PTU Question Paper , 2024

Subject : Chemistry (Solved)

1. Write a shoprt note on : (2×10)

(a) What is Huckel's rule, and how does it predict aromaticity in cyclic hydrocarbons?

Ans. Huckel’s rule was given by Erich Huckel in 1931 to find out the aromatic nature of the cyclic compounds. By applying Huckel’s rule one can find out if the given compound is aromatic, anti-aromatic or non-aromatic in nature. As per the rule a compound must fulfill the following requirements in order to have aromatic character-

a. The cyclic molecule or ion must be planar or nearly planar in nature.

b. It must have cyclic cloud of delocalized π electrons above and below the plane of the ring.

c. The cyclic compound must be completely conjugated i.e. the π electron cloud should include all the atoms of the ring.

d. The π electron cloud in the molecule must contain a total of $(4n + 2)$ π electrons where $n = 0, 1, 2, 3, 4, 5\ldots$

The cyclic planar hydrocarbons which have completely delocalized π electron cloud of $(4n + 2)$ π electrons ($2\pi, 6\pi, 10\pi, 14\pi\ldots$) are called aromatic hydrocarbons.

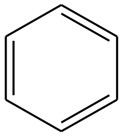
$n = 0$ $4n + 2 = 2\pi$

$n = 1$ $4n + 2 = 6\pi$

$n = 2$ $4n + 2 = 10\pi$

$n = 3$ $4n + 2 = 14\pi$

For example, benzene (C_6H_6) has completely delocalized electron cloud of 6π electrons above and below the plane of the ring so it is aromatic in nature.



Planar ring
4n + 2 Π electrons = 6Π electrons
Completely conjugated Π system
Aromatic in nature

Planar ring
4n + 2 Π electrons = 6Π electrons
Ring is not completely conjugated
Non-aromatic in nature

(c) How many 'H NMR signal will be obtained in:

(i) CH_3-CHCI-CH_3 (ii) CH_2CI-$CHCI_2$?

Ans. CH_3-CHCl-CH_3 :Two ^{1}H NMR signals.

It has two sets of chemically equivalent protons that will results into two ^{1}H NMR signals. The 6 -CH_3 protons have the same chemical environment so they will absorb at same frequency hence one signal. The -CHCl- proton has different chemical environment and thus will absorb at different frequency resulting into 2nd signal.

CH_3-CHCl-CH_3
A B A

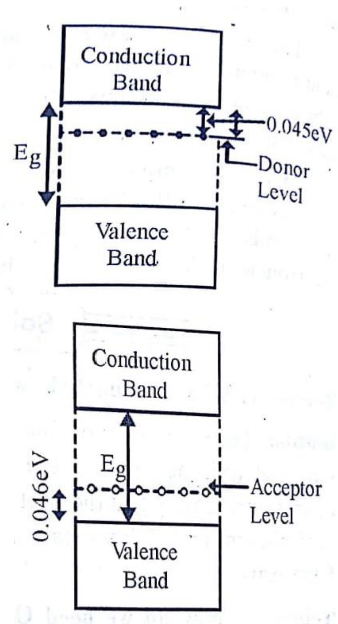
CH_2Cl-$CHCl_2$: Two ^{1}H NMR signals.

Again, the molecule has two sets of protons having different chemical environment and thus two ^{1}H NMR signals. The 2 -CH_2Cl protons have the same chemical environment so they will absorb at same frequency and the -$CHCl_2$ having different chemical environment will absorb at another frequency resulting into two ^{1}H NMR signals.

CH_2Cl-$CHCl_2$
A B

(b) How can you explain the effect of doping on the band structure of semiconductors?

Ans. Doping is the process of adding impurities to a semiconductor in order to increase the conductivity of a semiconductior. Doping increases the conducitivity of a semiconductor by increasing the number of electron or holes. For example, addition of a pentavalent dopant decrseases the band gap Eg (energy gap between valence band and conduction band) by creating the new donor level below the conduction band. Similalrly addition of a trivalent dopant decrseases the band gap Eg (energy gap between valence band and conduction band) by creating the new acceptor level above the valence band as shown in Fig. Energy level diagram of (a) n-type semiconductor (b) p-type semiconductor



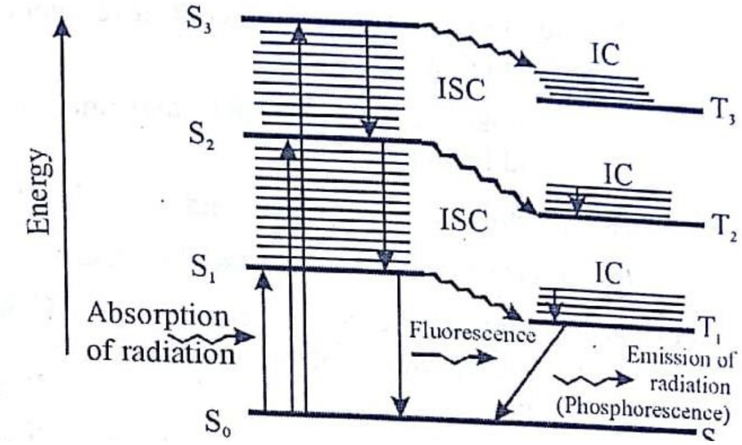
(d) What is Fluorescence? Explain with the help of Jablonskii diagram.

Ans. Fluorescence is the process of re-emission of light energy of linger wavelength immediately after the absorption of light energy. When a substance absorbs light, it gets excited to the higher energy level i.e. excited state. The excited molecule jump back from the excited singlet state to the ground state emitting the light of higher wavelength, fluorescence occurs.

$$S_1 \longrightarrow S_0 + hv$$

where S_1 is first excited singlet state and S_0 is ground state

It can be understood with the help of jablonskii diagram:

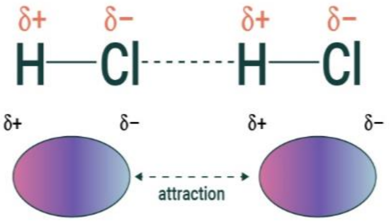


Jablonskii Diagram showing Fluorescence

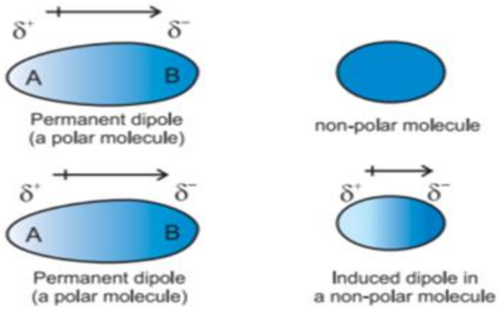
(e) What are different types of Van der Waal's forces?

Ans. There are mainly three types of Vander Forces:

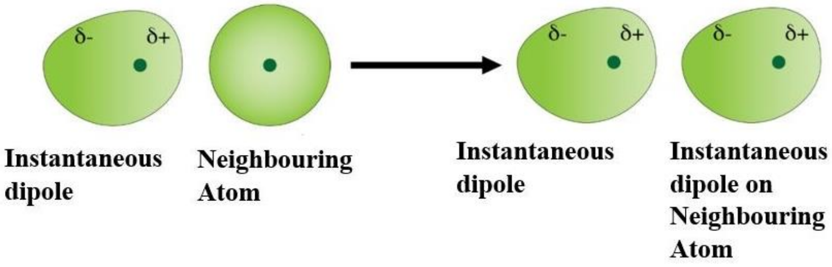
i) **Dipole-Dipole interactions:** Dipole-dipole interactions are present in the molecules having permanent dipoles i.e. in polar molecules. The word ‘dipole’ means two poles i.e. a positive and a negative pole. The attraction arises between the positive end (pole) of one molecule and the negative end (pole) of another molecule. These van der Waals forces due to electrostatic interaction between the dipoles are known as dipole-dipole interactions.



(ii) Dipole-induced dipole interactions: These attractions arise between the polar and non-polar molecules. The permanent dipole of the polar molecule induces the temporary dipole in non-polar molecule called induced dipole. The attractive force developed between dipole and induced dipole.



(iii) **Instantaneous dipole-instantaneous induced dipole forces (London forces or Dispersion forces):** These are present among the non-polar molecules like H_2, N_2, O_2 etc. For a small fraction of time, the electron cloud of a non-polar molecule becomes unsymmetrical. During which, it can undergo distortion resulting in the formation of an instantaneous dipole. This instantaneous dipole induces a new dipole in the neighbouring molecule (called induced dipole) which helps to sustain the original dipole. This gives rise to a weak attractive force between the instantaneous dipole and induced dipole. These forces are also called as London forces or dispersion forces or Van der Waal forces.



(f) Differentiate between Real gases and Ideal gases.

Ans.

Ideal Gases	**Real Gases**
1. These gases obey Boyle's Law and Charle's Law at all temperatures and pressures.	1. These do not obey gas laws at all temperatures and pressures.
2. Collision between the molecules of ideal gases are elastic.	2. Collision between the molecules of ideal gases are inelastic.
3. There are no intermolecular forces of attraction in ideal gas.	3. There are intermolecular forces of attraction in real gas.
4. These obey ideal gas equation i.e. $PV= nRT$	4. These obey Vander Waals equation i.e. $(P+ an^2/V^2)\ (V-nb) = nRT$
5. Ideal gases do not exist.	5. Real gas exist e.g. O_2, H_2, CO_2, N_2 etc.

(g) Distinguish between hard water and soft water.

