Time: 3 Hours   Max. Marks: 70

Instructions: *1) The question paper has two parts. Answer both the parts.*
2) Draw diagrams and write chemical equations wherever necessary

PART-A

Answer **any eight** of the following (8 X 2 = 16)
1. State Heisenberg's uncertainty principle
2. Write radial probability distribution curve for 1s electron.
3. Explainthe significance of wave function?
4. Define lattice energy.
5. What is inter-molecular hydrogen bonding? Give an example
6.How the electrical property of semi-conductors is explained based on band theory.
7. Cu^{2+} ion is coloured but Zn^{2+} ion is colourless. Give reason.
8. Explain Etard's reaction with an example.
9. How naphthalene is converted into phthalic acid. Give the equation.
10. Explain Huckel's rule of aromaticity with cyclopentadienyl anion as an example.
11. What is elimination reaction? Give an example
12. Give any two applications of neon

PART-B

Answer **any nine** of the following questions. (9 x 6 = 54)

13. a) Derive an expression for the energy of the first Bohr orbit in hydrogen atom
b) Define the term orbital in an atom. (4 + 2)

14. a) Explain the terms (i) Hamiltonian operator (ii) Laplacean operator.
b) Give any two limitation of Bohr's theory of atomic structure. (4 + 2)

15. a) What are quantum numbers? Explain their significance.
b) Calculate the wavelength of the wave associated with an electron moving with velocity $4.0 \times 10^6 \ ms^{-1}$, electronic mass $= 9.1 \times 10^{-31}$ kg, h $= 6.63 \times 10^{-34}$ Js. (4 + 2)

16. a) Set up Born-Haber's cycle for the formation of NaCl. Compute the calculation of lattice energy using this cycle.
b) Write the molecular electronic configuration of O_2 molecule. Predict its magnetic property.   (4 + 2)

17. a) Explain the shape of ammonia molecule based on VSEPR theory. -
b) Calculate the bond order of He_2^{+} ion. $(4 + 2)$

18. a) Explain SP^3 hybridization with $SiCl_4$ as example.
   b) Mention any two properties of ionic compounds. $(4 + 2)$

19. a) How does XeO_3 react with i) water ii) alkali
b) State and Explain Fajan's rule. $(4 + 2)$

20. a) What are Zeolites? Explain the molecular sieve property and base exchanger property of Zeolites.
b) What are interstitial compounds? $(4 + 2)$

21. a) Give reasons for the following: i) Transition metal ions form colored compounds.
                                    ii) Transition metal exhibits variable oxidation state.
b) Calculate the magnetic moment of Cr in Potassium dichromate. $(4 + 2)$

22. a) Describe ion exchange method for the separation of lanthanides.
b) What are transuranic elements? Give examples. $(4 + 2)$

23. a) Explain the orienting influence of nitro group in nitrobenzene towards electrophilic substitution reaction.
b) What is Ullmann's reaction? Give an example. $(4 + 2)$

24. a) Discuss the structure of benzene on the basis of molecular orbital theory.
b) Give a method for the preparation of Stilbene. $(4 + 2)$

25. a) Explain SN1 mechanism with an example.
b) Explain Saytzeff's rule with an example. $(4 + 2)$

CHEMISTRY –II
Model question paper-I- answers

1. State Heisenberg's uncertainty principle

Ans: It is impossible to know simultaneously both the velocity (momentum) and the position of the electron accurately. Also, the more precisely one of them is determined the more uncertain the other one becomes.

$$\Delta p \text{ X } \Delta x \geq h/4\pi$$

Where $\pm \Delta p$ is the uncertainty in measuring he momentum and $\pm \Delta x$ is the uncertainty in the position

2. Write the radial probability distribution curve for 1s electron.

Ans: Radial probability distribution of electron is obtained by plotting $4\pi^2 r^2 \varphi^2$ against distance from nucleus in case of 1selectron. The maximum in the graph indicates radius of maximum probability of electron. In case of H, it is 0.529Å
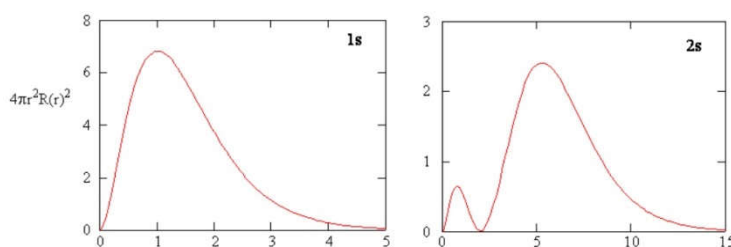
Diagram:

3. Explainthe significance of wave function?

Ans: The wave function ψ in schrodinger equation by itself has no significance except that it represent the amplitude of electron wave. Square of the wave function (ψ^2) gives the probability of finding an electron of a given energy E at a particular place around the nucleus. Thus it is possible to identify the space around the nucleus where there is a high probability of finding an electron with specific energy.

4. Define lattice energy.

Ans: lattice energy, U is defined as the enthalpy of formation of a mole of an ionic solid from free gaseous ions brought from infinity to their respective equilibrium sites in their crystalline lattice under standard conditions. It may also be defined as the change in energy that occurs when an ionic solid is separated into isolated ions in gas phase.

5. What is inter molecular hydrogen bonding? Give an example

Ans: A linking together of number of different molecules by hydrogen bonding is known a inter molecular hydrogen bonding.

Examples-HF, H_2O, NH_3, ROH etc

**6. Howthe electrical property of semi-conductors is explained based on band theory.**

Ans: In insulators and semiconductors the Fermi level is inside a band gap; however, in semiconductorsthe bands are near enough to the Fermi level to be thermally populated with electrons or holes. Semiconductors are defined by their unique electric conductive behavior, somewhere between that of a metal and an insulator.

7. Cu^{2+} ion is coloured but Zn^{2+} ion is colourless. Give reason.

Ans: Electronic configuration of Cu is $3d^{10} 4s^1$, valence electron of copper in Cu^{2+} is $3d^9$, number of unpaired electron is 1, and therefore it undergoes d-d transitions by absorption of energy in the visible region, so it is coloured whereas Electronic configuration of Zn is $3d^{10}$ $4s^2$, valence electron of zinc in Zn^{2+} is $3d^{10}$ number of unpaired electron is 0 and therefore it does not undergoes d-d transitions so it is colourless.
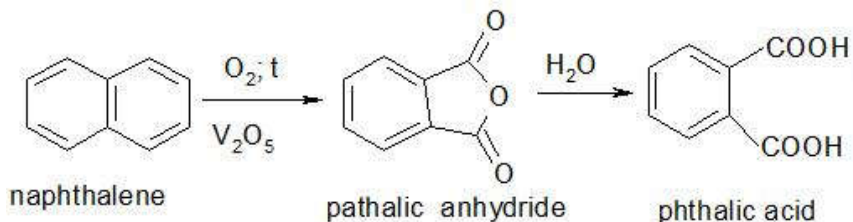
8. Explain Etard's reaction with an example.

Ans: Toluene on mild oxidation with an oxidant such as chromyl chloride gives benzaldehyde it is called Etard's reaction.
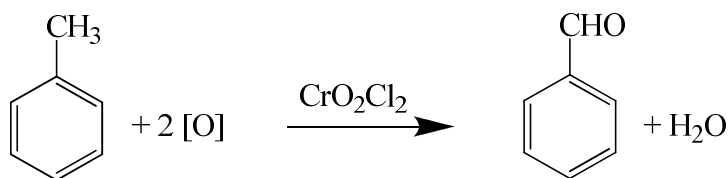

9. How naphthalene is converted into phthalic acid. Give the equation.

Ans: Potassium permanganate in acid solution or V_2O_5 oxidises naphthalene into phthalic acid.

10. Explain Huckel's rule of aromaticity with cyclopentadienyl anion as an example.

Ans: Huckel's rule = $(4n+2)\pi$ electrons where n = 0,1,2…..In case of cyclopentadienyl anion n=1. $(4n+2)\pi = (4x1+2)\pi = 6\pi$ electrons. Therefore it is aromatic.
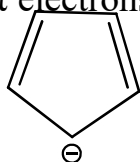
11. What is elimination reaction? Give an example.

Ans: An elimination reaction is one in which a molecule loses two atoms or groups, without being replaced by other atoms or groups.

　　Example: $CH_3CH_2Br + a/c\ KOH \rightarrow CH_2=CH_2$
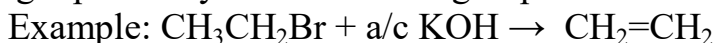
12. Give any two applications of neon.

Ans: Electrical discharge tubes, vacuum tubes, high voltage indicators, television tubes, helium-neon lasers, liquefied neon is used in cryogenic refrigerant etc.

