Solved Question Paper-Dec 2018

CHEMISTRY-I

Subject Code : BTCH-101-18

M.Code : 75343

Time:3Hrs.   Max. Marks : 60

SECTION-A

1. Answer briefly :

a) What is fluorescence?

Ans. When a substance is exposed to light or certain other radiations then the phenomenon of re-emitting the energy immediately after the absorption is known as fluorescence.

b) What do you understand by effective nuclear charge?

Ans. The effective nuclear charge is the net positive charge experienced by valence electrons.

 It can be approximated by the equation: $Z_{eff} = Z - S$,

Where Z is the atomic number and S is the number of shielding electrons

c) What is optical activity?

Ans. It is the ability of certain substance to rotate the plane of plane-polarized light as it passes through a crystal, liquid or solution. It occurs only when the substance is asymmetric in nature.

d) What is the essential condition for a molecule to be IR active?

(i) Molecule must have finite dipole moment. If it does not have dipole moment, some of its vibrations must produce an induced dipole moment.

(ii) Frequency of IR radiation must be equal to the vibrating frequency of a particular group or bond in the molecule.

e) Discuss entropy.

Ans. It is the measure of the level of disorder in a closed but changing system in which energy can only be transferred in one direction. Higher the energy means higher the disorderliness of the system.

f) What is the usefulness of Ellingham diagrams?

Ans. In metallurgy, the Ellingham diagram is used to predict the equilibrium temperature between a metal, its oxide, and oxygen — and by extension, reactions of a metal with sulfur, nitrogen, and other non-metals. The diagrams are useful in predicting the conditions under which an ore will be reduced to its metal. It involve the graph between free energy change and Temp.

g) What do you understand by polarizability?

Ans. The power of a cation to distort an anion is called polarizing power or polarisibility

Polarising power is denoted by alpha which is the ratio of induced dipole and electric field.
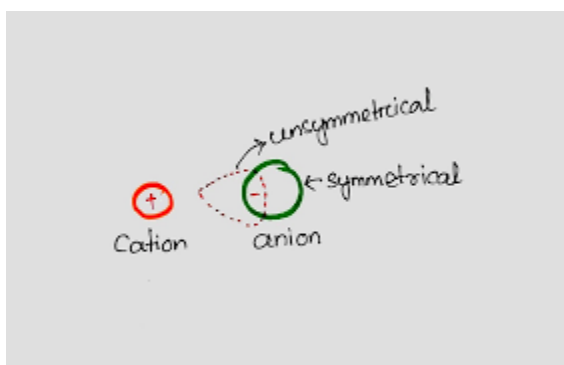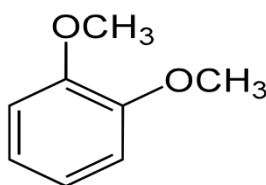

h) Write the electronic configurations for H2 and H2 + in term of molecular orbital theory.

Ans. the electronic configurations for H2 and H2 + in term of molecular orbital theory.
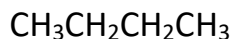
H2 = $(\sigma 1s)^2$

H2$^+$= $\sigma 1s)^1$
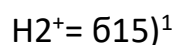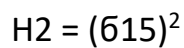
I) How many signals would you expect to see in the 1H NMR spectrum of the following:

It has two kinds of proton so have 2 signals

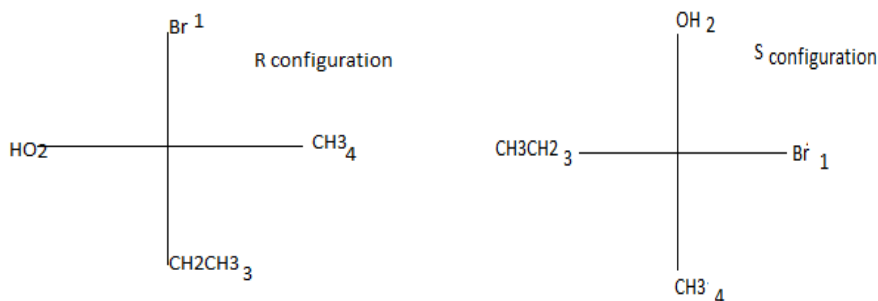It have two kinds of proton so have 2 signals

$$CH_3CH_2CH_2CH_3$$

j) Indicate whether each of the following structures has the R or S configuration. Assign priorities to each group. What is the relationship between the two structures?

Ans.

SECTION-B

Q2 a) Solve the Schrodinger wave equation for a particle in one-dimensional box. (6)

Particle in One Dimensional Box

Schrodinger wave equation is applicable for the translational motion of a particle (electron, atom or molecule) in space.

→ Electron in one Dimensional box is like flow of electron in a wire.

Consider a particle which moves along x-axis between $x=0$ and $x=a$ inside a box. The particle jumps between the walls of the box, but it does not loose energy when collides with the walls, so that energy should be constant.

V = Potential energy
V = Constant
V = ∞ at displacement

Starting Point $x=0$

→ Potential energy is infinite on both sides of the box.

→ Potential energy is constant at the centre (or inside) of the box.

As a particle cannot have infinite or unlimited energy it means it cannot exist outside the box. So ψ is zero for $x \leq 0$ and $x \geq a$.