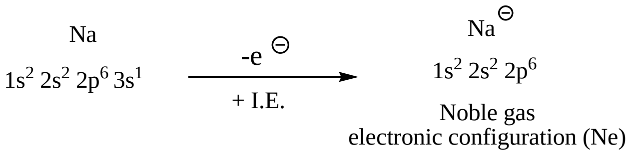
Ans.

Hard Water	Soft Water
1.Hard water does not form lather with the soap.	1. Soft water forms lather easily with the soap.
2. It contains dissolved salts of calcium and magnesium in it.	2. It does not contain dissolved salts of calcium and magnesium in it.
3. It lowers the cleansing quality of the soap.	3. It does not lower the cleansing quality of the soap.
4. It increases the boiling point of water due to presence of salts of Ca and Mg. Therefore more time and fuel is used for cooking.	4. Less time and fuel is used for cooking.

(h) How would you explain the fact that first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium?

Ans. Ionization enthalpy of an element is defined as the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom. It depends upon the atomic radii and effective nuclear charge. First ionization energy of sodium is lower than magnesium:

Na: (atomic no. 11)



Mg: (atomic no. 12)

$$\underset{1s^2\ 2s^2\ 2p^6\ 3s^2}{\mathrm{Mg}} \xrightarrow[+\ \mathrm{I.E.}]{-e^{\ominus}} \underset{1s^2\ 2s^2\ 2p^6\ 3s^1}{\mathrm{Mg}^{\ominus}}$$

In both Na and Mg the first electron has to be removed from 3s orbital. But the Na has larger atomic radii and less effective nuclear charge than Mg which leads to easy removal of electron from Na in comparison to Mg. In addition, Na attains the stable noble gas configuration of Neon ($1s^2\ 2s^2\ 2p^6$) after removal of one electron from Na. Thus, Na has lower first ionization energy than Mg. However, the 2nd ionization enthalpy of sodium is higher than magnesium. The 2nd electron from Na^+ has tom be removed from stable noble gas configuration in comparison to Mg^+ which attains the noble gas configuration after removal of 2nd electron. Thus, the conversion of Na^+ to Na^{2+} requires more energy in comparison to Mg^+ to Mg^{2+} which accounts for higher 2nd ionization enthalpy of Na than Mg.

$$\underset{1s^2\ 2s^2\ 2p^6}{\mathrm{Na}^{-}} \xrightarrow[+\ \mathrm{I.E}_2]{-e^{\ominus}} \underset{1s^2\ 2s^2\ 2p^5}{\mathrm{Na}^{2+}}$$

Noble gas
electronic configuration (Ne)

$$\underset{1s^2\ 2s^2\ 2p^6\ 3s^1}{\mathrm{Mg}^{-}} \xrightarrow[+\ \mathrm{I.E}_2]{-e^{\ominus}} \underset{1s^2\ 2s^2\ 2p^6}{\mathrm{Mg}^{2+}}$$

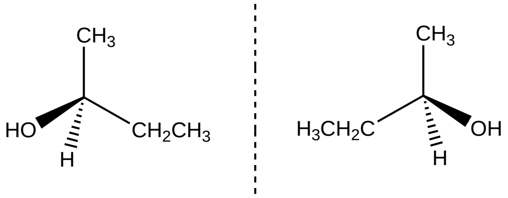
Noble gas
electronic configuration (Ne)

(i) What is enantiomerism? Explain with an example.

Ans. Optical isomers which are non-superimposable mirror images of each other are called enantiomers and the phenomenon is called enantiomerism. Enantiomers have identical physical properties but differ in their behaviour towards plane polarized light. One enantiomer rotates the angle of plane polarized light towards right and the other towards left but to the same extent. The isomer which rotates the angle towards right is called dextrorotatory and the one which rotates towards left is called laevorotatory compound. A molecule must satisfy the following conditions to show enantiomerism:

a. Molecule must not be superimposable on its mirror image.
b. Molecule must not be symmetrical it should be dissymmetric in nature i.e. it must not have centre of inversion and plane of symmetry.

Such a molecule is called optically active molecule. For example, the compound 2-butanol doesn't have any symmetry element. The molecule is non-superimposable on its mirror image and thus it is optically active and exists as a pair of enantiomers.



Non-superimposable: Optically active
(pair of enantiomers)

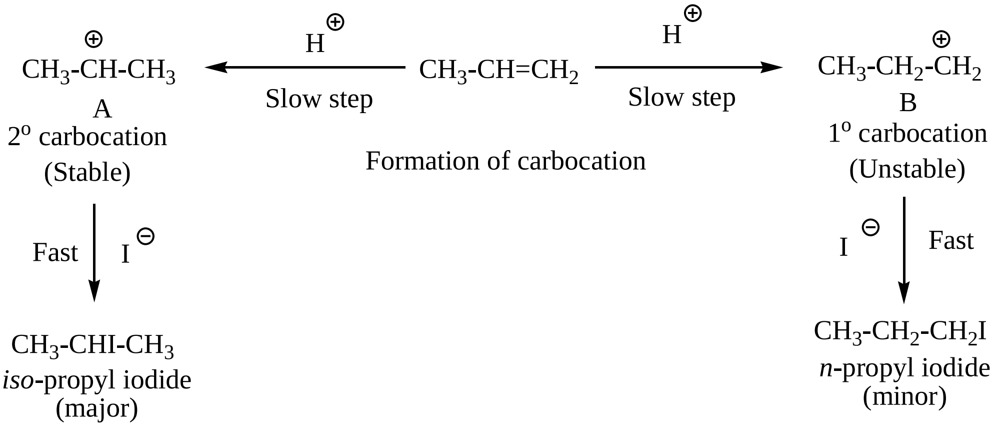
(j) What is Markownikov's addition?

Markownikov's rule states the electrophilic addition of unsymmetric reagent to unsymmetrical alkene. Alkenes are unsaturated molecules so they show addition reactions. They are electron rich molecules due to presence of loosely bounded π-electrons. So, they show electrophilic addition reactions. The rule states that when addition across an unsymmetrical ethylenic bond takes place and there is possibility of formation of two products, in the major product the positive part of the attacking reagent goes to the carbon with the greater number of hydrogen atoms and negative part goes to the other end of the double bond which carries lesser number of hydrogen atoms. For example, the addition of HI to the propylene gives us mixture of *n*-propyl iodide (minor) and *iso*-propyl iodide (major)

$$CH_3\text{-}CH{=}CH_2 \quad + \quad HI \longrightarrow \underset{\substack{n\text{-propyl iodide}\\ \text{(minor)}}}{CH_3\text{-}CH_2\text{-}CH_2I} \quad + \quad \underset{\substack{iso\text{-propyl iodide}\\ \text{(major)}}}{CH_3\text{-}CHI\text{-}CH_3}$$

The addition initiates by the slow addition of proton (H^+) to one of the doubly bonded carbon atoms to form either carbocation A or B. Carbocation A is secondary (2°) carbocation whereas carbocation B is a primary carbocation (1°). As 1° carbocation is less stable than 2° one, the reaction favours the formation of 2° carbocation which upon fast reaction with iodide ion gives us *iso*-propyl iodide as major product. On the other hand, the carbocation B upon interaction with iodide ion leads to the formation of *n*-propyl iodide as minor product.

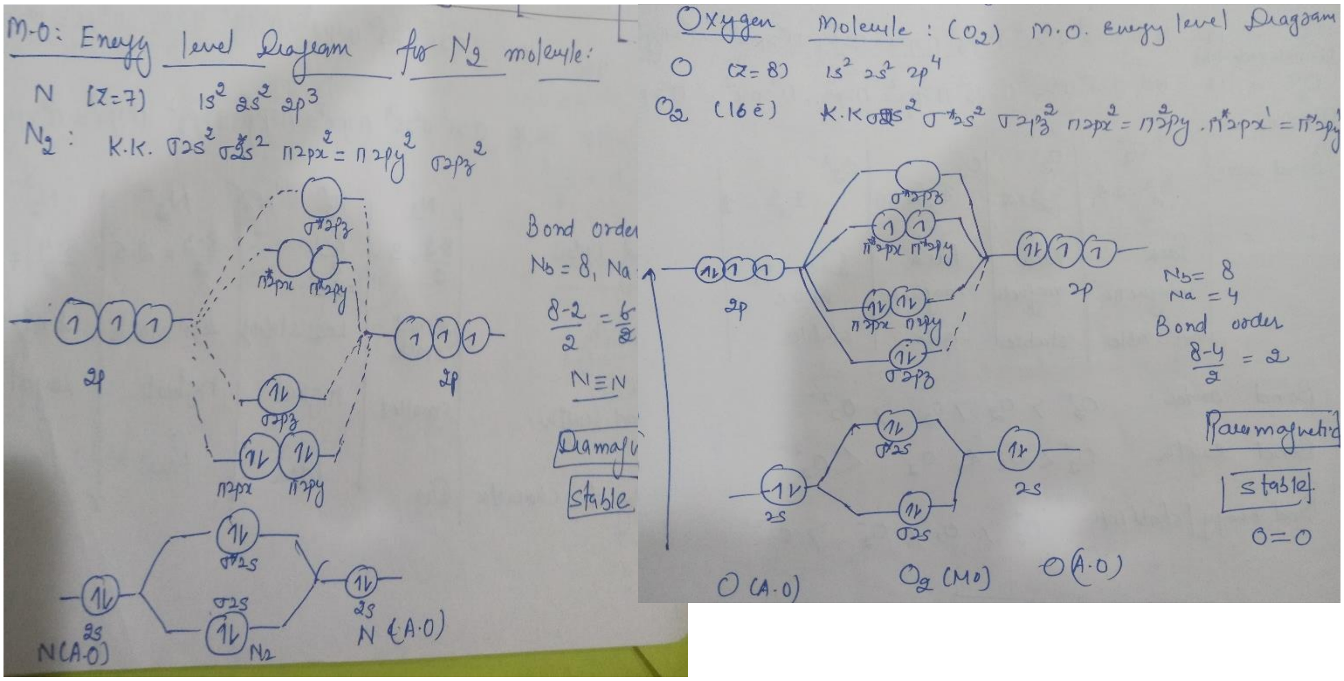
On the basis of mechanistic details, Markownikov's rule can be explained as: If there is a possibility of formation of two intermediates in a reaction, the major product will come from the more stable intermediate.



