चौधरी PHOTOSTAT

Hi, My Name is

CHEMISTRY IAS DIAS

Important topics for
2006:-

- Derivation of Schrödinger equⁿ
- Shape of s,p and d-orbitals. (see prepared one)
- quantum no·s and their significance (see prepared)
- Difference between 3s, 3p and 3d orbitals
  (Remember the plot) it is difficult
  to draw.

- do remember 1s, 2s wave functions
  and also 2p$_x$, 2p$_y$, 2p$_z$ wave functions

- imp Example 3
  Calculation of $\langle r \rangle$ for 1s and 2s

Note:-

$$\int_0^\infty x^h e^{-\alpha x} dx = \frac{h!}{\alpha^{h+1}} \qquad (\alpha > 0)$$

1.) Atomic Structure [Civil Services Exam Questions]:→

1.) Write note on: Quantum mechanical approach to Pauli's principle.
[8 marks] [1976]

2.) Write notes on:- Zero point Energy, Hamiltonian operator, Normalisation of function. [24 marks] [1976]

3.) ~~State~~ Derive the energy levels for an electron in a one-dimensional box and point out how this model can be used to account for spectral properties of conjugated polyenes. [16 marks] [1977]

4.) Write short note on: Pauli's exclusion Principle. [20 marks] [1971]

5.) State Heisenberg's uncertainty principle. How is the occurence of zero-point energy of the particle in a box is in accordance with the Heisenberg's uncertainty principle?
[20 marks] [1980]

6.) For a hydrogen atom in a one-dimensional box, 1 nm long, Calculate the value of the quantum number of the energy level for which the energy is equal to $\frac{3}{2}kT$ at 300 K.
[20 marks] [1980]

7.) Calculate the de Broglie wavelength of an electron that has been accelerated by a potential difference of 1000 volts.
[30 marks] [1980]

8.) What is the interpretation of ψ (wave function) and ψ^2 (square of wave equation)
[10 marks] [1980]

9.) Give an account of the molecular orbital theory and point out the difference between this and valence bond theory
[40 marks] [1981]

10.) Draw the molecular orbital diagram of the oxygen and the nitrogen molecules and calculate the bond order in each case.
[20 marks] [1981]

11.) Illustrate, with examples, non-bonding and anti-bonding orbitals. [20 marks] [1981]

12.) What is Schrödinger wave equation? Show how it can be solved for the case of a free particle in a rectangular three - dimensional box. [40 marks] [1981]

13.) Write the Schrödinger equation for hydrogen atom, giving the meaning of the terms. [20 marks] [1983]

14.) Explain and illustrate the meaning of the terms: Eigenfunction, and eigen value; bonding, antibonding and non-bonding orbitals. [20 marks] [1984]

25.) A particle of mass m is confined to a three-dimensional box defined by $V = 0$ for $0 \leq x \leq a, 0 \leq y \leq b, 0 \leq z \leq c$
$= \infty$ otherwise.
Find the allowed energy levels of the particle [30 marks] [1984]

26.) Draw rough diagrams to illustrate the nature of the radial distribution functions for the following hydrogenic orbitals and give the magnitude of the orbital angular momentum of the electron in each of these orbitals: 1s, 2s, 2p, 3p and 3d. [20 marks] [1985]

17.) What is a normalized wave function? [5 marks] [1986]

18.) What are the important conclusions from the 'particle in a one-dimensional box.' [30 marks] [1986]

19.) A particle of mass m is confined to a one-dimensional box of unit length (i.e. $0 \leq x \leq 1$). Derive expressions for i) the allowed energy levels, and ii) the average (expectation) value of x for $n=3$, state where n is a quantum number

20.) Considering an electron of mass 9.1×10^{-28} gm moving with a velocity v. for an uncertainty of 1 Å in its position, what is the inherent uncertainty in its velocity? [15 marks] [1988]

21.) Explain normalized and orthogonal wave functions.
[15 marks] [1988]

22.) Show that the application of Schrödinger equation to the problem a particle confined to a one dimensional box, leads to discrete energy levels. [40 marks] [1988]