At the centre (or inside Box)
$$V = 0$$

Inside box Schrodinger's wave equation for one dimensional motion.
$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad —(1)$$

Outside the box $V = \infty$. By putting the value of $V (V=\infty)$ in
$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-\infty)\psi = 0 \quad —(2)$$

$E \to 0$ (as P.E is infinite)

so equation (2) becomes
$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(-\infty)\psi = 0$$

$$\frac{d^2\psi}{dx^2} - \infty \psi = 0$$

$$\frac{d^2\psi}{dx^2} = \infty \psi$$

$$\psi = \frac{1}{\infty}\frac{d^2\psi}{dx^2} = 0$$

So outside the box $\boxed{\psi = 0}$. It means Particle can not go outside the box.

Inside the box $V = 0$. So equation (1) becomes

$$\frac{d^2\psi}{dx^2} + \frac{8m\pi^2 m}{h^2}(E-0)\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \quad —(3)$$

Acc to Quantum Mechanics for a given scale of system E is constant.

So equation (3) becomes
$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \text{where}$$

$$k^2 = \frac{8\pi^2 m}{h^2}E \quad —(5)$$

k^2 is independent of x and constant.

Now Generally
$$\psi = A\sin kx + B\cos kx \quad —(4)$$
For different values of A, B and k ψ have many values.

Applying boundary conditions $\psi = 0$ at $x=0$ and $x=a$

① $\psi = 0$ when $x=0$ equation ④ becomes
$0 = A\sin(0) + B\cos(0)$
$B = 0$

Now equation ④ becomes
$\psi = A\sin kx$ —⑤ when $B=0$

② $\psi = 0$ when $x=a$ equation ⑤ becomes
$0 = A\sin ka$
$\sin ka = 0$

This equation holds good only when values of ka are integral multiples of π i.e.
$ka = n\pi$

$k = \frac{n\pi}{a}$ equation ⑤ becomes

Putting the value of k from ⑥ to ⑤

$$\psi = A\sin\left(\frac{n\pi x}{a}\right) \quad —⑨$$

Expression for Eigen function and hence for Eigen values equation Ⓐ becomes
$$E = \frac{k^2 h^2}{8\pi^2 m} = \left(\frac{n\pi}{a}\right)^2 \times \frac{h^2}{8\pi^2 m}$$

$$E = \frac{n^2 h^2}{8ma^2} \quad n = 1, 2, 3, 4 \ldots \quad —⑩$$

Hence equation ⑨ and ⑩ are the solution of the Schrodinger equation for a particle in a box.

In equation ⑨ value of a is determined by using normalisation of wave function.

$$\int \psi\psi^* d\tau = 1 \quad —⑪$$

$\psi = \psi^*$

Putting the value of ψ from equation ⑨ into ⑪

$$\int_0^a A^2\sin^2\left(\frac{n\pi}{a}x\right)dx = 1$$

$$A^2\int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx = 1$$

$$A^2 \frac{a}{2} = 1$$

$$A = \sqrt{\frac{2}{a}}$$

Hence $\psi = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$

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b) What will happen if the walls of the one-dimensional box are suddenly removed?

Ans. Walls of one dimensional box are suddenly removed then the particle will be free and no external force is acting on it so potential energy of particle will be zero.

. [V=0] in above equation.

Q.3 With the help of a diagram, explain the splitting of d-orbital energy levels in tetrahedral ligand field? Account for the non-existence of tetrahedral complexes with low spin configurations. (6)

Ans. The splitting of fivefold degenerate d orbitals of the metal ion into two levels in a tetrahedral crystal field is the representation of two sets of orbitals as T_d. The electrons in $d_x{}^2\text{-}y^2$ and $d_z{}^2$ orbitals are less repelled by the ligands than the electrons present in d_{xy}, d_{yz}, and d_{xz} orbitals. As a result, the energy of d_{xy}, d_{yz}, and d_{xz} orbital set are raised while that os the $d_x{}^2\text{-}y^2$ and $d_z{}^2$ orbitals are lowered.

- There are only four ligands in T_d complexes and therefore the total negative charge of four ligands and hence the ligand field is less than that of six ligands.
- The direction of the orbitals does not coincide with the directions of the ligands approach to the metal ion.

Thus, the repulsions in tetrahedral coordination compound yield two energy levels:

- t_2– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with higher energy
- e – set of two orbitals ($d_x{}^2\text{-}y^2$ and $d_z{}^2$) with lower energy
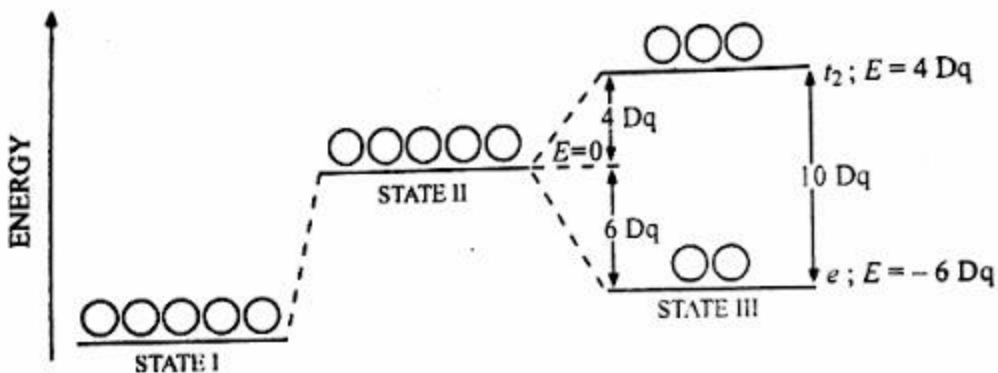
Low spin configurations are rarely observed in tetrahedral complexes. The crystal field stabilisation energy for tetrahedral complexes is lower than pairing energy. Energy gap between the two energy levels i.e. 'e' and 't2' in tetrahedral complex is very low. Almost of that of octahedral complex, so the energy of promotion becomes less expensive than the election pairing energy. Hence electron will always go to higher states avoiding pairing, so low spin tetrahedral complex are not generally formed.