SECTION-B

2. (a) Give the molecular orbital energy level diagram of O_2 and N_2. Comment on the bond order and magnetic characteristics of these molecules.

Ans. Molecular orbital Diagram for O_2 and N_2 is given below along with their bond order and magnetic characteristics



(b) Define wave function and give its significance.

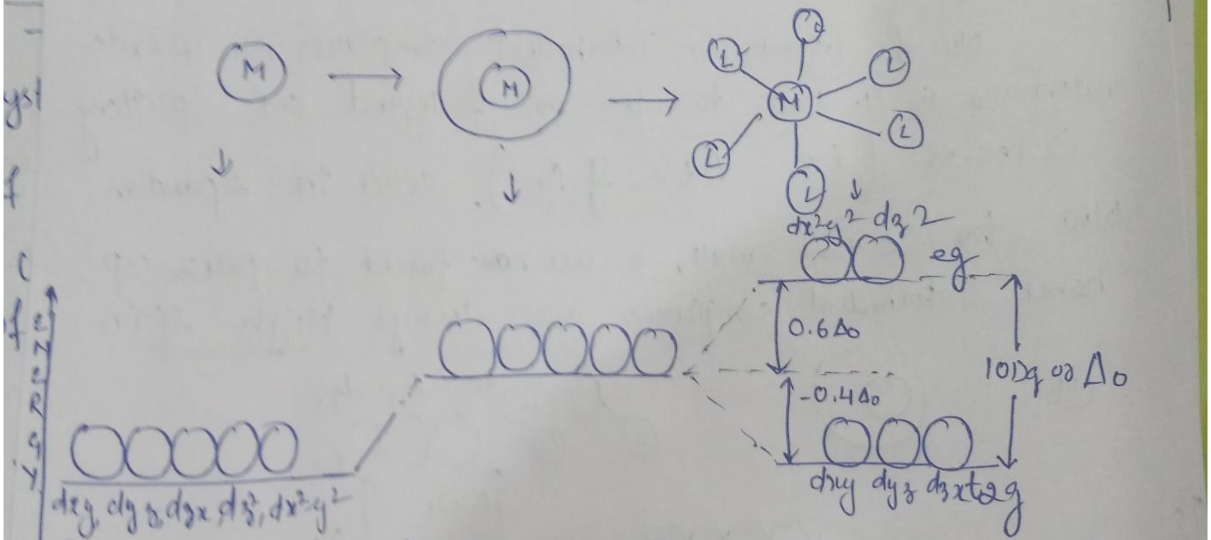
Ans. The wave function is the variable quantity of matter wave. Just like in light waves electromagnetic field vary in space and time, in sound waves, pressure varies in time and space the wave function varies in electron wave or matter wave. Wave function is represented by ψ. It describes the behavior of matter wave as a function of space and time.

It has no direct physical significance as it is not an observable quantity. However, its value of wave functions is related to the probability of finding the matter particle at a given point in space at a given time.

3. (a) Explain the crystal field splitting of orbitals in octahedral and tetrahedral fields complexes.

Ans. In octahedral complexes, six ligands approach the central metal ions. The ligand field results into splitting of degenerate d- orbitals in two sets as shown in figure

In octahedral complexes, two sets of d-orbitals are formed ① one set of three orbitals of lower energy i.e. t2g and other set of two orbitals of higher energy i.e. eg. CF Spitting of octahedral complexes is shown in fig.



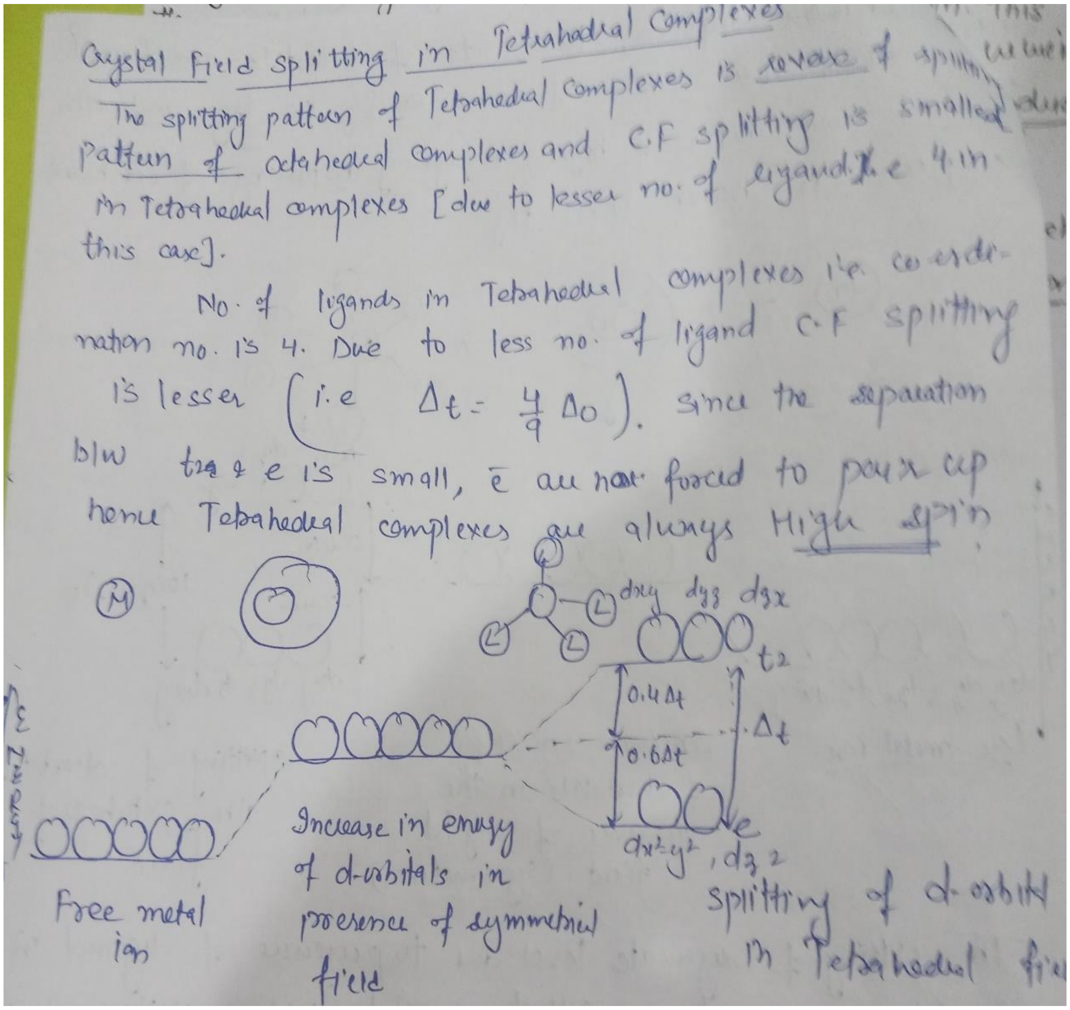
Free metal ion

Increase in energy of d-orbitals in the presence of crystal field (symmetrical)

splitting of d-orbital in Octahedral field.

The splitting of degenerate level due to presence of ligand in a definite geometry is called crystal field splitting. It is denoted by Δ_o. [Δ → energy separation, O → octahedral)

In octahedral system, energy of two eg orbitals ↑es by 0.6 or 6Dq and energy of three t2g orbital ↓es by 0.4Δ_o or 4

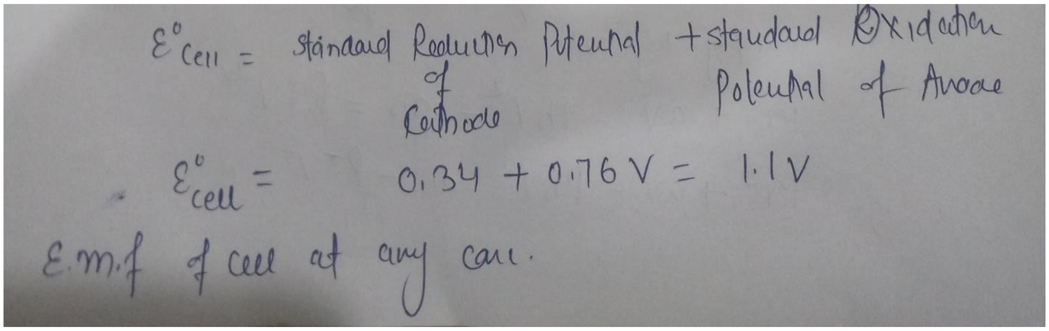


Crystal Field splitting in Tetrahedral Complexes

The splitting pattern of Tetrahedral Complexes is reverse of splitting pattern of octahedral complexes and C.F splitting is smaller in Tetrahedral complexes [due to lesser no. of ligand. i.e 4 in this case].