23.) Calculate the energy of a photon of radiation of wavelength 150 nm. [5 marks] [1989]

24.) The wavefunction for the ground state of the hydrogen atom is $\psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$. Derive an expression for the probability of finding the electron inside a sphere of radius a_0 centered at the nucleus. [15 marks] [1990]

25.) The energy levels for a particle of mass m in a one-dimensional box of length L are given by the equation $E_n = \frac{n^2 h^2}{8 m L^2}$. Considering $m = 1.0 \times 10^{-30}$ kg, and $L = 5.0 \times 10^{-10}$ m and $h = 6.6 \times 10^{-34}$ Js, calculate the frequency of light which may raise the particle from n=5 to n=6. Is it possible for n to be equal to zero? [15 marks] [1990]

26.) What are the conditions on the solution of Schrödinger equation for its acceptance as a wave function? [10 marks] [1991]

27.) Draw the radial part of the wave-functions for hydrogen atoms with n=3, l=2; n=3, l=0; n=2, l=1 in different ways. [15 marks] [1991]

28.) What are degeneracies of the following orbitals for hydrogen-like atoms? i) n=2, ii) n=3

Topics important for this year :-

→ Born Haber Cycle (see prepared one)

→ Born- Lande Equation (prepared)

→ M.O. of CO and BeH₂

→ Comparison beth VBT & MOT (prepared)

→ VBT & its application.   (Prashant's notes)

2.) Chemical Bonding :→

1.) Write short notes on Born-Haber Cycle. [1978]

2.) Discuss the nature of the Chemical Bond [20 marks] [1972]

3.) HCl has dipole moment 1.03 debye. If the bond length is 1.275 Å, calculate the percentage ionic character of H-Cl bond.

$(e = 4.80 \times 10^{-10}$ e.s.u; 1 debye $= 10^{-18}$ e.s.u-cm)

[20 marks] [1978] [1985]

4) What are the bond orders in the following molecules and ions? He_2, O_2, O_2^+ and O_2^-

[20 marks] [1980]

5) What is dipole moment? How can it be used for ascertaining:-
i) the symmetry of the molecule ii) bond angles iii) ionic character

[20 marks] [1980]

6.) Give an account of the molecular orbital theory and point out the difference between this and valence bond theory.

[40 marks] [1981]

7.) Draw the molecular orbital diagram of the oxygen and the nitrogen molecules and calculate the bond order in each case.

[20 marks] [1981]

8.) Illustrate, with examples, non-bonding and anti-bonding orbitals.

[20 marks] [1981]

9.) Draw the energy level diagrams for the molecular orbitals in F_2 and CO molecules and obtain the bond order in each case.

[20 marks] [1981]

10.) Write the electronic configurations of O_2^{2-} and Id_2^+ and the molecular orbital representations of He_2^+ and 1,3-butadiene.

[20 marks] [1983]

11.) Using molecular orbital diagrams, deduce the bond orders in O_2, O_2^- and O_2^{2-}. Arrange the three in the order of increasing bond energy.

[20 marks] [1984]

12.) Explain and illustrate the meaning of the terms: bonding, anti-bonding and non-bonding orbitals. [10 marks] [1984]

13.) Give an account of the valence bond treatment of hydrogen molecule and explain its essential differences with the M.O. method. [40 marks] [1985]

14.) Define the dipole moment of a molecule. Discuss the application of dipole moment data for eliciting information about molecular structure and partial ionic charcter of a bond. [20 marks] [1985]

15.) Explain, giving examples, bonding, anti-bonding and non-bonding orbitals. [15 marks] [1986]

16.) Why is it not possible to visualize a stable He_2 molecule? [5 marks] [1986]

17.) Describe a method of determining the dipole moment of the molecule of a compound in solution state. [30 marks] [1986]

18.) Give the essential features of valence bond and molecular orbital theories. [30 marks] [1986]

19.) Arrange the following molecules in order of increasing bond length: O_2, O_2^+, O_2^-. Which molecule will have greater bond dissociation energy, N_2 or N_2^+? Give reasons for your answers. [20 marks] [1987]