PART-B

Answer any nine of the following questions. $(9 \times 6 = 54)$

13. a) Derive an expression for the energy of the first Bohr orbit in hydrogen atom.   4m

Ans: Bohr pictured the hydrogen atom as a system containing a single electron with charge 'e'. It rotates in a circular orbit of radius 'r' around a nucleus of charge Ze, Z is the effective charge of the nucleus or the atomic number.

We know that, $r = \varepsilon_o n^2 h^2/\pi m e^2 z$ and $v^2 = Ze^2/4\pi\varepsilon_o mr$, $KE = \frac{1}{2} mv^2$, $PE = Ze^2/4\pi\varepsilon_o r$ 1m

 $KE = 1/2m(Ze^2/4\pi\varepsilon_o mr) = Ze^2/8\pi\varepsilon_o r$

Total energy $E = Ze^2/8\pi\varepsilon_o r - Ze^2/4\pi\varepsilon_o r$ 1m

  $E = - Ze^2/8\pi\varepsilon_o r$ 1m

Substituting for the value of r

$E = -Z^2 e^4 m/8\varepsilon_o^2 h^2 n^2$ for the 1st Bohr orbit, n=1, then, $E = -Z^2 e^4 m/8\varepsilon_o^2 h^2$ 1m

b) Define the term orbital in an atom.   2m

Ans: The 3d space around the nucleus where the probability of finding the electron is maximum.

14. a) Explain the terms   4m

(i) Hamiltonian operator: the total energy of a sysyem is equal to the sum of kinetic and potential energies in classical mechanics. This is generally written as H

$$H = E_k + E_p$$

   The corresponding operator is $\hat{H}$, called as Hamiltonian operator.

$$\hat{H}\psi = E\psi$$
$$H = (-h^2/8\pi^2 m)\,\nabla^2 + E_p$$

   Where H is representing the total energy of the system, E – numerical value of energy

(ii) Laplacean operator: it is the second order differential operator in three dimensional spacial coordinate. It is denoted by ∇.

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

b) Give any two limitations of Bohr's theory of atomic structure.   2m

Ans: Any two of the following:

1.It fails to explain the spectra and energy of atoms containing more than one electron.

2. It predicts the origin of only one spectral line from an electron between any two energy states but multiple or fine structure of spectral lines remains unexplained.

3. This theory has no explanation for splitting of spectral lines in electric field (stark effect) and in magnetic field (Zeeman effect).

4. The magnitude of energies of the stationary states in atom containing more than one electron cannot be accurately calculated by the application of bohr's theory

5. It does not throw light on the arrangement and distribution of electrons in atoms other than hydrogen.

6. A great drawback of this theory is its ability to explain molecule formation.

15. a) What are quantum numbers? Explain their significance.   4m

Ans: Quantum numbers are used to describe the distribution of electrons in an atom. The solution of schrodinger wave equation for the hydrogen atom is characterized by 3 integral values n,l,m which are designated as principal, azimuthal, and magnetic quantum numbers. These quantum numbers are the identification numbers for the electron in an atom as they fully describe the position and energy o an electron in the atom.

Principal quantum number (n): this signifies the energy level or the principal shell to which on electron belongs. It is denoted by 'n' which takes integral values 1,2,3………… the letters K,L,M,N,…… are also used.

Azimuthal or angular momentum quantum number (l): this gives the angular momentum of the electron in its processional momentum around the nucleus. It gives the shape of the orbital. Since the angular momentum depends on the kinetic energy, the valueof this quantum number depends on the value of n. it can take values $l = 0$ to (n-1) for a given value of n. the azimuthal quantum numbers $l = 0,1,2,3$ are symbolized by s,p,d and respetively.

Magnetic quantum number (m) : In the presence of a magnetic field the orbital motion of the electron orient itself in the different directions. The component of the angular momentum vector along the directions of the applied field has quantized values called magnetic quantum numbers. Thus the values of 'm' depend upon the magnitude of 'l'. For a particular value of 'l' , 'm' takes$(2l + 1)$ values ranging from $-l$ to $+l$incliding zero.

Spin quantum number: it explains the multiplets in the spectrum. Electron not only moves in an orbit around the nucleus but also spins on its own axis. The angular momentum due to spin can have only 2 valurs $+1/2$ or $-1/2$ depending upon clockwise or anti-clockwise spinning motions.

b) Calculate the wavelength of the wave associated with an electron moving with velocity 4.0 x 10^6 ms^{-1}, electronic mass = 9.1x 10^{-31} kg, h = 6.63 x 10^{-34}Js.   2m

Ans: $\lambda = h/mv$

v = 6.63 x 10^{-34}Js/(9.1x 10^{-31} kg x 4.0 x 10^6 ms^{-1}) = 1.8 x 10^{-10}m = 0.18 nm.

16. a) Set up Born-Haber's cycle for the formation of NaCl. Compute the calculation of lattice energy using this cycle.4 m
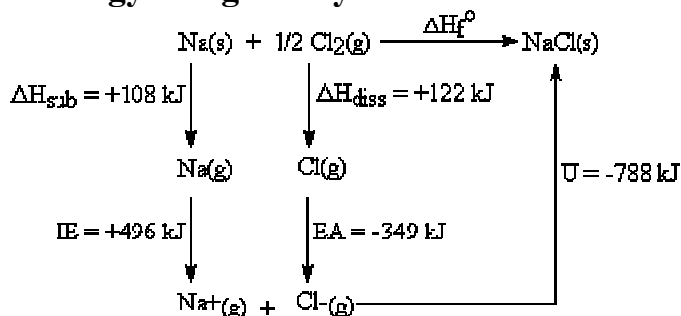
$\Delta H_f^\circ = \Delta H_{sub} + IE + \Delta H_{diss} + EA + U$

Ans: $\Delta H_f^\circ = 108 + 496 + 122 - 349 - 788 = -411$ kJ/mole
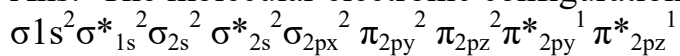
$$\Delta H_f = \Delta H_s + I + 1/2\Delta H_d + E.A + U$$
$$\text{Lattice energy, } U = \Delta H_f - \Delta H_s - I - 1/2\Delta H_d - E.A$$

$$U = -411 - 108 - 496 - 122 + 349)$$
$$U = -788 KJ/mol.$$

b) Write the molecular electronic configuration of O_2 molecule. Predict its magnetic property.

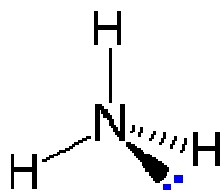Ans: The molecular electronic configuration of O_2 molecule is

$\sigma 1s^2 \sigma^*{}_{1s}{}^2 \sigma_{2s}{}^2 \sigma^*{}_{2s}{}^2 \sigma_{2px}{}^2 \pi_{2py}{}^2 \pi_{2pz}{}^2 \pi^*{}_{2py}{}^1 \pi^*{}_{2pz}{}^1$

Bond order $= [(10-6)/2] = 2$

There are two unpaired electrons. Thus it is paramagnetic in nature,

17. a) Explain the shape of ammonia molecule based on VSEPR theory.4 m

Ans: In NH_3, the central N atom has four electron pairs in the outer shell. A regular tetrahedral configuration with a bond angle $109°28'$ is expected but actual bond angle is $107°$. One of the orbitals has a lone pair of electrons. According to VSEPR theory, the force of repulsion between a lone pair and bonded pairs is more than the force of repulsion between two bonded pair of electrons. This results in the lone pair causing the three bonded pairs to be pushed closer together which decreases the bond angle from $109°28'$ to $107°$ and the shape of molecule is pyramidal in which he nitrogen atom lies at the centre, the three H atoms form the base while the lone pair forms apex of the pyramid.


b) Calculate the bond order of He^{2+} ion.   **2m**

The molecular electronic configuration of He^{2+} molecule is $\sigma 1s^2 \sigma^*{}_{1s}{}^1$.

The bond order $= \frac{1}{2}(N_b - N_a) = (2-1)/2 = 0.5$

18. a) Explain SP^3 hybridization with $SiCl_4$ as example. 4m

Ans: The electronic configuration of silicon in its ground state is $1s^2 2s^2 2p^6 3s^2 3p^2$ with two unpaired electrons. In excited state, paired electron from 3s orbital is shifted to empty 3p orbital. It has four unpaired electron i.e, one 3s and three 3p orbitals undergoes sp^3 hybridization. Sp^3 hybrid orbitals of silicon with one electron overlap with 2p orbital of Cl atoms to form four Si-Cl bonds. The molecule is tetrahedral with a bond angle $109°28'$.
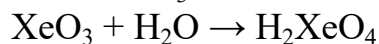
Structure:
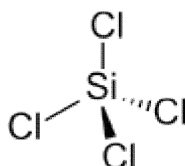
b) Mention any two properties of ionic compounds. **2m**
Ans: Any two of the following:
1.Very stable, have high melting and boiling point.
    2. Hard and brittle.
    3. Good conductors of electricity in molten stateand in aqueous solution.
    4. Soluble in polar solvents.