No. of ligands in Tetrahedral complexes i.e. co-ordination no. is 4. Due to less no. of ligand C.F splitting is lesser (i.e $\Delta_t = \frac{4}{9}\Delta_o$). since the separation b/w t_2 & e is small, $\bar{e}$ are not forced to pair up hence Tetrahedral complexes are always High spin

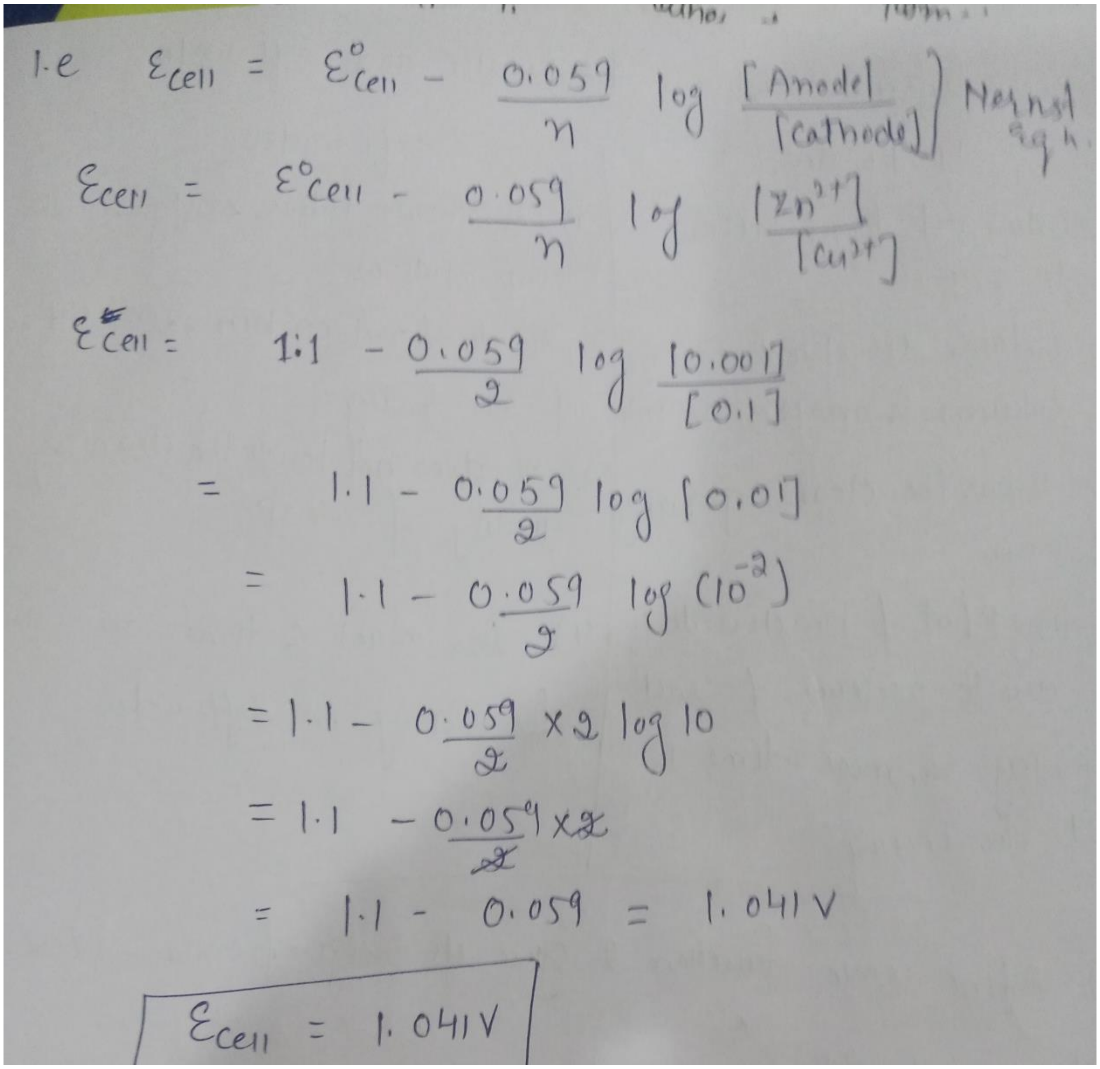
(b) Calculate the emf of the cell Zn/ Zn 2+ (0.001M) || Cu2+ (0.1M)/ Cu. The standard potential of Cu/Cu2+ half-cell is +0.34 V and Zn/Zn2+ is 0.76 V.



E^0_{cell} = standard Reduction Potential of Cathode + standard Oxidation Potential of Anode

E^0_{cell} = 0.34 + 0.76 V = 1.1 V

E.m.f of cell at any conc.



i.e $E_{cell} = E^{0}_{cell} - \frac{0.059}{n} \log \frac{[Anode]}{[Cathode]}$ Nernst eqn.

$$E_{cell} = E^{0}_{cell} - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.1 - \frac{0.059}{2} \log \frac{[0.001]}{[0.1]}$$

$$= 1.1 - \frac{0.059}{2} \log [0.01]$$

$$= 1.1 - \frac{0.059}{2} \log (10^{-2})$$

$$= 1.1 - \frac{0.059}{2} \times 2 \log 10$$

$$= 1.1 - \frac{0.059 \times \cancel{2}}{\cancel{2}}$$

$$= 1.1 - 0.059 = 1.041 V$$

$$\boxed{E_{cell} = 1.041 V}$$

4. (a) What are the different factors which affect the value of λ_{max} and intensity of spectral lines?

Ans. The wavelength at which a molecule absorbs maximum in the UV-visible range is called λ_{max}. In the UV-visible range the excitation takes place in the electronic energy levels. On absorption of energy, the electron excites from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). So, the value of λ_{max} depends upon the HOMO and LUMO energy gap.

$$E = h\nu \qquad (c = \nu\lambda)$$

$$E = hc/\lambda$$

$$E \propto 1/\lambda$$

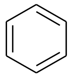
The energy is inversely proportional to the wavelength. So, decrease in the HOMO-LUMO energy gap leads to increase in λ_{max} and vice-versa. The various factors which affect the position and intensity of spectral lines are:

1) **Bathochromic shift and hyperchromic effect:** A decrease in the HOMO-LUMO gap causes increase in the λ_{max} value called as bathochromic or red shift. It is also accompanied by increase in the intensity of spectral lines which we term as hyperchromic effect.

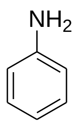
I. **Conjugation of two or more chromophoric groups:** Conjugation of double bonds or two chromophores lowers the HOMO-LUMO energy gap which in turn requires less energy for the electronic transition and thus shifting the absorption towards higher λ_{max} and also increasing the intensity of spectral lines. For example, π to π^* transition-

$CH_2{=}CH{-}CH{=}CH_2$ $\lambda_{max} = 217$ nm
$CH_2{=}CH_2$ $\lambda_{max} = 175$ nm

II. **Attachment of an auxochrome to the chromophore:** An auxochrome attached to a chromophore extends the conjugation and thus shifts the absorption to longer wavelength. For example $-NH_2$ attached to the benzene ring shifts the λ_{max} from 255 nm to 280 nm.

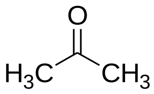


$\lambda_{max} = 255$ nm



$\lambda_{max} = 280$ nm

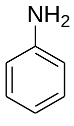
III. **Low polarity solvent:** A low polarity solvent increases the energy of non-bonding electrons (n) and in turn decreases the energy gap between n and π^*, leading to shifting of λ_{max} to higher wavelength. For example, n to π^* absorption in carbonyl compounds-



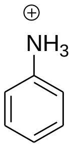
λ_{max} = 264 nm (H_2O)
λ_{max} = 279 nm (Hexane)

2) **Hypsochromic shift and hypochromic effect:** An increase in the HOMO-LUMO energy gap will lead to decrease in the λ_{max} called as hypsochromic or blue shift which is also accompanied by decrease in the intensity of spectral lines known as hypochromic effect.

I. **Removal of conjugation:** Removal of conjugation increases the HOMO-LUMO energy gap and thus shifting the absorption to shorter λ_{max}. For example, protonation of aniline shifts the λ_{max} from 280 nm to 203 nm.

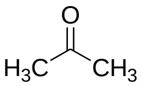


λ_{max} = 280 nm



λ_{max} = 203 nm
(No lone pair of electrons
so no conjugation)

II. **Solvent of high polarity:** High polarity solvent decreases the energy of non-bonding electrons and thus increasing the n and π^* energy gap and shifting the absorption to shorter λ_{max}. For example, n to π^* transition in acetone-



λ_{max} = 279 nm (Hexane)
λ_{max} = 270 nm (Ethanol)
λ_{max} = 264 nm (H_2O)

b) What are auxochromes and chromophores? Explain with suitable examples.