b) Discuss the relationship that exists between crystal field splitting and pairing energy in determining whether a given complex will be high or low spin.

Ans. Filling of d-orbitals takes place in the following manner; the first three electrons are arranged in t_{2g} level as per the Hund's rule. The fourth electron can either enter into t_{2g} level giving a configuration of $t_{2g}^4 e_g^0$ or can enter the e_g orbital giving a configuration of $t_{2g}^3 e_g^1$. This depends on two parameters magnitude of crystal field splitting, Δ_o and pairing energy, P. The possibilities of two cases can better be explained as:

- $\Delta_o > P$ – Electron enters in the t_{2g} level giving a configuration of $t_{2g}^4 e_g^0$. Ligands producing this configuration are known as strong field ligands and form low spin complexes.

- $\Delta_o < P$ – Electron enters in the e_g level giving a configuration of $t_{2g}^3 e_g^1$. Ligands producing this configuration are known as weak field ligands and form high spin complexes.

High Spin and Low Spin

The complexion with the greater number of unpaired electrons is known as the high spin complex, the low spin complex contains the lesser number of unpaired electrons. High spin complexes are expected with weak field ligands whereas the crystal field splitting energy is small Δ. The opposite applies to the low spin complexes in which strong field ligands cause maximum pairing of electrons in the set of three t_2 atomic orbitals due to large Δ_o.

- High spin – Maximum number of unpaired electrons.
- Low spin – Minimum number of unpaired electron

Q.4 Discuss the principle of electronic spectroscopy. Explain with reference to CH2=CH2, 1, 3- butadiende and carbonyl compounds. (6)

Ans. Basically, electronic spectroscopy is an analytical technique to study electronic structure and dynamics in atoms and molecules. When any excitation source such as X-rays, or any other it will eject an electron from an inner shell of an atom. i.e. it is based upon the phenomenon of photo electric emission.

In case of carbonyl compounds whose absorption range is 1760-1665 cm-1 due to stretching vibration of c = 0 band. It has characteristic high intensity and a few other functional groups in this region. Exact wave number of c=0 stretch can give us clues as to whether the compound is ketone, aldehyde or carboxylic acid.

In case of ethane band intensities is 640-3260 cm-1. The probable transition occurs from $\pi \rightarrow \pi^*$ at 170-190 nm.

In case of 1,3- butadiene absorption range at 217 nm. Which is in u.v.ddz range. This corresponds to a $\pi \rightarrow \pi^*$ transition.

b) What is fluorescence? Discuss its applications in medicine.

Ans. When a substance is exposed to light or certain other radiations then the phenomenon of re-emitting the energy immediately after the absorption is known as fluorescence.

(i) The structure of protein can be studied by measuring the closeness of fluorescent groups in protein.
(ii) It is used in fluorescent microscope and X-ray diagnosis.

(iii) It is also used in determination of uranium in salts in field of nuclear research.

## Q5 a) What are van der Waals forces? Discuss them briefly.

Ans. Van der Waals forces -Van der Waals forces are driven by induced electrical interactions between two or more atoms or molecules that are very close to each other. Van der Waals interaction is the weakest of all intermolecular attractions between molecules

The Following types of intermolecular forces exist between the molecules of different substances:

1. Dipole-Dipole Interactions

2. Dipole –Induced Dipole Interactions (London Dispersion Forces)

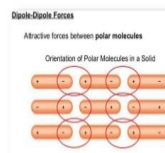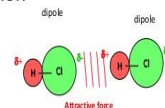3. Ion –Dipole Interactions

4. Ion-Induced Dipole Interactions

Types of intermolecular forces:

1. Dipole-Dipole interactions -These Interactions result when two dipolar molecules interact with each other through space. When this occurs, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second polar molecule. This type of interaction between molecules accounts for many physically and biologically significant phenomena such as the elevated boiling point of water.
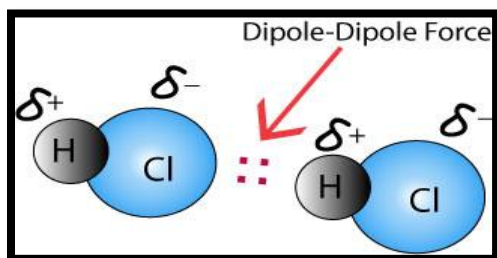
Dipole-Dipole Attraction
- Attractive forces that exist between molecules that have permanent dipoles.
- These exist in any polar substance.
- Weaker than Ion-Dipole force
- Increased polarity, stronger dipole-dipole attraction

2. Dipole –Induced Dipole Interactions (London Dispersion Forces):

The London dispersion force is the weakest intermolecular force. The London dispersion force is a temporary attractive force that results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles. This force is sometimes called an induced dipole-induced dipole attraction.