19. a) How does XeO_3 react with i) water ii) alkali 4m
Ans: i) with water: XeO_3 reacts with water gives xenic acid
$$XeO_3 + H_2O \rightarrow H_2XeO_4$$
ii) With alkali: XeO_3 reacts with alkali undergoes disproportionation to give perxenate ion.
$$4XeO_3 + 12\ OH^- \rightarrow Xe + 3\ XeO_6^{4-} + 6H_2O$$
$$4XeO_3 + 12\ NaOH \rightarrow Xe + 3\ Na_4XeO_6 + 6H_2O$$

b) State and explain Fajan's rule.   **2m**
Ans: i) A small positive ion favourscovalency. In small positive ion, the charge density is more and ion is highly polarizing and very good at distorting the negative ion.
ii) A large negative ion favourscovalency. In a large negative ion, the outermost electrons are shielded from the nucleus by the inner core of electron and are highly polarizable.
iii) Large charge on either or both ions favourscovalency. A high charge increases the extent of polarization.
iv)Polarization and hence covalency is favoured when the positive ion does not have noble n gas configuration.

20. a)What are Zeolites? Explain the molecular sieve property and base exchange property of Zeolites.   **4m**
Ans: Zeolites are alumino silicates having general formula $M_{x/n}[(AlO_2)_x(SiO_2)_y]zH_2O$
Where M is a cation like Na^+, K^+, Ca^{2+}.
They have a three dimensional network with a honey comb like structure. In zeolites the cations move freely the open pore structure and can be exchanged with other cations. The presence of open pore structure makes zeolites acts as base exchanger. Example - softening of hard water. Certain zeolites are used to exchange calcium ions present in hard water.
Zeolites acts as molecular sieves because the open channels have diameters in the range of 40-70nm. These channels absorbs gases other water vapours. The cross section of these channels is used to separate gaseous mixture.
Base exchange property: The hydrogen form of zeolites (prepared by ion-exchange) are powerful solid-state acids, and can facilitate a host of acid-catalyzed reactions, such as isomerisation, alkylation, and cracking. The specific activation modality of most zeolitic catalysts used in petrochemical applications involves quantum-chemical Lewis acid site reactions.

b) Write a note on interstitial compounds? **2m**

Ans: Interstitial compounds are the compounds where small non-metallic atoms like H, B, C, N etc are able to fit into the interstitial sites of transition metal lattices. These are non-stoichiometric compounds.

Example: $TiH_{1.8}$, $ZrH_{1.9}$, $VH_{1.6}$ etc.

21. a) Account for the following: **4m**

i) Transition metal ions form colored compounds.

   Transition elements form coloured compounds in solid state and in solution. It is due to the presence of incompletely filled d orbitals. In the transition metals, the d orbitals split into two sets with one of lower energy and other with higher energy. Colour of substances arises invariably from the property of unpaired electrons to absorb light of certain wavelength in the region of visible light (400-750nm). The electrons present in the lower energy absorb the visible light of certain wavelength and jump into higher energy. This is called d-d transition of electron. The colour of the transmitted [i.e, colour of the substance] light is complimentary colour to that of the absorbed light.

ii) Transition metal exhibits variable oxidation state.

Transition elements show variable oxidation state. The common oxidation state is +2 due to the removal of ns electron. Higher oxidation state are due to loss of one or more (n-1)d electron in addition to ns electrons. The energy difference between ns and (n-1) is small. Therefore in addition to ns electron, (n-1) electron can also be removed. The maximum oxidation state of 3d series transitions metal is equal to the number of valence electrons in ns and (n-1) d electrons. Manganese exhibits maximum of +7 oxidation state, but decreases in the later elements. Number of oxidation state increases from Sc to Mn and decreases. Mn shows maximum oxidation state +7. From Sc to Mn number of unpaired 'd'electrons increases and after Mn pairing of electrons starts.

**b) Calculate the magnetic moment of Cr in Potassium dichromate. 2m**

Ans : The oxidation state of Cr in potassium dichromate is +6. The electronic configuration of Cr is $3d^5 4s^1$. In case of potassium dichromate, Cr^{+6} has $3d^0$ electronic configuration. Since d orbital does not contain any unpaired electron it is diamagnetic in nature.

n =0 therefore magnetic moment $\mu = \sqrt{n(n+2)} = 0$,

where n is number of unpaired electrons.

22. a) Describe ion exchange method of the separation of lanthanides. **4m**

Ans: This method is most effective and raid method for the separation of lanthanides. A synthetic cation exchange resin contains functional group like COOH or SO_3H group. The resin is packed in a long column fixed in vertical position. A solution of mixture of lanthanide ions is allowed to flow through it. Lanthanide ions replace (M^{3+} ions) H^+ of resins.

 $M^{3+} + 3R\text{-}H \rightarrow R_3(M) + 3H^+$
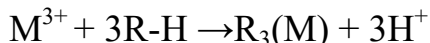
H^+ ion flows down the column and move out of the column. The cation which has the maximum capacity to undergo exchange process is held near the top and other cations are held further down the column in the order of their decreasing capacities to undergo exchange process. Then buffered solution of citric acid/ammonium citrate is passed through the

column. As the citrate solution moves down the column, lanthanide ions in the resin come out and form citrate complex.

M(resin)$_3$ + 3H(citrate) → 3H-resin + M(citrate)$_3$
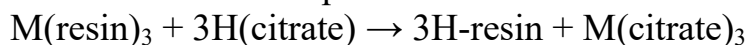
The first citrate complex comes out is one which was least firmly held on the resin. It is followed by other complex components in the order of increasing strengths with which they are held by resins. Thus the last component comes out is one which is most firmly held by the resin. In case of lanthanides, ionic radii decrease from La^{3+} to Lu^{3+} ion due to lanthanide contraction. Smaller ion held more firmly by the resin. La^{3+} ion is attached to resin more firmly than Lu^{3+}. Therefore Lu^{3+}-citrate complex comes out first and La^{3+} complex comes out last. The process is repeated several times and all lanthanides are separated. Then lanthanide ions are recovered from the complex by adding dilute HCl.

$$La(citrate)_3 + 3H^+ \rightarrow La^{3+} + 3citric\ acid$$
$$Lu(citrate)_3 + 3H^+ \rightarrow Lu^{3+} + 3\ citric\ acid$$
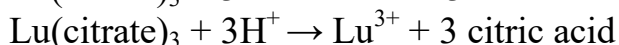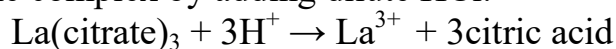
**b) What are transuranic elements? Give examples.**   **2m**

The transuranium elements (also known as transuranic elements) are the chemical elements with atomic numbers greater than 92 (the atomic number of uranium). All of these elements are unstable and decay radioactively into other elements.
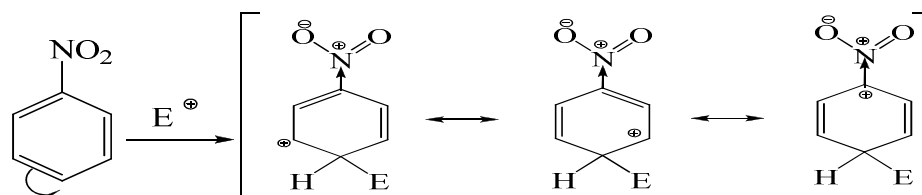
Examples Neptunium , Plutonium, Americium, Curium. etc

23. a) Explain the orienting influence of nitro group in nitrobenzene towards electrophilic substitution reaction. (4 + 2)
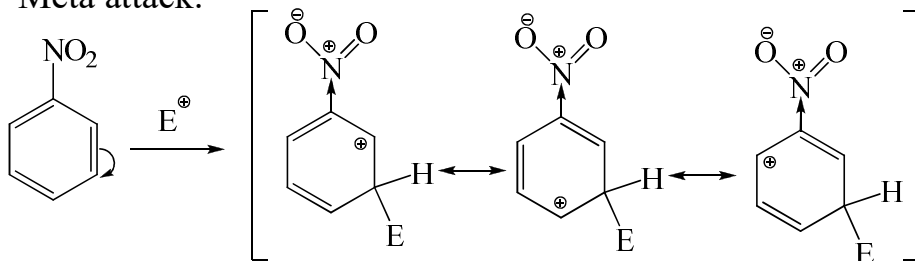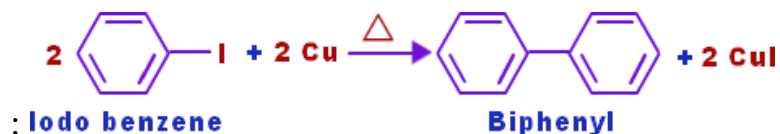
Ans: Ortho attack:
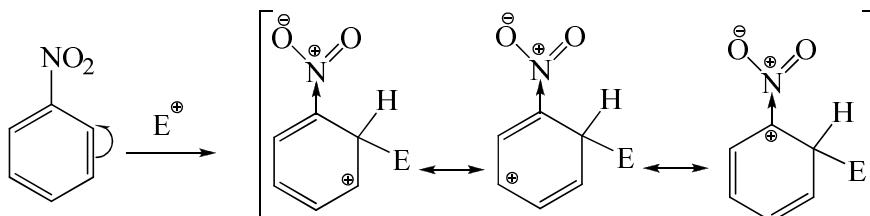
Para attack:

Meta attack:

Since ortho and para results resonance forms which are less stable compared to meta forms which are more stable. Hence nitro groupmeta orienting;

b) What is Ullmann's reaction? Give an example.
Ans: Two molecules of iodo benzene is heated with copper powder biphenyl is obtained.
This reaction is called **Ullmann's reaction**

24. a) Discuss the structure of benzene on the basis of molecular orbital theory.   4m
Ans: The structure of benzene molecule is obtained from a consideration of the bond orbitals in the molecule.
1. In benzene, each carbon atom is sp2 hybridized and bonded to two neighboring carbon atoms and one hydrogen atom by sigma (σ) bond.
2. It is a flat, symmetrical molecule with all carbon and hydrogen atoms lying in the same plane. Every bond angle is 120°.
3. Each carbon atom has a fourth orbital- a p orbital perpendicular to the plane of the regular hexagon.
4. Each unhybridized p orbital consists of two lobes one above and one below the plane of the ring.
5. The p orbital of one carbon atom overlap with the p orbital of the adjacent carbon atom forming π bond.
6. The p orbital overlap is extended to all six carbon atoms, resulting in the formation of a delocalized π bond. This delocalization of electrons of six p orbitals form two continuous doughnut shaped electron clouds, one lying above and the other below the plane of the hexagonal ring.
   Diagram:

π electrons delocalized around the ring, above and below the plane
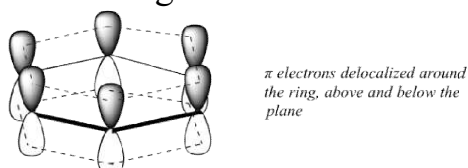
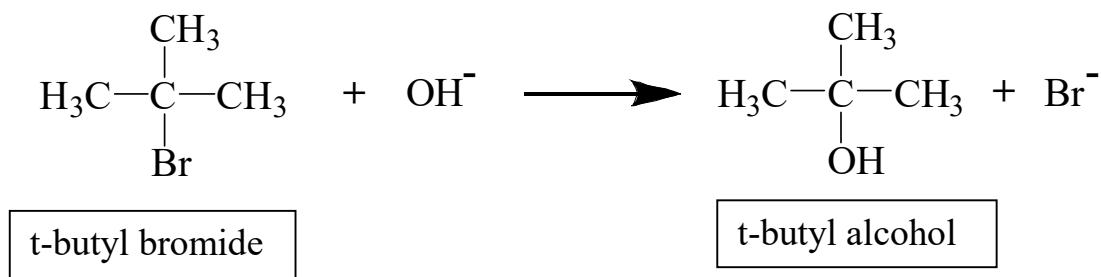**b) Give a method for the preparation of Stilbene.**
Ans: when benzyl triphenylphosphonium chloride reacts with benzaldehyde in the presence of conc. NaOH to form a mixture of cis stilbene and trans stilbene.
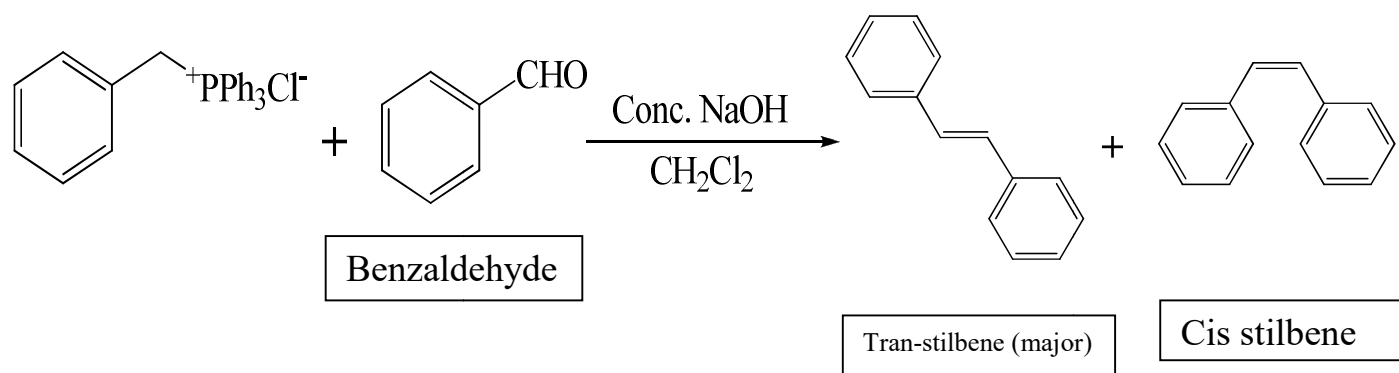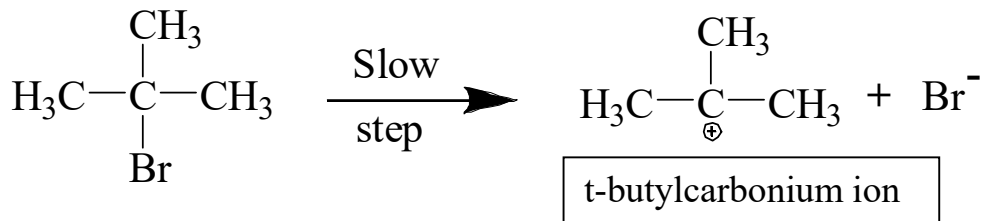
25. a) Explain S$_N$1 mechanism with an example.   4m

Ans: Nucleophilic substitution reaction that follow I order kinetics i.e,rate of reaction depends on the concentration of alkyl halide alone and takes place in two steps are called S$_N$1 mechanism.
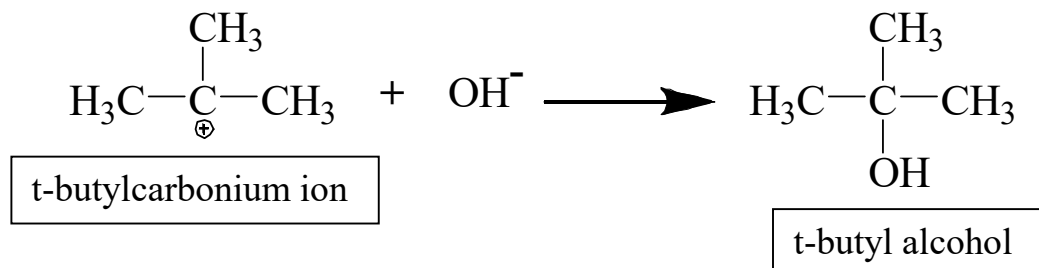
Example: Hydrolysis of tertiary butyl bromide with alkali forms tertiary butyl alcohol

Reaction:

$$H_3C-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + OH^- \longrightarrow H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + Br^-$$

| t-butyl bromide | | t-butyl alcohol |

Step 1: Formation of carbocation: In presence of polar solvents the alkyl halide ionizes to form a planar carbocation. The step forms rds and slow step.

$$H_3C-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[\text{step}]{\text{Slow}} H_3C-\overset{\overset{CH_3}{|}}{\underset{\oplus}{C}}-CH_3 + Br^-$$
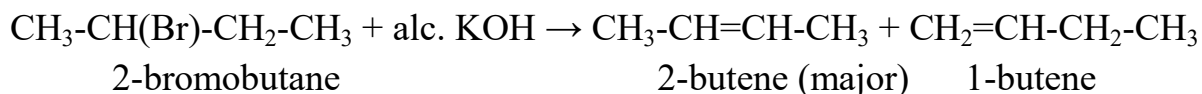
| t-butylcarbonium ion |

Step2: Attack of carbocation: Since the carbocation is planar, the nucleophile can attack on either sides forming the final product tertiary butyl alcohol. Racemization is observed in the mechanism

$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\oplus}{C}}-CH_3 + OH^- \longrightarrow H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

| t-butylcarbonium ion | | t-butyl alcohol |

b) Explain Saytzeff's rule with an example.   **2m**

Ans: During dehydrohalogenation reaction, halogen from one carbon atom and hydrogen from adjacent carbon atom are eliminated in the form of HX. If the dehydrohalogenation of alkyl halides can yield more than one alkene, then the product is the most highly substituted alkene.