Ans. **Chromophores:** Any group which displays absorption of electromagnetic radiations in the UV-visible range (200-800 nm) is called a chromophore. In terms of electronic transition chromophores are of two types:

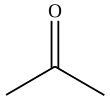
i. π – π* transitions: Chromophores which contain π electron undergo π – π* transitions in the UV-visible range e.g. conjugated π system. An isolated double bond in alkene absorbs around 170 nm (λ_{max} = 170 nm) which doesn't come under the UV-visible range. But the conjugation of two or more double bonds decreases the HOMO (π) – LUMO (π*) energy gap and thus the λ_{max} comes in the UV-visible range. For example,

Ethene
(Isolated double bond) $H_2C{=}CH_2$ λ_{max} = 170 nm

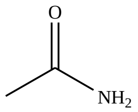
1,3-Butadiene
(Conjugated system)

$H_2C{=}\underset{H}{C}{-}\underset{H}{C}{=}CH_2$ λ_{max} = 217 nm

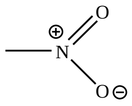
ii. n – π* transitions: Chromophores which contain unsaturated heteroatom have both π and n (non-bonding electrons) electrons so they can undergo π – π* as well as n – π* transitions e.g.



n - π* λ_{max} = 285 nm
π - π* λ_{max} = 180 nm



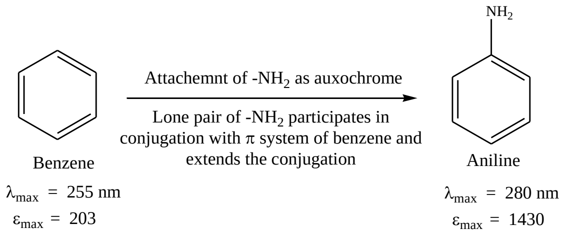
n - π* λ_{max} = 220 nm
π - π* λ_{max} = 178 nm



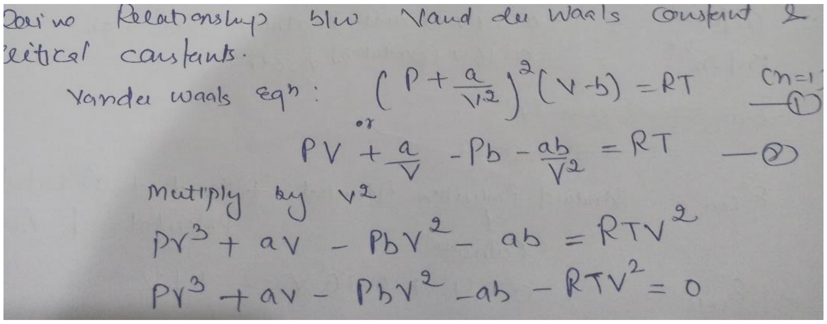
n - π* λ_{max} = 274 nm

$-N{=}N-$ n - π* λ_{max} = 338 nm

Auxochrome: An auxochrome is a group which itself doesn't show electronic transition in absorb in UV-visible range (doesn't act as chromophore) but when attached to a chromophore it shifts the absorption maximum (λ_{max}) towards longer wavelength i.e. bathochromic shift along with an increase in the intensity of absorption (hypsochromic effect). Auxochromes are saturated group of atoms having at least one heteroatom which contain one or more non-bonding electrons. The non-bonding electrons extends the conjugation upon attachment with the chromophore and thus decreasing the HOMO-LUMO energy gap and shifting the λ_{max} towards higher wavelength e.g. -OH, -NH_2, -OR, -NHR, -NR_2 groups.



5. (a) Derive relation between Van der Waals constants and critical constants.



Derive Relationship b/w Vand der Waals constant & critical constants.

Vander waals eqn : $\left(P+\frac{a}{V^2}\right)^2(V-b)=RT$ (n=1) —①

or

$PV+\frac{a}{V}-Pb-\frac{ab}{V^2}=RT$ —②

mutiply by V^2

$PV^3+aV-PbV^2-ab=RTV^2$

$PV^3+aV-PbV^2-ab-RTV^2=0$

①

Arranging in descending Powers of V.

$$PV^3 - PbV^2 - RTV^2 + aV - ab = 0 \quad \text{— ③}$$

, ① ,

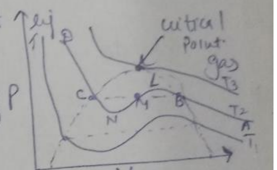
Dividing ③ by P, we get

$$V^3 - bV^2 - \frac{RTV^2}{P} + \frac{aV}{P} - \frac{ab}{P} = 0$$

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \quad \text{— ④}$$

eq ④ is a cubic eqn. below certain values of T, eq ④ has 3 real roots. As the T ↑es all root approaches each other & become identical as shown in P-V plot ↑fig

From graph we can see, there are 3 unequal roots at point B, M, C. ~~Poi~~ (For curve ABLMN (D))



Isotherms of CO2

(Curve ABLMNCD)

Values of Volumes at Point B → saturated vapour ~~Press~~ phase

C → liquid phase

M → No physical meaning

As Temp. ↑es T_2 to T_3 the curved portion reduced to a point where all values of V become identical correspond to critical ~~Temperature~~ point.

Hence at critical point Volume correspond to critical volume ie V_c.

at critical Point we can write

$$[(a-b)^3 = a^3 - 3a^2b + 3ab^2 - b^3]$$

$$(V - V_c)^3 = 0$$

$$V^3 - 3V^2V_c + 3 \cdot V \cdot V_c^2 - V_c^3 = 0 \quad \text{— ⑤}$$

at critical point $T = T_c$ (Critical Temp), $P = P_c$ ↘critical Pressure.

Putting. $T = T_c$ & $P = P_c$ in eqn ④

$$V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \quad — ⑥$$

Comparing cofficient of equal power of V in ⑤ & ⑥

$$3V_c = b + \frac{RT_c}{P_c} \quad — ⑦$$

$$3V_c^2 = \frac{a\cancel{V}}{P_c} \quad — ⑧$$

$$V_c^3 = \frac{ab}{P_c} \quad — ⑨$$

Divide ⑨ by ⑧

$$\frac{V_c^3}{3\cancel{V_c^2}} = \frac{\cancel{a}b}{\cancel{P_c}} \times \frac{\cancel{P_c}}{\cancel{a}}$$

$$\boxed{V_c = 3b} \quad — ⑩$$

Putting value of V from ⑩ into ⑧

$$3.(3b)^2 = \frac{a}{P_c}$$

$$27b^2 = \frac{a}{P_c}$$

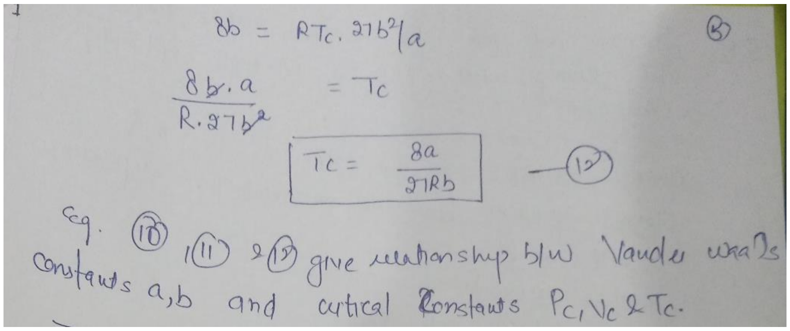
$$\boxed{P_c = \frac{a}{27b^2}} \quad — ⑪$$

ing value of P_c & V_c from ⑩ & ⑪ into ⑦

$$3 \times 3b = b + R.T_c \times \frac{27b^2}{a}$$

$$9b = b + RT_c\frac{27b^2}{a}$$

$$b - b = RT_c\, 27b^2/a$$



⑤

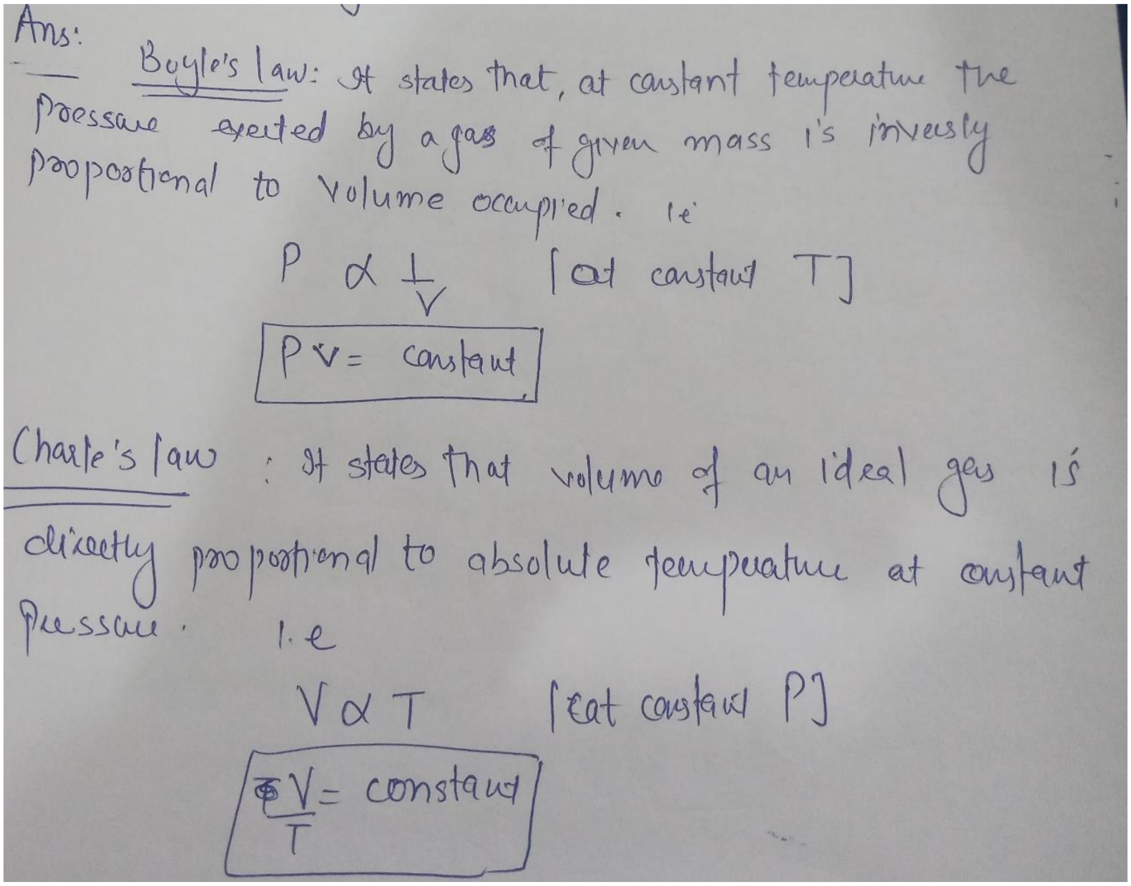
$$8b = RT_c . 27b^2/a$$

$$\frac{8\cancel{b}.a}{R.27\cancel{b}^2} = T_c$$

$$\boxed{T_c = \frac{8a}{27Rb}} \quad \text{—⑫}$$

eq. ⑩, ⑪ & ⑫ give relationship b/w Vander waal's constants a, b and critical constants P_c, V_c & T_c.