20.) Use molecular orbital to write down the electronic configuration of NO molecule and discuss the bonding. Will NO^- be paramagnetic or dimagnetic? [10 marks] [1987]

21.) Use valence bond method to discuss the electronic structure of hydrogen molecule. Use this example to discuss the relative merits and demerits of valence bond and molecular orbital (MO) methods. [40 marks] [1987]

21.) Explain how dipole moment data can be used for eliciting information about molecular structure and partial ionic character of a bond. Give suitable examples for your answer.   [20 marks] [1987]

22.) Using MO ~~di~~ energy diagrams, determine the bond order and comment on the magnetic property (paramagnetic or diamagnetic) of H_2^+, He_2^+, N_2 and O_2. [20 marks] [~~45 mar~~ 1988]

23) How does Born-Haber cycle enable evaluation of lattice energy of a crystal.   [20 marks] [1988]

~~24~~) Using MO approach write the electronic configurations of N_2^+, NO^+, CO, O_2^+, and F_2. Also calculate the bond order in each case.   [10 marks] [1989]

25.) If the equilibrium bond length in HCl is 1.2476×10^{-10} m, calculate the dipole moment in debye (D) units. Also, if the calculated dipole moment is 1.08 D, comment on the ionic character of the bond.   [5 marks] [1989]

26.) Draw the molecular orbital diagram for carbon monoxide and use the aufbau principle to put in the appropriate number of electrons. Is CO^+ likely to be more stable than CO.   [5 marks] [1990]

27.) Give the population of σ, π, π^* orbitals for CO and NO. Predict the effect on bond energy of each for the removal of an electron and for the addition of an electron.   [20 marks] [1992]
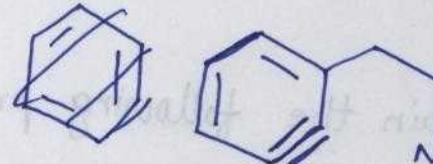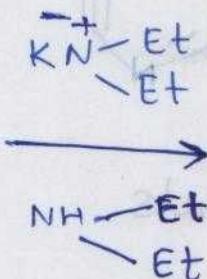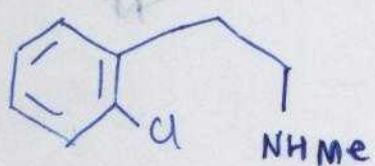
28.) The equilibrium <u>intermdecular-</u> distance for $NaCl(g)$ molecule is 0.286 nm. What is the maximum value of the dipole moment possible? How do you explain the difference between this and the actual value?   [15 marks] [1992]