Example:

CH$_3$-CH(Br)-CH$_2$-CH$_3$ + alc. KOH → CH$_3$-CH=CH-CH$_3$ + CH$_2$=CH-CH$_2$-CH$_3$

2-bromobutane   2-butene (major)   1-butene

Time: 3 Hours   Max.Marks: 70
Instructions: 1) The question paper has two parts. Answer both the parts.
2) Draw diagrams and write chemical equations wherever necessary.

PART-A

Answer **any eight** of the following (8 X 2 = 16)
1. Write Schrodinger wave equation and indicate the terms
2. Explain wave partical duality
3. Write the shapes of the orbital when l=0 and l=1
4. Mention the type of hybridization of the central atom in the following. a. $BeCl_2$ b.PCl_5
5. Write Born - Lande equation for the calculation of lattice energy and indicate the terms involved
6. Explain intra molecular hydrogen bonding with an example
7. Calculate the magnetic moment of Fein ferrous sulphate (Z of iron =26).
8. Give an example for Diels alder reaction
9. How naphthalene converted to phthalic anhydride
10. Explain Birch reduction.
11. What is Hofmann elimination reaction. Give an example.
12. Give a method of preparation of XeO_3

PART-B

Answer **any nine** of the following questions. (9 x 6 = 54)
13. a) Give the postulates of quantum mechanics.
b) Differentiate between orbit and orbital. (4 + 2)

14. a)Set up Schrodinger equation for particle in one dimensional box and solve for the variables.
b)What are radial probability and angular probability distributions?(4 + 2)

15. a) Explain Eigen values and Eigen functions in Quantum mechanics?
    b) Calculate the energy associated with Bohr's 3rd orbit given the energy of Bohr's first orbit is -2.17 x 10^{-18}J.(4 + 2)

16. a) Explain the shape of water molecule on the basis of VSEPR theory.
b) Define the terms: i) Bond length ii) Bond angle. (4 + 2)

17.a) Define lattice energy. Set up Born Haber's cycle for the calculation of lattice energy ofMagnesium oxide.
    b) Explain the type of bonding in dry ice and iodine crystals.   (4 + 2)

18. a) Discuss the hybridization involved in the formation of BF_3.
b) What are bonding and antibonding molecular orbitals?(4 + 2)

19. a) How is Helium isolated from natural gases?
b) HF has higher boiling point than HCl why? (4 + 2)

20. a) What are silicates? Explain different types of silicates with an example
   b) Why Cu^{2+} ion is more stable than Cu^{+}? (4 + 2)

21. a) Explain the characteristics of transition elements with respect to
(i) Complex formation   (ii) Magnetic properties.
b) What is lanthanoid contraction? Mention any two of its consequences .(4 + 2)

22.a) Explain the electronic configuration and oxidation states of lanthanides.
b) Why f-block elements are called as inner transition elements?(4 + 2)

23. a) Explain the orienting influence of –OH group in phenol.
   b)how anthracene is converted into anthraquinone(4 + 2)

24. a) Explain the mechanism of nitration of benzene.
b) Define antiaromaticity. (4 + 2)

25. a) Explain the mechanism of E_1 reaction with a suitable example.
b) Between chlorobenzene and benzyl chloride which is more reactive and why. (4 + 2)

CHEMISTRY –II
Model question paper-II- answers

1. Write Schrodinger wave equation and indicate the terms.
Ans: Schrodinger wave equation is
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0,$$
Where m = mass of electron, V = potential energy, E = total energy, h = plank constant, ψ = amplitude function or wave function.

2. Explain wave particle duality.
Ans: de-Broglie's hypothesis proposes dual nature of matter. Wave–particle duality is the concept that every elementary particle or quantic entity may be partly described in terms not only of particles, but also of waves. It expresses the inability of the classical concepts "particle" or "wave" to fully describe the behavior of quantum-scale objects.

3. Write the shapes of the orbital when l=0 and l=1.
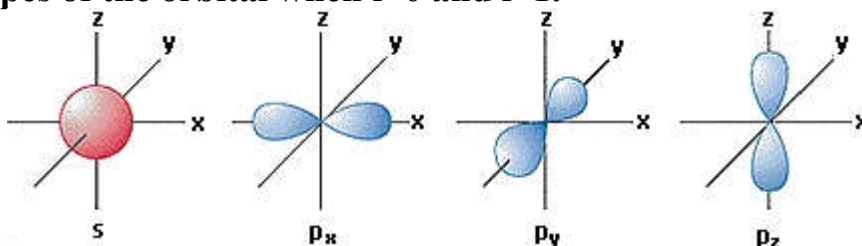
s orbital shape when l=0,   Any one shape of p orbital when l=1

4. Mention the type of hybridization of the central atom in the following.
i) $BeCl_2$ – sp hybridization.   ii) PCl_5 – sp^3d

5. Write Born - Lande equation for the calculation of lattice energy and indicate the terms involved.
Ans:

$$U = \frac{N_A M z^+ z^- e^2}{4\pi\varepsilon_o r}\left(1 - \frac{1}{n}\right)$$

N_A = Avogadro constant;
M = Madelung constant, relating to the geometry of the crystal;
z+ = charge number of cation
z– = charge number of anion
e = elementary charge, $1.6022\times10{-19}$ C
ε_0= permittivity of free space
r_0= distance to closest ion
n = Born exponent whose value depends on the type of the ion.

6. Explain intra molecular hydrogen bonding with an example.

Ans: The bond arises due to electrostatic forces of attraction between H and an electronegative element present in the same molecule which results in ring formation or chelation is called intra molecular hydrogen bonding.

Example: 2-nitrophenol, salicylaldehyde, acetoacetic ester etc

7. Calculate the magnetic moment of Iron in ferrous sulphate (Z=26)

Ans: From the equation of magnetic moment: $\mu = \sqrt{n(n+2)}$; Iron in ferrous sulphate has the configuration: $[Ar]\ 3d^6$; n= number of unpaired electrons = 4; $\mu = \sqrt{4(4+2)}$;   1m

Hence $\mu = 4.898$BM. 1m

8. Give an example for Diels alder reaction

Ans: The Diels-Alder reaction is a conjugate addition reaction of a conjugated diene to an alkene (the dienophile) to produce a cyclohexene.Ex: The simplest example is the reaction of 1,3-butadiene with ethene to form cyclohexene:
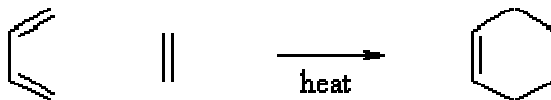

9. How naphthalene is converted into phthalic anhydride.

Ans: Naphthalene undergoes oxidation when treated with oxygen and vanadium pentoxide at 450°C yields phthalic anhydride.
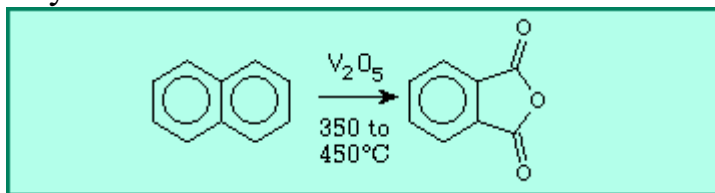

10. Explain Birch reduction.

The Birch reduction is an organic reaction where aromatic rings undergo a 1,4-reduction to provide unconjugated cyclohexadienes. The reduction is conducted by sodium or lithium metal in liquid ammonia and in the presence of an alcohol.
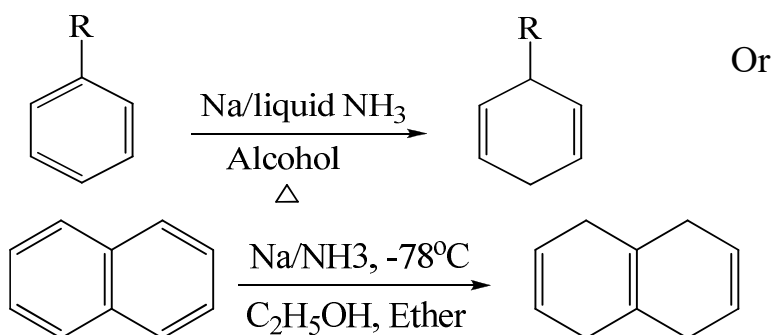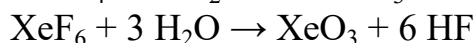
11. Give a method of preparation of alkyl halide from alcohol.