(b) Explain Boyle's law and Charle's Law.



Ans:

Boyle's law: It states that, at constant temperature the pressure exerted by a gas of given mass is inversely proportional to volume occupied. i.e

$$P \propto \frac{1}{V} \quad [\text{at constant } T]$$

$$\boxed{PV = \text{constant}}$$

Charle's law: It states that volume of an ideal gas is directly proportional to absolute temperature at constant pressure. i.e

$$V \propto T \quad [\text{at constant } P]$$

$$\boxed{\frac{V}{T} = \text{constant}}$$

SECTION-C

6. (a) Compare the hot lime soda process and the zeolite process of water softening with respect to the principle involved, advantages and limitations.

Ans. Hot lime soda process and zeolite process of water softening are two major water softening technologies. Both are discussed below-

1**. Hot lime soda process:**

Principle: It is based upon the precipitation of hard water upon addition of lime (CaO) and Soda (Na_2CO_3) at high temperatures of 108-116°C. The precipitation of Calcium takes place as its carbonate and magnesium as its hydroxide as shown in the following reactions:

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

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$$

Advantages

1. It is very economical.

2. Increase the pH of soft water so that softer water does not corrode the water pipes.

3. Along with hardness removal, remove the quantity of other minerals.

Limitations

1. Does not remove the hardness completely therefore the soft water cannot be used in boilers.

2. Large amount of sludge is form after precipitation, and sludge disposal in another issue.

3. Careful handling and skilled supervision is required.

2. Zeolite process: Zeolite is a micro-porous material made of aluminosilicates having formula $Na_2O.Al_2O_3.\ nSiO_2.xH_2O$

Principle: It is based upon exchange of Ca^{2+} and Mg^{2+} ions present in hard water with ion exchanger resin i.e. zeolite. Here hard water is passed through the column containing zeolite bed. The sodium ions present in zeolite are replaced by Ca^{2+} and Mg^{2+} ions of hard water.

$$Na_2Ze + Ca^{2+} \longrightarrow Ca\text{-}Ze + 2Na^{+}$$

(Zeolite)

$$Na_2Ze + Mg^{2+} \longrightarrow Mg\text{-}Ze + 2Na$$

Zeolite gets inactivated when all Na^{+} ions are replaced by Ca^{2+} and Mg^{2+} ions. Then zeolites are regenerated by passing the brine solution through it.

$$Ca\text{-}Ze + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$

$$Mg\text{-}Ze + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$

Advantages

1.Remove the hardness completely.

2.No precipitation of impurities take place hence no sludge in formed

3. Less time and less skill and small equipment is required.

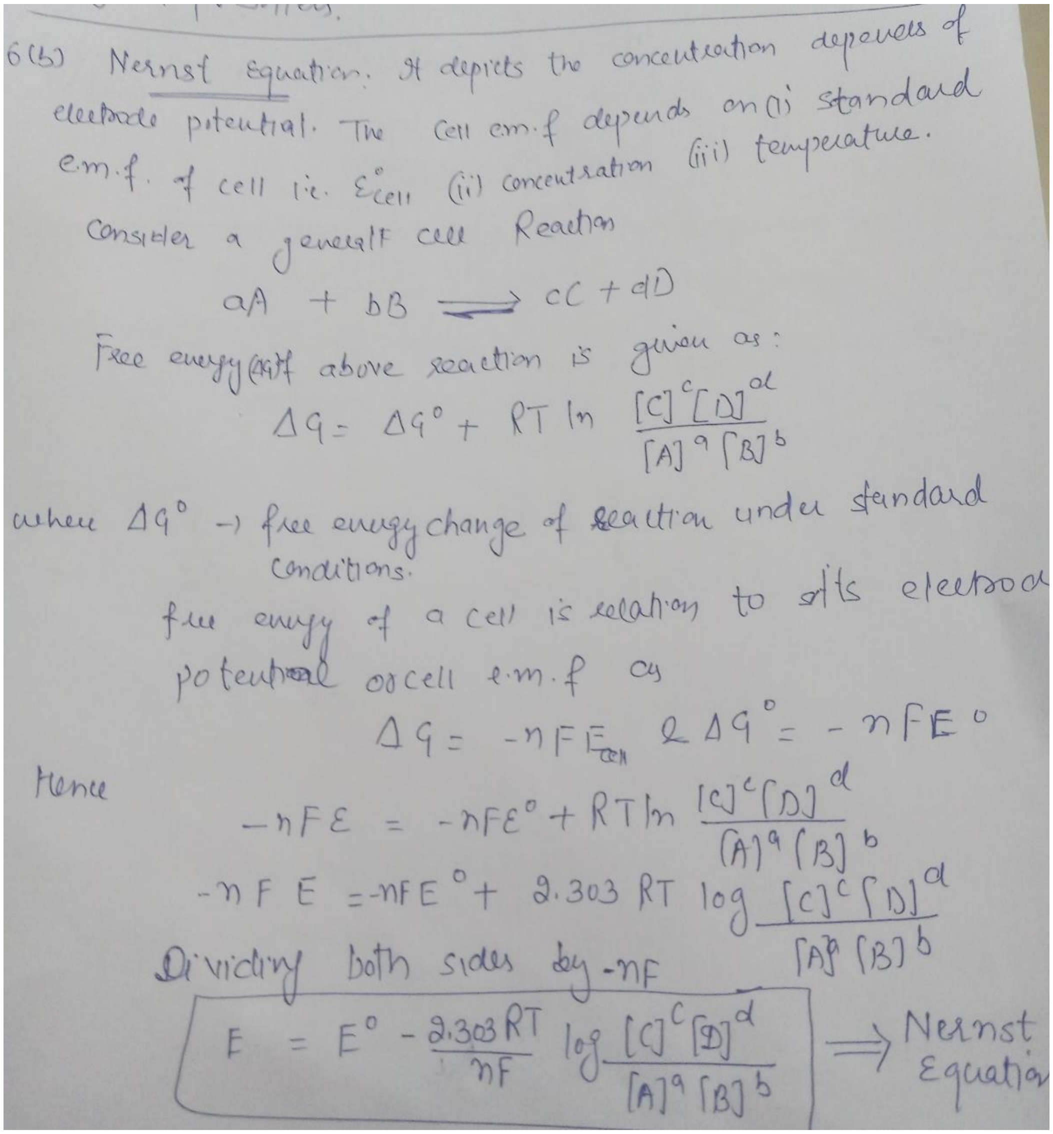
Limitations

1. Treated water contains more sodium than lime soda process.

2. It replaces only Ca^{2+} and Mg^{2+} but leaves acidic ions like HCO_3^{-} and CO_3^{2-}. Such soft water causes the corrosion of boilers.

3. High turbid water cannot be used.

(b) Derive the Nernst equation for the calculation of cell e.m.f.



6(b) Nernst Equation. It depicts the concentration depends of electrode potential. The cell e.m.f depends on (i) standard e.m.f. of cell i.e. E°_{cell} (ii) concentration (iii) temperature.

Consider a general cell Reaction

$$aA + bB \rightleftharpoons cC + dD$$

Free energy (ΔG) of above reaction is given as:

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where ΔG° → free energy change of reaction under standard conditions.

free energy of a cell is relation to its electrod potential or cell e.m.f as

$$\Delta G = -nFE_{cell} \quad \& \quad \Delta G^{\circ} = -nFE^{\circ}$$

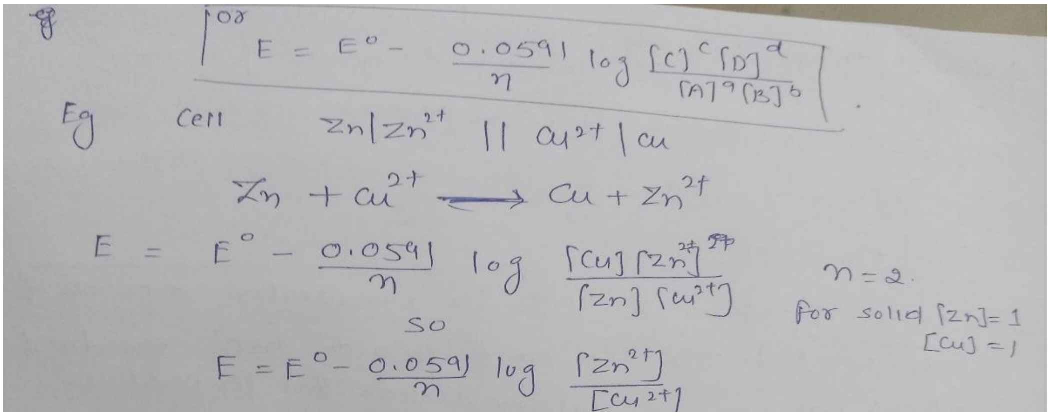
Hence

$$-nFE = -nFE^{\circ} + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$-nFE = -nFE^{\circ} + 2.303\, RT \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Dividing both sides by $-nF$

$$\boxed{E = E^{\circ} - \frac{2.303\,RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}} \Longrightarrow \text{Nernst Equatio}$$



or

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Eg Cell $Zn|Zn^{2+} \| Cu^{2+}|Cu$

$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$$

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[Cu][Zn^{2+}]}{[Zn][Cu^{2+}]}$$

$n = 2.$

For solid $[Zn] = 1$

$[Cu] = 1$

so

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

7. (a) Define the term electronegativity. How does it vary in the periodic table?