These forces are weaker than other intermolecular forces and do not extend over long distances. The strength of these interactions within a given molecule depends directly on how easily the electrons in the molecules can move (i.e., be polarized). Large molecules in which the electrons are far from the nucleus are relatively easy to polarize and therefore possess greater dispersion.
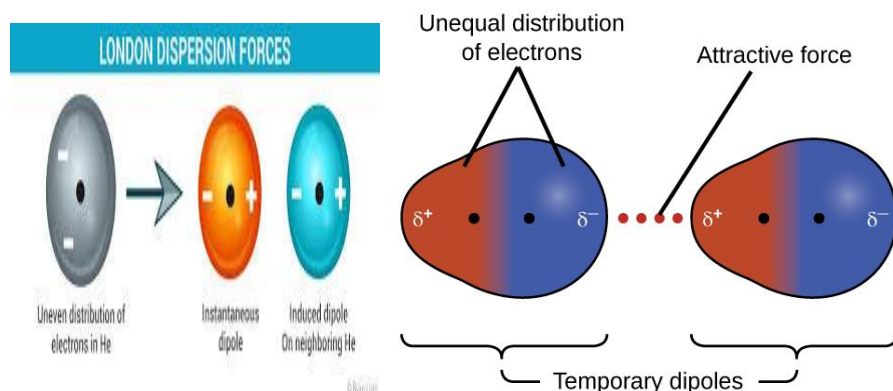
3. Ion-Dipole Interaction

Ion-dipole interaction occurs when an ion encounters a polar molecule. In this case, the charge of the ion determines which part of the molecule attracts and which repels. A cation or positive ion would be attracted to the negative part of a molecule and repelled by the positive part. An anion or negative ion would be attracted to the positive part of a molecule and repelled by the negative part.

Example: An example of the ion-dipole interaction is the interaction between a Na^+ ion and water (H_2O) where the sodium ion and oxygen atom are attracted to each other, while the sodium and hydrogen are repelled by each other.

Example: When NaCl is mixed with water in a beaker, the polar H_2O molecules are attracted to the sodium and chloride ions in the beaker. The strength of this interaction depends on:

- The magnitude of the <u>dipole moment</u>
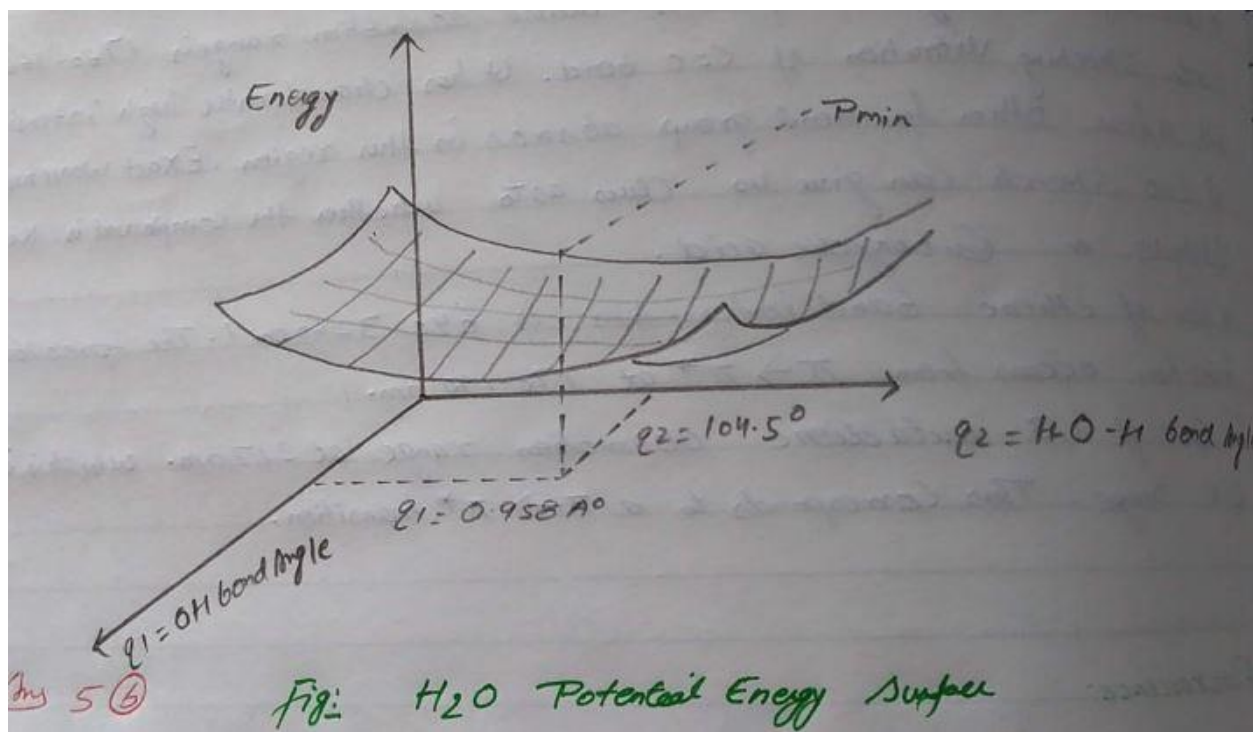- Size of the polar molecule
- The size and charge of an ion

4. Ion Induced Dipole Interactions

In this type of interaction, a non-polar molecule is polarized by an ion placed near it. The non-polar molecules, upon obtaining a charge, behave as induced dipoles. This interaction between an ion and an induced dipole is known as ion-induced dipole interaction.

b) What do you understand by potential energy surface? Explain with an example.