Ans: The Hofmann elimination is an organic reaction used to convert an amine with a β-hydrogen to an alkene using methyl iodide, silver oxide and water under thermal conditions.
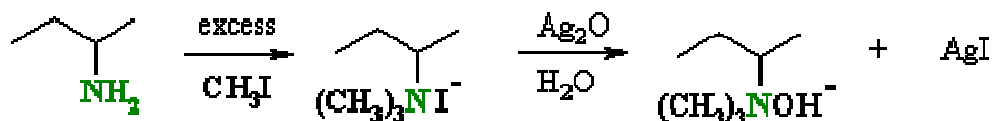
12. Give a method of preparation of XeO$_3$.

Ans: By heating xenon tetrafluoride with water:

$6XeF_4 + 12H_2O \rightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$

$XeF_6 + 3 H_2O \rightarrow XeO_3 + 6 HF$

PART-B

Answer any nine of the following questions. (9 x 6 = 54) 13.a) Give the postulates of quantum mechanics.4m

Ans: Any three from the following:

i) The physical state of a system at time t is fully described by the wave function $\psi(x,y,z,t)$.this wave function is a function of position co-ordinates and possibly time.

ii) The possible wave function $\psi(x,y,z,t)$ are obtained by solving appropriate schrodinger equation.

iii) The wave function $\psi(x,y,z,t)$, its first derivative and second derivative are continuous, finite and single valued for all values of x.The wave function $\psi(x,y,z,t)$ is normalized which means $\int\psi\psi^* = 1\psi^*$ is the complex conjugate of ψ.

iv) Every dynamical variable corresponding to a physically observable quantity can be represented by a linear operator.

v) Quantum mechanical operators corresponding to physical properties are obtained from the classical expressions in terms of variable and converting them to operators using set of procedures

b) Differentiate between orbit and orbital.   2m

Ans: Any one difference

ORBIT	ORBITAL
1.It is well-defined circular path followed by electron around nucleus.	1.It is a region of space around the nucleus where the probability of finding an electron is maximum.
2. It represents two dimensional motion of electron around nucleus.	2. It represents three dimensional motion of electron around nucleus.
3. The maximum no. of electrons in an orbit is $2n^2$.	3. The maximum no. of electrons in an orbital is 2.
4.Orbit is circular in shape.	4. Orbitals have different shapes.

14. a) Set up Schrodinger equation for particle in one dimensional box and solve for the variables.4m

Ans: Consider a single particle say an electron of mass 'm', confined to one dimensional box

of length 'a'. The walls of this box are formed by potential energy barriers, infinitely high that the particle cannot escape. The potential energy out-
side is infinite but inside the box, it is zero: i.e., V(x)=0

V≠ V=a   V=∞   Schrodinger equation is: $d^2\Psi/dx^2 + 8\pi^2 m(E-V) \Psi/h^2 = 0$;
∞   since V(x)=0; $d^2\Psi/dx^2 + 8\pi^2 mE\Psi/h^2 = 0$
or $d^2\Psi/dx^2 + k^2 \Psi = 0$; where $k^2 = 8\pi^2 mE/h^2$ is a constant
x≠0 |x=a   independent of x.

The solutions of the second order differential equation of the above type is
        Ψ = A Cos kx+ B Sin kx; where A and B are the two arbitrary constants.
   The value of these constants can be determined by considering the fact outside the box; V=∞; the Schrodinger equation then becomes: $d^2\Psi/dx^2 + 8\pi^2 m(E-\infty) \Psi/h^2 = 0$
This is possible if the particle is outside the box, but it cannot be, since it is present or confined inside the box.
    By one of the postulates of quantum mechanics, Ψ must be continuous function of x. Hence Ψ must be zero at the walls of the box, that is x=0 and x=a, as there can be no variation in the values of Ψ at the walls of the box.
    ∴. Ψ=0 at x=a , At x=0, the equation Ψ = A Cos kx + B Sin kx   becomes
                0 = A Cos k.0+ B Sin k.0; 0=A, Since Cos 0=1.
                Hence, Schrodinger equation is : Ψ = B Sin kx
Again, at the other wall, that is x=a, Ψ=0, therefore 0=B Sin ka; or Sin ka =0
B cannot be zero as it leads to Ψ being equal to zero everywhere which is not acceptable
 Hence, Sin Ka =0 = Sin nπ; that is   ka = nπ; Or k = nπ/a where n=1,2,3…..
The solution of Schrodinger equation is: $\Psi = \Psi_n$ = B Sin[nπx/a], where n is the quantum number.   Hence k = nπ/a ……(1)   and $k^2 = 8\pi^2 mE/h^2$ -------(2) from earlier equation
equating both; $8\pi^2 mE/h^2 = n^2 \pi^2 /a^2$; rearranging we get   **E = $n^2 h^2/8ma^2$**
n=1,2,3….., E corresponds to the energy of the particle in one dimensional box.

b) What are radial probability and angular probability distributions?   2m
Radial Distribution function: The probability of distribution of electrons in an orbital is represented by plotting a graph of Ψ^2 Vs distance from the nucleus 'r'.   This way ofrepresentation is prominent and informative by radial distribution functions. It givesthe total probability of finding electrons in a spherical shell between r and r+dr insteadof a point location.
Angular wave function This wave function corresponds to Y((θ,Φ) depends on the angles θ and Φ. It is a function of the quantum numbers l and m.The wave functions for p atomic orbitals depends on the angular co-ordinates θ and Φ in addition to r. From the probability plots, it is observed that the probability of finding a $p_z$electron is maximum along z axis, it is zero in the X-Y plane which is called the nodal plane. A nodal plane separates the two lobes. The atomic orbital shape as dumb-bell.

15. a) Explain Eigen values and Eigen functions in Quantum mechanics?   **4m**

Ans:<u>Eigen Values and Eigen functions</u>:   The Schrodinger equation can have several solutions. Out of these only some are acceptable. The solutions that give acceptable values of the total energy are calledEigen values. The corresponding wave functions for which these solutions are applicable are called Eigen functions or wave functions.

   The wave function (Ψ) must satisfy the following conditions: 1) It must have definite values 2) It must be single valued   3) Its first derivative must be continuous with respect to its variables. When these conditions are satisfied, it is a well behaved function.
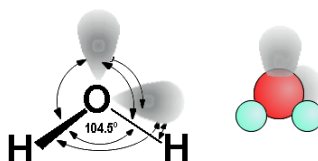
b) Calculate the energy associated with Bohr's 3rd orbit given the energy of Bohr's first orbit is -2.17 x 10^{-18}J.   **2m**

Ans: $E = -Z^2e^4m/8\varepsilon_o^2h^2n^2$ given 1^{st}bohr orbit E = -2.17 x 10^{-18}J, for 3rd orbit n =3 therefore E = -2.17 x 10^{-18}J / $(3)^2$ = -0.241 x 10^{-18}J.

16 a) Explain the shape of water molecule on the basis of VSEPR theory.   **4m**
Ans:

<u>Water</u>

The central atom is oxygen, attached to two hydrogen atoms. The oxygen atom, after sharing two electrons with each hydrogen atom, is left with four electrons not taking part in bonding, and these form two non-bonding pairs of electrons. Their combined repulsive influences on the two H-O bonds result in a smaller bond angle (104.5°) than expected for a regular tetrahedron.An electrostatic repulsion exits between the bonded electrons and the non-bonding pairs (NBPs) on the oxygen. This repulsion pushes the bonds away from the NBPs creating the bond angle of 104.5∘ (**VSEPR structure**). The resulting **water molecule** is actually a special version of the tetrahedral **shape**Since there are only three atoms, they must necessarily lie in one plane, and so water is a planar molecule.

b) Define the terms:
2mBond length: The **bond length** is **defined** to be the average distance between the nuclei of two atoms bonded together in any given molecule. A **bond angle** is theangle formed between three atoms across at least two **bonds**.