(a) In a covalent bond in heteronuclear molecule the different atoms have different tendencies to attract the bonded pair of electrons towards itself. This property of an atom to attract the shared pair of electrons in a molecule towards itself is called electronegativity. Greater the ability of an atom to attract electrons in a bond, larger is the value of its electronegativity. Electronegativity of an element depends upon its effective nuclear charge.

Variation of electronegativity down a group: Electronegativity decreases as we move from top to bottom in a group. While going down in a group the nuclear charge increases but with each element a new principal shell is added causing increase in the atomic radii which overcomes the increase in nuclear charge. This results into decrease in effective nuclear charge as a result of which the electronegativity continuously decreases down a group.

Variation of electronegativity along a period: Electronegativity increases along a period. As we move from left to right the nuclear charge increases by one unit with every element but the electron enters in the same shell which leads to decrease in the atomic radii. As a result, the effective nuclear charge increases along a period and consequently electronegativity increases.

(b) Ionization enthalpy decreases in a group from top to bottom. Why?

Ionization enthalpy of an element is defined as the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom.

$$M(g) \quad + \quad \text{Ionization enthalpy} \longrightarrow M^{+}(g) \quad + \quad e$$

It gives a measure of the ease with which an atom can lose an electron and change into a cation. The smaller the value of ionization enthalpy, easier it is to remove the electron from the atom. It depends upon the attractive force between nuclei and the last valance electron. There is a gradual decrease in the ionization energy when we from top to bottom down a group. The nuclear charge continuously increases down the group but the atomic size also increases due to addition of another shell with each element. The increase in the shell number leads to increase in the shielding effect on the outermost electron due to an increase in the number of inner electrons. The effect of increase in the atomic size and shielding effect is much more than the effect of increases in the nuclear charge. As a result, the attractive force for outermost electron continuously decreases as we go down the group which leads to gradual decrease in the ionization enthalpy down a group.

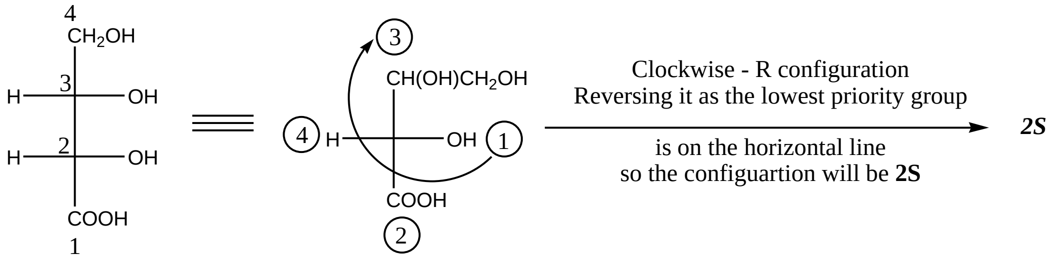
(c) Electron gain enthalpies of noble gases are positive. Why?

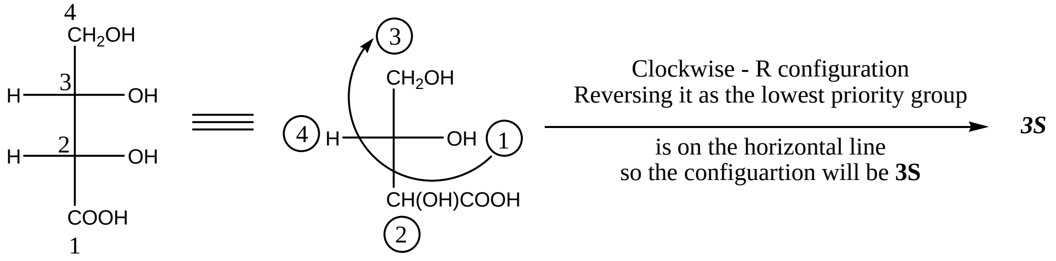
(a) The electron gain enthalpy is defined as the amount of energy released when an electron is added to an isolated gaseous atom.

$$X(g) \xrightarrow{e} X^{-}(g) \quad + \quad \underset{\text{(Electron gain enthalpy)}}{\text{Energy}}$$

The magnitude of the electron gain enthalpy measures the ability of an atom to hold the additional electron. If an atom has more tendency to hold the electron, a large amount of energy will be released leading to a negative value of electron gain enthalpy and on the other hand if an atom has no tendency to hold the electron energy has to be provided from outside for the electron gain which leads to positive value of electron gain enthalpy. The electron gain enthalpy of noble gases is zero. The noble gases have stable electronic configuration of ns^2 np^6 and have no tendency to take an extra electron because that will destabilize the electronic configuration. Consequently, the incoming electron does not feel any attraction for the nucleus. Thus, for the noble gases to gain electron there is absorption of energy which leads to positive values of their electron gain enthalpies.

8. (a) Assign R or S configuration of each of the following compounds:

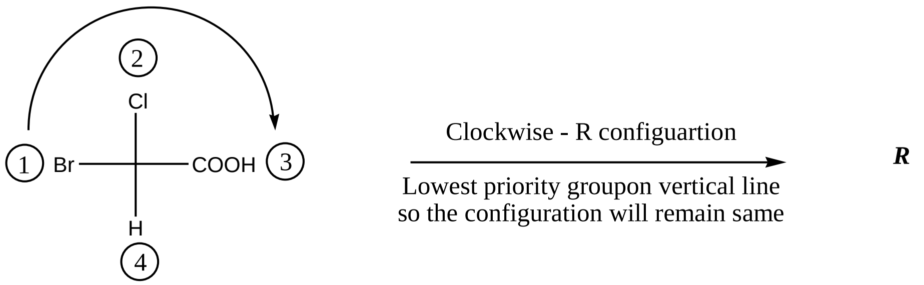




C-2: First, we will give the priority order to the groups attached to the C-2. Now going from 1 to 3 there is clockwise movement which indicates R configuartion, but the least priority group is on the horizontal line so reversing it as per the golden rule it comes ***2S***.

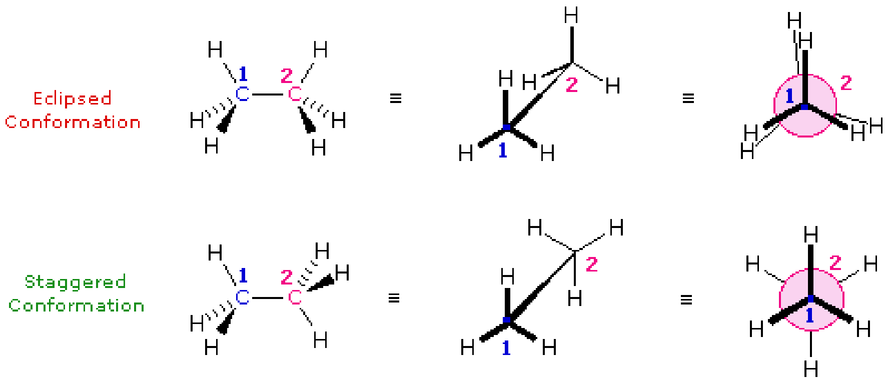
C-3: Again, we will give the priority order to the groups attached to the C-3. Now going from 1 to 3 the configuration comes R, but the least priority group is on the horizontal line so reversing it as per the golden rule it comes ***3S***.

In the similar manner,



(b) Give the conformational analysis of ethane with potential energy diagram for various suitable conformations of it.

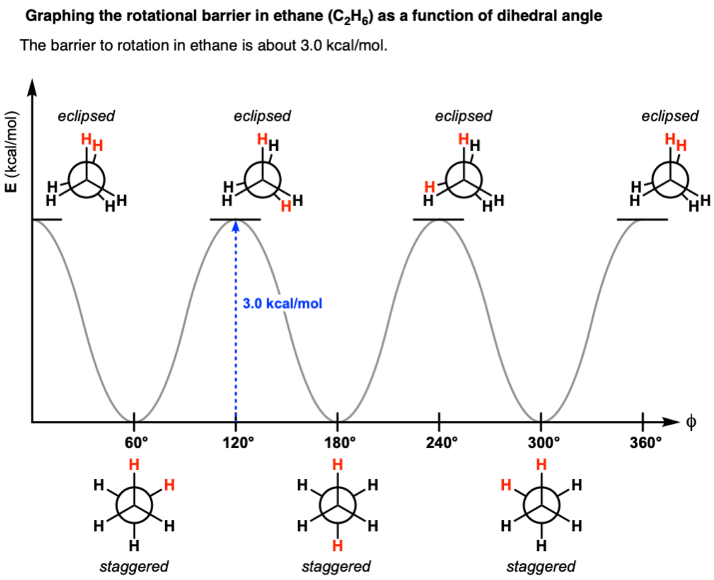
Ans. In ethane molecule (CH_3-CH_3) the two carbon atoms are connected by a σ-bond. If one of the methyl groups in ethane molecule is kept fixed and the other is rotated about the C-C bond, a large number of momentary arrangements of the hydrogen atoms on one carbon with respect to the hydrogen atoms on the other carbon atom in space are obtained which represent conformations of ethane. In all these conformations, the basic structure of ethane molecule and various bond angles and bond lengths remain the same. Out of the infinite possible conformations of ethane only the two extreme ones are important called staggered and eclipsed conformations.