Ans. It is a mathematical function that gives the energy of a molecule as a function of its geometry. Energy as a function of one or more coordinates is defined.If there is only one coordinate the system is called as pot. energy surface or curve. Vaues of energies of a system depends on the degrees of freedom.Pot. energy surfaces are of two types repulsive and attractive

In case of H_2O the geometry is defined by two bond length and a bond angle. Bond length is the same then the graph of E versus two geometric parameters q1=O-H bond length q2= the H-O-H bond angle will represent the potential energy surface of water.

Fig: H_2O Potential Energy Surface

(Labels on figure: Energy; Pmin; $q_2 = 104.5°$; $q_2 = H-O-H$ bond Angle; $q_1 = 0.958 A°$; $q_1 = OH$ bond Angle; Ans 5(b))

SECTION-C

Q6 a) Calculate the solubility product of AgBr in water at 25°C from the cell : +
Ag,Ag Br | AgBr , Ag (sat.soln.) (s) + 0.07 ; 0.80 ==The standard potentials are E
V E V AgBr Ag Ag Ag , , (4)

Ans. AgBr(S) +e⁻   Ag(s) +Br⁻(aq) ; E^0 R=0.07 V

Ag(s) ⟶   Ag⁺(aq) +e⁻ ; E^0 L=0.80 V

Overall reaction

AgBr(S)⟶   Ag⁺(aq)+ Br⁻(aq)

E^0 = E^0 R- E^0 L

-0.73 V

Nerst equation

0.0591 log [(Ag⁺)(Br⁻)]

=0.059   log Ksp

=log Ksp=E^0/0.0591

=-0.73V/0.0591

Ksp=4.81×10^{-11}

b) What advantages does the use of "ion-exchange resin" provide over "zeolite process" for softening of hard water?

Ans. Advantages of ion exchange method over zeolite method

Zeolite method replace ca2+ and mg2+ ions by Na+ ions but all acidic impurities eg: HCo3- and Co32- are present as such. But in case of ion exchange resin, even these impurities are also removed properly.

Soft water produced by zeolite method has 10-15 ppm hardness which can't be used in high pressure boiler, but by ion exchange method water of hardness as low as 2 ppm is obtained which can be used in high pressure boilers.

Gases can also be removed by ionexchange which cannot be removed in zeolite process

Ion exchangers are more effective in removing hardness rather than zeolite

Q7 a) Explain the concept of hard soft acids and bases. (4)

Ans. Hard Soft Acids and Bases (HSAB) Principle is a qualitative concept introduced by Ralph Pearson to explain the stability of metal complexes.
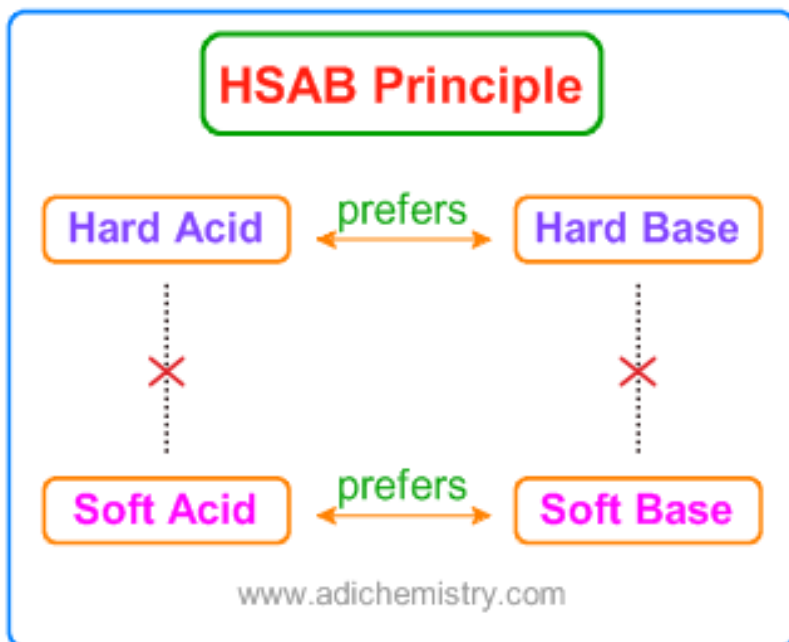
❖ The large electronegativity differences between hard acids and hard bases give rise to strong ionic interactions.

❖ The electronegativities of soft acids and soft bases are almost same and hence have less ionic interactions. i.e., the interactions between them are more covalent.

❖ The interactions between hard acid - soft base or soft acid - hard base are mostly polar covalent and tend to be more reactive or less stable. The polar covalent compounds readily form either more ionic or more covalent compounds if they are allowed to react.