17. a) Define lattice energy. Set up Born Haber's cycle for the calculation of lattice energy of Magnesium oxide.4m
Ans: The **lattice energy** of a crystalline solid is usually defined as the energy of formation of the crystal from infinitely-separated ions and as such is invariably positive. The precise value of the lattice energy may not be determined experimentally, because of the impossibility of preparing an adequate amount of gaseous ions or atoms and measuring the energy released during their condensation to form the solid. However, the value of the lattice energy may either be derived theoretically from electrostatics or from a thermodynamic cycling reaction.-
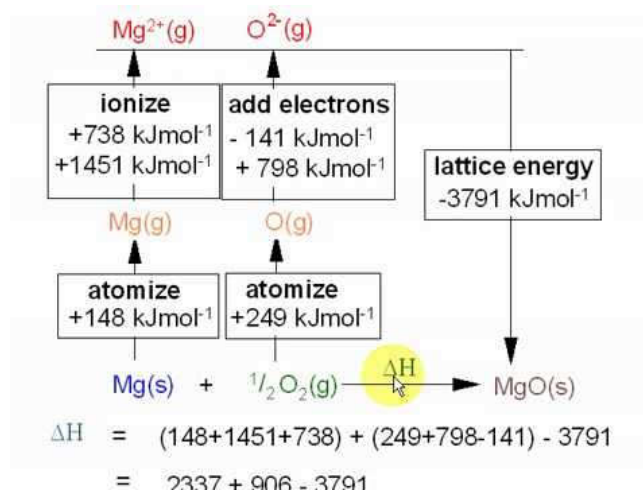
$$\Delta H_f = \Delta H_s + 1/2\Delta H_d + I.E1 + I.E2 + E.A1 + E.A2 + U$$

$$U = \Delta H_f - \Delta H_s - 1/2\Delta H_d - I1 - I2 - E.A1 - E.A2$$

**b) Explain the type of bonding in dry ice and iodine crystals.** **2m**
A material that has a very low melting point and that will not conduct electricity either as a solid or when molten consists of molecules that are close-packed, bump-in-hollow and that are attracted to each other by weak van der Waals attractions. Examples include carbon dioxide (CO_2, dry ice), iodine (I_2), and naphthalene (mothballs). The electrons are constrained to the well-defined groups of atoms that constitute the molecules. The atoms within the molecules are linked together by strong covalent bonds. The weak attractions between the molecules, termed London forces, arise from the charge asymmetry in the moleculesthat result from the
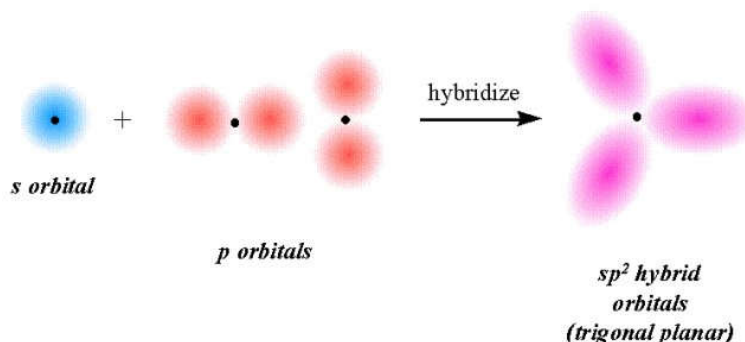polarizability of their electron clouds.

18. a) Discuss the hybridization involved in the formation of BF$_3$. **4m.**
Ans: **BF$_3$** 1. Boron electron configuration:
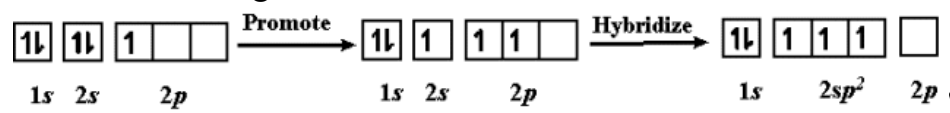
2. The three sp^2 hybrid orbitals have a trigonal planar arrangement to minimize electron repulsion

s orbital

p orbitals

sp^2 hybrid orbitals (trigonal planar)

b) What are bonding and antibonding molecular orbitals?2m
Bonding Molecular Orbital: Bonding molecular orbital is formed by the addition of overlapping of atomic orbitals. The wave function of the bonding MO may be written as:
Ψ **(MO) = ΨA + ΨB.**Atomic orbitals having same sign forms the Bonding molecular orbital when the lobes of them combines. Therefore, electrons in the bonding MO contribute to attraction between the two atoms. It has lower energy than the isolated atomic orbitals.
Anti-Bonding Molecular Orbital: Anti-bonding molecular orbital is formed by the subtraction of overlapping of atomic orbitals. The wave function for the anti-bonding MO may be written as:Ψ **(MO) = ΨA – ΨB.**Atomic orbitals having opposite sign forms the Bonding molecular orbital when the lobes of them combines. . Therefore, the electrons in anti-bonding MO contribute to repulsion between the atoms. It has higher energy than the isolated atomic orbitals.

19. a) How is Helium isolated from natural gas?
4mAns: Natural gas contains as much as 7% He along with other hydrocarbon, CO_2, N_2. CO_2 is removed by reaction with concentrated potash (KOH). The gases are liquifed when most of the hydrocarbon gets liquefied. The residual gas mixture consists of N_2, He and a small amount of methane. The mixture is compressedto100 atm and cooled to73K when except helium, the other gases gets liquefied. 99% pure helium is obtained. This is further purified by cooling to 3K and passing over activated charcoal. All the gases except He are absorbed and pure He is obtained.

b) HF has higher boiling point than HCl why?   **2m**
Ans: HCl,HF molecule has intermolecular hydrogen bonding. Electronegativity of F_2 is very high and it has very small atomic size hence HF has stronger bonding whereas Cl_2 has larger atomic size and it is less electronegative than F_2. Hence HCl has weaker hydrogen bonding. Stronger the hydrogen bonding higher the boiling point. Hence HF has higher BP than HCl.

20. a) What are silicates? Explain different types of silicates with an example.   **4m**
Ans**:**Silicates are the salts of silicic acid having the basic tetrahedral skeletal structure: SiO_4^{4-}. Silicates are classified based on their linkage structures as
1. Orthosilicates: These are having the discrete silicate units SiO_4^{4-}. In the crystal lattice, the oxygens of each silicate unit are co-ordinates round the metal ions forming a neutral structure.
Ex: 1. Zircon: $ZnSiO_4$
2. Pyrosilicates: These contain units of disilicate ions $Si_2O_7^{6-}$ which are formed by the conden-sation of two silicate units through an oxygen atom. Ex: Thortveitite $Sc_2Si_2O_7$.
3. Cyclic silicates: These contain two oxygen atoms per silicate anion that is SiO_4^{2-} tetrahedron is shared, a cyclic structure is obtained. Of these $Si_6O_{18}^{6-}$ is important.
Ex: Beryl: $Be_3Al_2Si_6O_{18.}$

4. Chain silicates: In these silicates, two oxygen atoms per silicate tetrahedron are shared forming a polymeric anion chain. They contain the primary unit of SiO_3^{2-}
Ex: Pyroxene mineral like diopsideCaMg $(SiO_3)_2$.
5. Sheet silicates: The silicates that results due to cross linking of silicate tetrahedron through oxygen atoms can be extended to three oxygen atom per silicon atom when two dimensional sheets are formed. They are having the basic unit of $Si_2O_5^{2-}$
Ex: Talc: $Mg_2(Si_2O_5)_2.Mg(OH)_2$.
6. Three dimensional silicates: This type of silicates arises when there is cross linking of all the four oxygen atoms in the silicate anion forming a three dimensional structure having the basic skeletal unit SiO_2- $(SiO_2)_n$. Ex: Quartz.

b) Why Cu^{2+} ion is more stable than Cu^+?   **2m**
Ans: Cu^+ ion is having the electronic configuration of $[Ar]3d^{10}$ configuration where all the electrons are paired up. where as Cu^{2+} is having the configuration of $[Ar]3d^9$ and Cu^{2+} is more stable than Cu^+ because of its high enthalpy of hydration.

21. a) Explain the characteristics of transition elements with respect to   **4m**
(i) Complex formation: Transition metals has the tendency to form complexes withsome inorganic anions and also with neutral molecules. The formation of complexes arises because of the formation of co-ordination bonds between electron donor molecules or ions called ligands and electron deficient transition metal cation having variable oxidation states.
Ex: 1. $Cu(NH_3)_4SO_4$ 2. $K_4Fe(CN)_6$.
(ii) Magnetic properties: As evident from the electronic configuration of transition metals and their ions having unpaired electrons in (n-1) d orbitals. As the number of unpaired electrons increases from one to five from Sc to Mn, the paramagnetic character increases, shown by the increase in magnetic moment calculated by using the equation: $\mu=\sqrt{n(n+2)}BM$. From Mn onwards the magnetic property decreases since the electrons are paired up. The last element in the series Zn is diamagnetic even in ionic state Zn^{2+} as there are no unpaired electrons.

b) What is lanthanide contraction? Mention any two of its consequences .   **2m**
Ans: The atomic and ionic radii decrease as we move across the lanthanoid series. The steady decrease in the atomic and ionic radii of the lanthanides is called lanthanide contraction. Due to ineffective shielding of 4s electrons there is a gradual increase in the attraction of the nucleus for the peripheral electron with increase in atomic number. Consequently, there is a contraction in atomic and ionic radii.
1. The chemistry of lanthanoides (physical and chemical) are similar.
2. The transition elements of 4d and 5d series shows close resemblance in their properties compared to 3d series. It is because, they have almost equal atomic radii.