Eclipsed conformation: Each of the carbon atoms on the back carbon lies exactly behind each of the hydrogen atoms on the front carbon. In other words, the dihedral angle between the C-H bonds of two carbons is 0^o (superimposed on each other). As a result, the non-bonded hydrogen atoms are quite close (229 pm) which leads to repulsion between their σ electron clouds. This raises the energy of the eclipsed conformation.

Staggered conformation: Each of the hydrogen atoms on the front carbon lies exactly in between each of the hydrogen atoms on the back carbon which means the dihedral angle between the C-H bonds of two carbons is 60^o. In this conformation the non-bonded hydrogen atoms on two carbons are as far apart as possible (310 pm) which makes the repulsions between their σ electron clouds minimum. This lowers the energy of staggered conformation in respect to eclipsed conformation and makes it more stable.

The staggered conformation of ethane is 12.55 KJ mol^{-1} (3 kcal mol^{-1}) more stable than the eclipsed conformation. This energy barrier is not very large and the two conformations are readily interconvertible at room temperature.



Potential energy diagram and interconversion of conformations of ethane by rotation of C-C σ bond

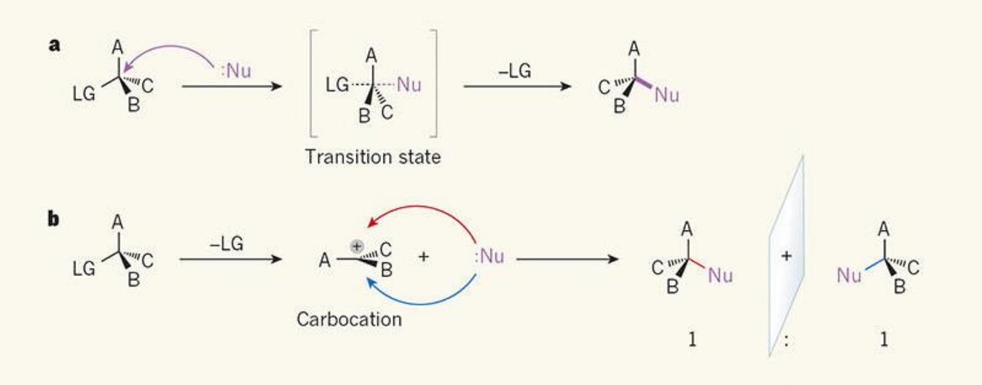
9. (a) Differentiate between SN$_1$ and SN$_2$ reactions.

(a) Differentiate between S_N2 and S_N1 reactions.

S_N2 and S_N1 are nucleophilic substitution reactions in which electron rich chemical species replaces another electron rich chemical group. The attacking reagent is called nucleophile (Nu) whereas the group which leaves the molecule is called leaving group. For example, the nucleophilic substitution reactions shown by alkyl halides.

S_N2 ⟶

S_N1 ⟶



S.No.	S_N2 Substitution Nucleophilic Bimolecular	S_N1 Substitution Nucleophilic Unimolecular
1. Number of steps	It is a single step concerted reaction where the bond formation and bond breakage take place in the same step.	It is two-step process where the first step involves the bond breakage (formation of carbocation) and the second involves the bond formation.
2. Reaction kinetics	The rate of the reaction depends upon the concentration of nucleophile as well as reactant that's why bimolecular (2nd order kinetics).	The slower step is the rate determining step of the reaction which involves only reactant so the rate of the reaction depends upon the concentration of reactant only that's why unimolecular (Ist order kinetics).

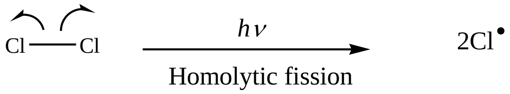
3. **Formation of transition state or intermediate**	It takes place *via* transition state formation which cannot be isolated.	It takes place *via* the formation of carbocation intermediate which can be isolated under freezing conditions.
4. **Nature of the alkyl halide**	It is sensitive to steric factors. The order of the reactivity of alkyl halides is methyl > 1^o > 2^o > 3^o halides.	It is not sensitive to steric factors. The order of the reactivity of alkyl halides is 3^o > 2^o > 1^o > methyl halide which follows the stability of carbocation.
5. **Nucleophilic attack**	The nucleophile exclusively attacks from the back side of the leaving group.	The carbocation is planar in nature so the nucleophile can attack from both the sides of the molecule.
6. **Stereochemistry of the product**	It involves complete inversion of configuration.	In case of optically active alkyl halides, it leads to the formation of racemic mixture.
7. **Rearrangement**	No formation of rearranged products as it is a one step process.	There is formation of rearranged products due to involvement of carbocation.
8. **Nature of nucleophile**	It is favoured by the strong nucleophiles like CN^-, RO^- etc.	It does not depend upon the strength of nucleophile but favoured by mild nucleophiles like H_2O, CH_3COOH.
9. **Concentration of nucleophile**	It is favoured by high concentration of nucleophiles.	It does not depend upon the concentration of nucleophiles.
10. **Polarity of the solvent**	It is favoured by solvents of low polarity or non-polar solvents.	It is favoured by solvents of high polarity
11. **Nature of the leaving group (halide ion)**	It does not depend upon the leaving capacity of halide ion.	The halide should be good leaving group. The order of the reactivity for various halides is I^- > Br^- > Cl^- > F^-.

(b) Give the mechanism of the following reaction:

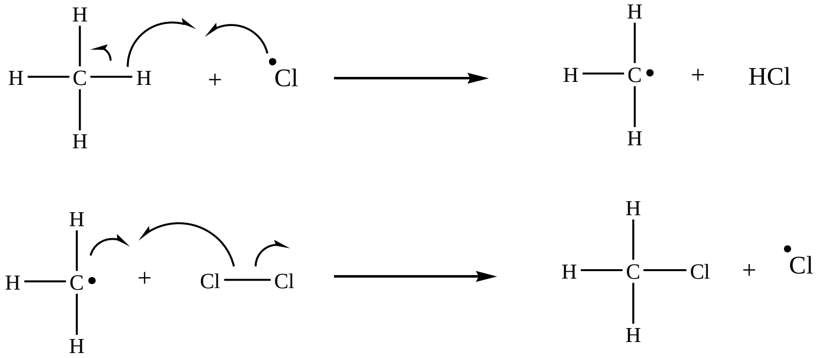
$$CH_4 \quad + \quad 4Cl_2 \xrightarrow{h\nu} CCl_4$$

This is chlorination of methane which proceeds through free radical mechanism. In this methane (CH_4) and Cl_2 is either heated or subjected to UV light which leads to replacement of all the H atoms of methane with -Cl group. A free radical reaction consists of three steps:

1. Chain initiation: When subjected to UV light Cl_2 absorbs energy and undergoes homolytic fission producing chlorine free radicals ($Cl^{\cdot}$).



2. Chain propagation: The chlorine free radical then collides with methane molecule and abstracts hydrogen producing methyl free radical ($CH_3^{\cdot}$) and HCl molecule. The methyl free radical then further reacts with a molecule of chlorine for the formation of methyl chloride (CH_3Cl) and another chlorine free radical.



The above two steps are repeated over and over again and the chain gets propagated. A single photon of light absorbed by Cl_2 can bring about the conversion of a large number of molecules into CH_3Cl. That’s why these reactions are called chain reactions.

When sufficient amount of methyl chloride has been formed, the chlorine free radical produced in chain propagation step has a great possibility of colliding with a molecule of methyl chloride rather than methane. The chloride free radical upon colliding with methyl chloride produces a new free radical (CH_2Cl) which further collides with Cl_2 molecule for the formation of methylene chloride and another free radical. These steps continue till all the hydrogen atoms are substituted by Cl atoms.

$$CH_3Cl + Cl^{\bullet} \longrightarrow {}^{\bullet}CH_2Cl + HCl$$

$${}^{\bullet}CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^{\bullet}$$

$$CH_2Cl_2 + Cl^{\bullet} \longrightarrow {}^{\bullet}CHCl_2 + HCl$$

$${}^{\bullet}CHCl_2 + Cl_2 \longrightarrow CHCl_3 + Cl^{\bullet}$$

$$CHCl_3 + Cl^{\bullet} \longrightarrow {}^{\bullet}CCl_3 + HCl$$

$${}^{\bullet}CCl_3 + Cl_2 \longrightarrow CCl_4 + Cl^{\bullet}$$

3. Chain termination: The chain reactions come to a halt if two same or different free radicals combine without producing new free radicals. For example,

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

$${}^{\bullet}CH_3 + Cl^{\bullet} \longrightarrow CH_3Cl$$