Applications of Hard/Soft Theory

1. Stability of a complex –

A complex would be more stable if metal and ligand, both are hard or soft.

eg – 1. AgI_2^- is stable but AgF_2^- is not.

$Ag^+ + 2I^- \rightarrow AgI_2^-$
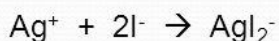
SA   SB   Stable complex

$Ag^+ + 2F^- \rightarrow AgF_2^-$

SA   HB   Unstable

2. $[CoF_6]^{3-}$ is more stable than $[CoI_6]^{3-}$

    HA-HB   HA-SB

b) Discuss the geometry of the following : BF_3, H_2O

Ans. BF3=trigonal plannar . Central atom boron has three valence electron. At the time of formation of BF3 molecule, each electron in valence shell of B. atom forms a bond pair with F. atom. As a result, the control boron atom is surrounded by three bond pairs and molecule adopts trigonal planar geometry.Bond angle is 120 degree

H_2O molecule is bent or regular. The central atom O of water has six valence electrons. The bond angle in H20 molecule is 104.5

Geometry of BF₃ Molecule

Trigonal Planar
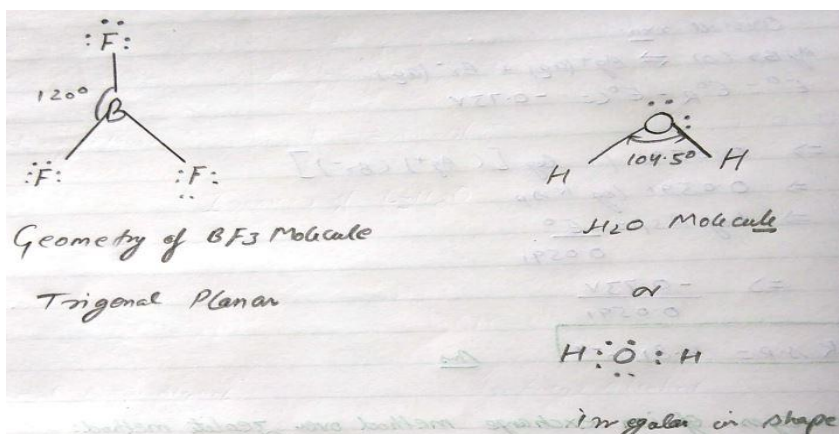
H₂O Molecule

Q.8 What is optical activity? What is the essential condition for a compound to be optically active? Explain. (4)

Ans. Optical activity is the ability of a chiral molecule to rotate the plane of plane-polairsed light, measured using a polarimeter. A simple polarimeter consists of a light source, polarising lens, sample tube and analysing lens.
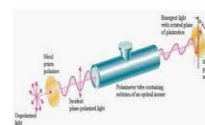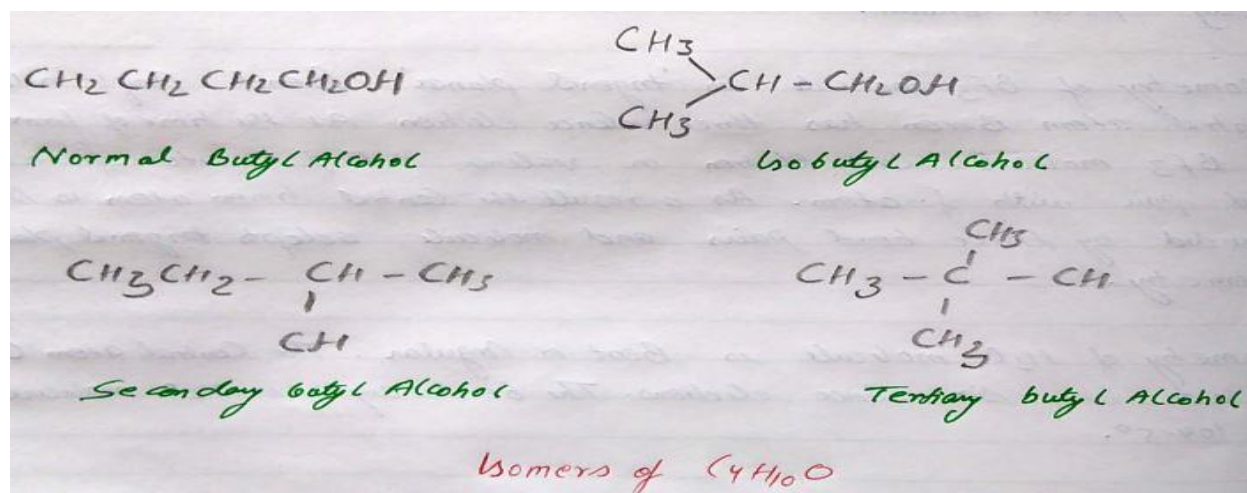

- It should have a chiral carbon centre with all four groups different.
- Compound and its mirror should be non-super imposable.
- Molecule should not have any plane of symmetry.

b) Draw structural isomers for C3H8O and C4H10 ?