22. a) Explain the electronic configuration and oxidation states of lanthanides.   4m

Ans: **i) Electronic configuration**: The lanthanoids involve the gradual filling of 4f subshell in their atoms, since the energies associated with 4f and 5d subshells for these elements are very close. Lanthanum, the first element has the outer configuration of $5d^1 6s^2$. In the fourteen elements which follow it, the electrons are successively added to 4f subshell, with some exceptions.

ii) oxidation states: Generally the common oxidation states of lanthanides are +3 because the ionization enthalpies of the first three ionization enthalpies for each element belonging to lanthanoid family are low. The ionic character of Ln^{3+} dominates in the compounds. Ln^{2+} and Ln^{4+} ions are less stable. i) Ce, Tb and Pr shows +4 oxidation states which are exceptions. ii) Eu and Yb attain f-7 and f-14 configurations attaining +2 oxidation states.

b) Why f-block elements are called as inner transition elements?   2m

Ans: The elements in which the valence electron enters in anti penultimate energy level i.e., (n - 2) f are known as f - block elements. This name is because of the position of the valence electron is in the f - orbital. Since the last electron enters into (n - 2)f - orbital which is inner to the penultimate shell (For d-block elements), they are called inner transition elements. Hence, the general electronic configuration for these elements is $(n-2)f^{1-14}$, $(n-1)d^{0-1}$, ns^2.
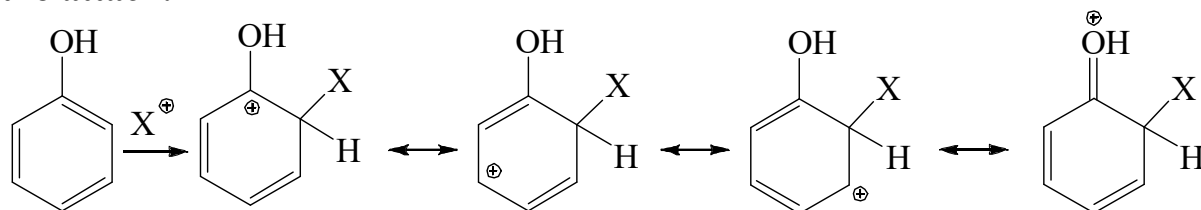
23. a) Explain the orienting influence of –OH group in phenol.4m

Ans: OH group in phenols ortho, para directing group. In phenol, electrophilic attack at the p-position give rise to an intermediates represented by
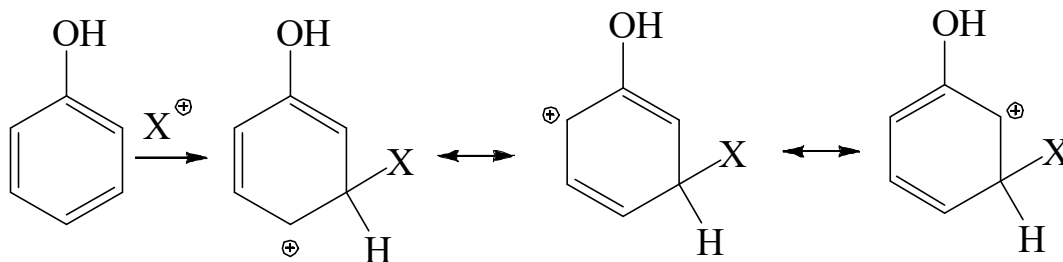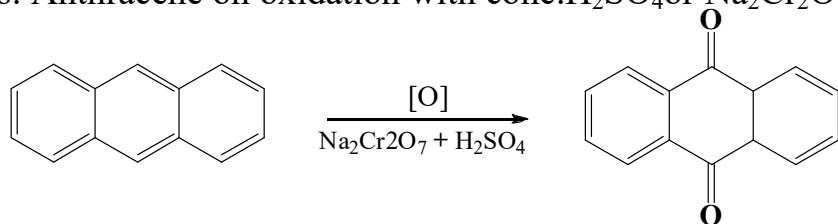
Para attack:
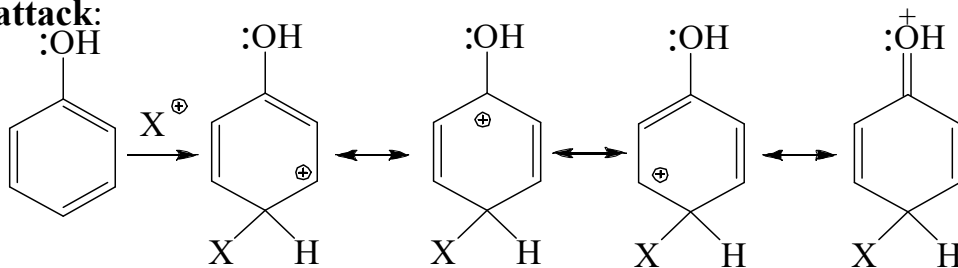
ortho attack:

Meta attack:

Since ortho and para results four resonance forms which are stable compared to meta forms which produces three forms. Hence OH group is ortho para orienting;

b) How anthracene is converted into anthraquinone.2m

Ans: Anthracene on oxidation with conc.H_2SO_4or $Na_2Cr_2O_7/H_2SO_4$ yields anthraquinone.

**24. a) Explain the mechanism of nitration of benzene.**   **4m**

Ans: Benzene on heating with mixture of conc. Nitric acid and con sulphuric acid gives nitrobenzene.

STEP-1: generation of electrophile (formation of nitronium ion)

Nitric acid reacts with .H_2SO_4 to generate NO_2^+ ion as an electrophile.

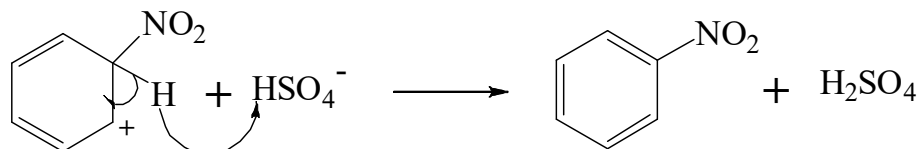$$HNO_3 + H_2SO_4 \rightarrow H2O + NO_2^+ + HSO_4^-$$
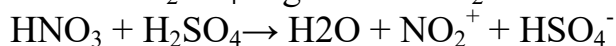
STEP-2: Benzne attacks nitonium ion to form carbocation which is resonance stabilized.
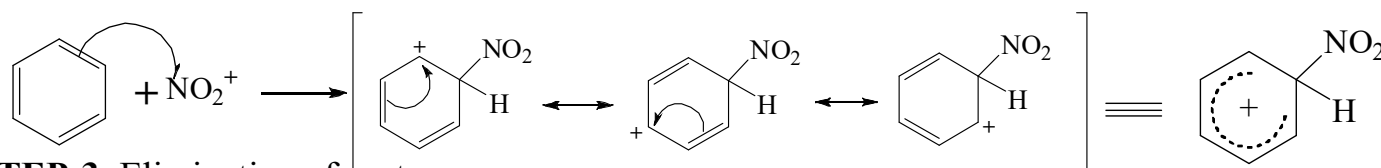
STEP-3: Elimination of proton.

HSO_4^- ion abstracts a proton from carbocatin and electron returns to the ring to regenerate aromatic ring. Catalyst is regenerated.

b) What is anti-aromaticity, Give an example   **2m**

Ans: **Anti-aromaticity** is a characteristic of a cyclic molecule with a π electron system that has higher energy due to the presence of 4n electrons in it. **or**

Anti-aromaticity is a characteristic of a cyclic, planar molecule with a complete conjugated π-electron system within the ring having 4n π-electrons where n is any integer within the conjugated π-system.

**25. a) Explain the mechanism of E1 reaction with a suitable example.**   **4m**

Ans: Elimination reaction in which the rate determining step involves only one species are called E1 reactions. These reactions generally take place in twostepsand follow first order kinetics.

Example: t-butyl chloride is treated with alcoholic KOH it undergoes E1 mechanismto give 2-methylpropene.

Step:1 formation of t-butyl carbonium ion

$CH_3-C-(CH_3)_2Cl \rightarrow (CH_3)_3C^+ + Cl^-$
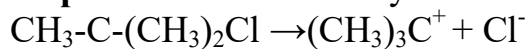
Step:2 loss of proton from adjacent or β carbon.

$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_2-C=CH_2$
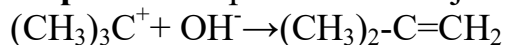
b) Between chlorobenzene and benzyl chloride which is more reactive and why.   2m

Ans: Benzyl chloride is more reactive than chlorobenzene because in benzyl chlorideCl atom is attached to sp^3 hybridized carbon atom, the resonance stabilization of aromatic ring is less resonance stabilized. Where as in chlorobenzene Cl atom is attached to sp^2 hybridized carbon atom, the resonance stabilization of aromatic ring is more resonance stabilized as a result removal of chlorine is difficult in chlorobenzene.