Ans. Isomers of C3H8O

Isomers of C3H8O

Isomers of C4H10

$CH_2 CH_2 CH_2 CH_2OH$

Normal Butyl Alcohol

$CH_3 CH_2 - CH - CH_3$
$\qquad\qquad |$
$\qquad\qquad CH$

Secondary Butyl Alcohol

CH_3
$\quad \searrow CH - CH_2OH$
CH_3

Isobutyl Alcohol

$\qquad\qquad CH_3$
$\qquad\qquad |$
$CH_3 - C - CH$
$\qquad\qquad |$
$\qquad\qquad CH_3$

Tertiary butyl Alcohol
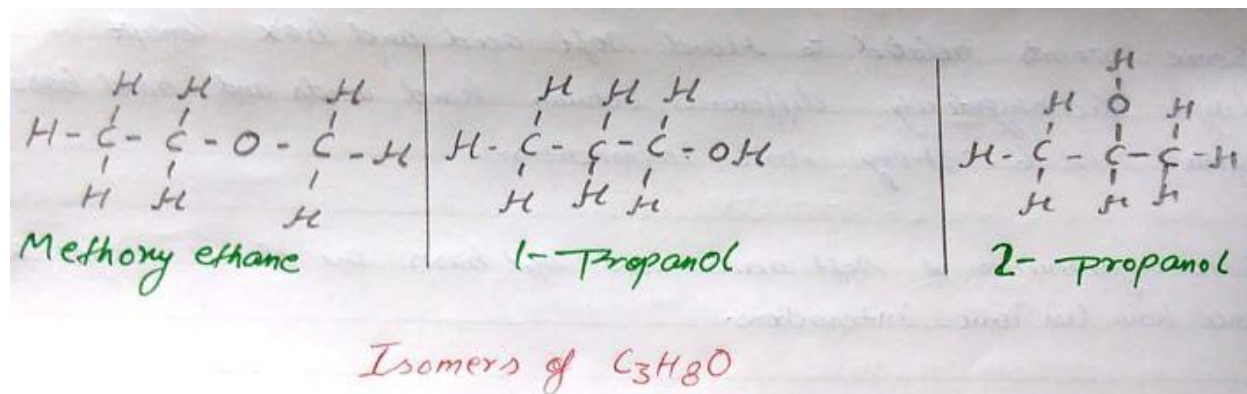
Isomers of C4H10O

Q9 a) Discuss the synthesis of a commonly used drug molecule by taking a suitable example. (3)

Ans. Preparation of Aspirin

It act as an anti analgesic, antipyretic and anti-inflammatory drug.

Aspirin is used to treat pain like headache, muscle pain, toothache and also used to reduce fever or inflammation in case of arthritis. It is sometimes used to treat or prevent heart attacks, strokes, and chest pain (angina).

Aspirin is synthesized by using acetylation reaction which follows electrophillic substitution mechanism in which electrophile attack on the molecule.

Two types of acetylating agents are used to synthesis Aspirin: Acetic anhydride and Acetyl chloride
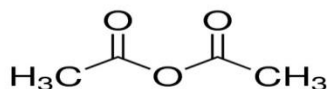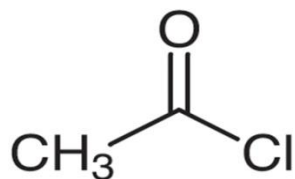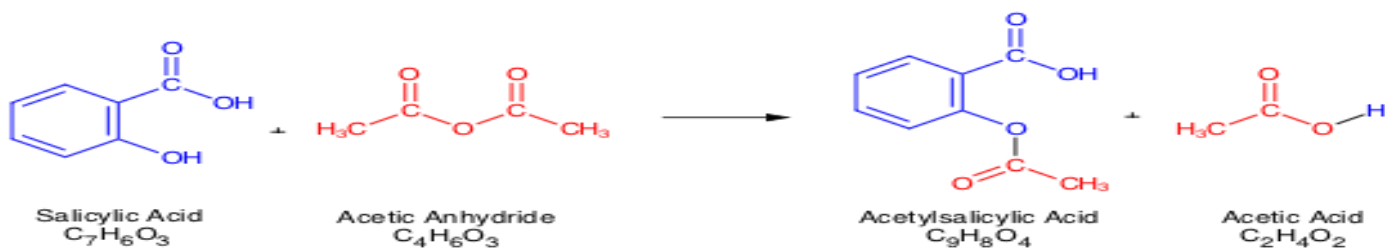

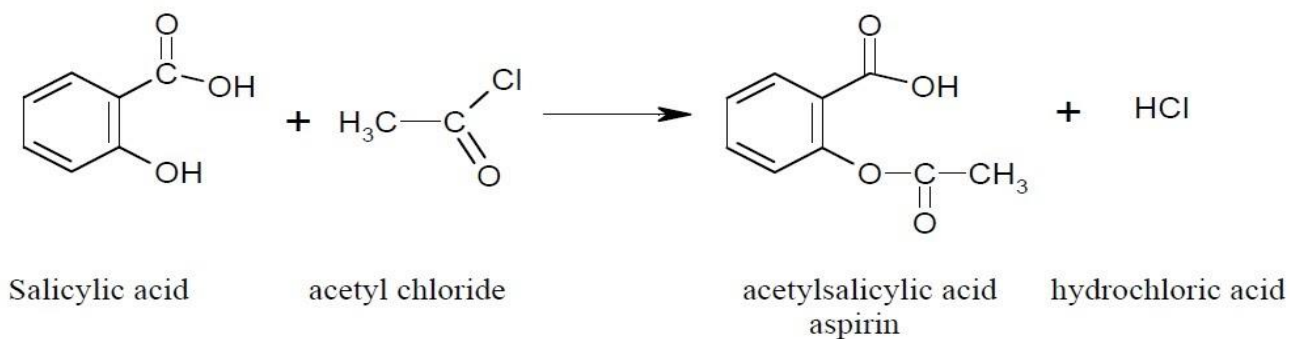Acetyl chloride   acetic anhydride

Types of acetylation:

One is with acetic anhydride and second with acetyl chloride

1. Using acetic anhydride

Salicylic Acid $C_7H_6O_3$ Acetic Anhydride $C_4H_6O_3$ Acetylsalicylic Acid $C_9H_8O_4$ Acetic Acid $C_2H_4O_2$

2. using acetyl chloride   PYRIDINE

Salicylic acid   acetyl chloride   acetylsalicylic acid aspirin   hydrochloric acid

- APPARATUS USED: beaker, measuring cylinder, conical flask, ice cubes, glass rod, filter paper, weighing balance, funnel, Hot plate, thermometer and oven.

- CHEMICALS REQUIRED:

1. Acetylation with acetic anhydride

a) Salicylic acid = 5 gm

b) Acetic anhydride = 8 ml

c) Conc. H_2SO_4 = 2-3 drops   RESULT=yield=11 g

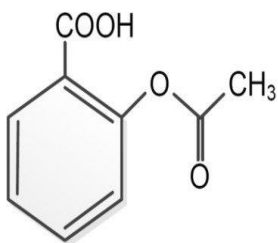1. Acetylation with acetyl chloride

a) Salicylic acid = 5 gm

b) Pyridine = 4 ml

c) Acetyl chloride = 4 ml   RESULT=yield = 10 g

Structural formula of Aspirin

Aspirin is obtained by the acetylation of Salicylic acid (o-hydroxy benzoic acid) with acetic anhydride or acetyl chloride in the presence of little concentrated sulphuric acid or pyridine respectively

PROCEDURE:

Acetylation with acetic anhydride

1. Place 5 gm of salicylic acid and 7 ml of acetic anhydride in a small absolutely dry conical flask.
2. Add 2-3 drops of conc. H_2SO_4 and rotate the flask for through mixing.
3. Warm the conical flask on a water bath to about 50-60ºC, while shaking, for about 15 minutes.
4. Allow the mixture to cool and stir occasionally.
5. Add about 80 ml of water, stir well and filter at the pump.
6. Recrystallize the crude product from a mixture of equal volume of Hot water and ethanol.

Melting point = 136-137ºC.

b) Discuss the SN2 mechanism of alkyl halides in terms of kinetics, stereochemistry and reactivity of alkyl halides.

Ans. Bimolecular nucleophilic Substitution Reactions:

What is an S_N2 Reaction?

The S_N2 reaction is a nucleophilic substitution reaction where a bond is broken and another is formed simultaneously. Two reacting species are involved in the rate determining step of the reaction. The term 'S_N2' stands for – Substitution Nucleophilic Bimolecular.

S_N2 Reaction Mechanism:

This reaction proceeds through a backside attack by the nucleophile on the substrate. The nucleophile approaches the given substrate at an angle of 180° to the carbon-leaving group bond. The carbon-nucleophile bond forms and carbon-leaving group bond breaks simultaneously through a transition state.

Now, the leaving group is pushed out of the transition state on the opposite side of the carbon-nucleophile bond, forming the required product. It is important to note that the *product is formed with an inversion of the tetrahedral geometry at the atom in the centre.*

The S_N2 reaction mechanism for the nucleophilic substitution of chloroethane with bromine acting as the nucleophile is illustrated below.
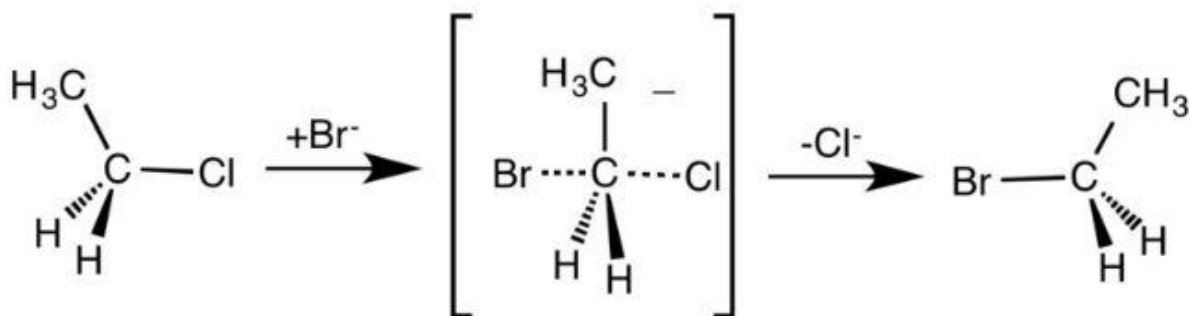
- SN2 reactions are

- bimolecular with simultaneous bond-making and bond-breaking steps.

- SN2 reactions do not proceed via an intermediate.

- SN2 reactions give inversion of stereochemistry at the reaction centre. Steric effects are particularly important in SN2 reactions.