Benzyne

Ex.)
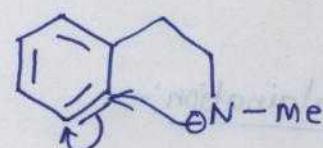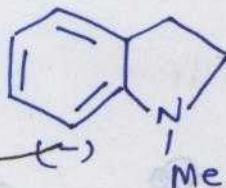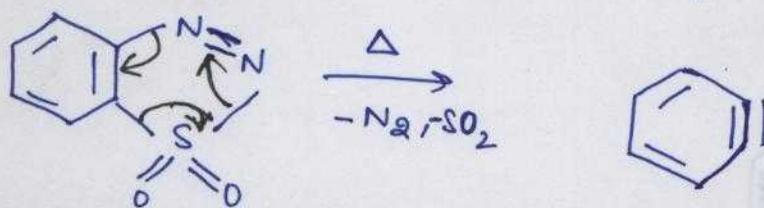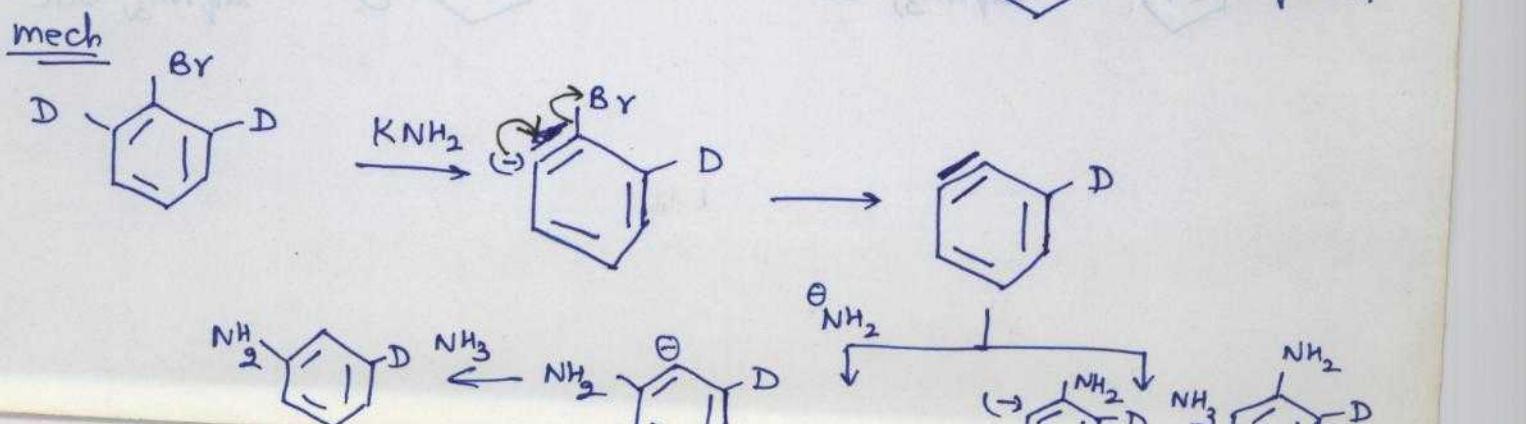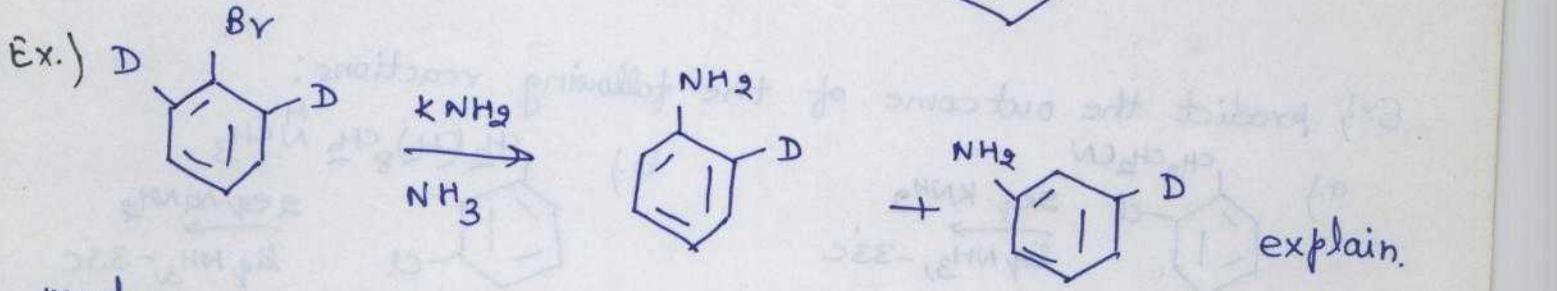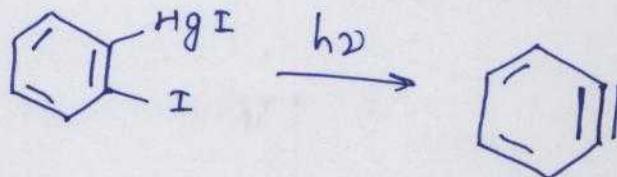
Benzyne can form in various steps:-

i)

$$\xrightarrow[-N_2, SO_2]{\Delta}$$

ii) Photolysis:-

$$\xrightarrow{h\nu}$$

Ex.) D

$$\xrightarrow[NH_3]{KNH_2}$$

explain.

mech


$$\xrightarrow{KNH_2}$$
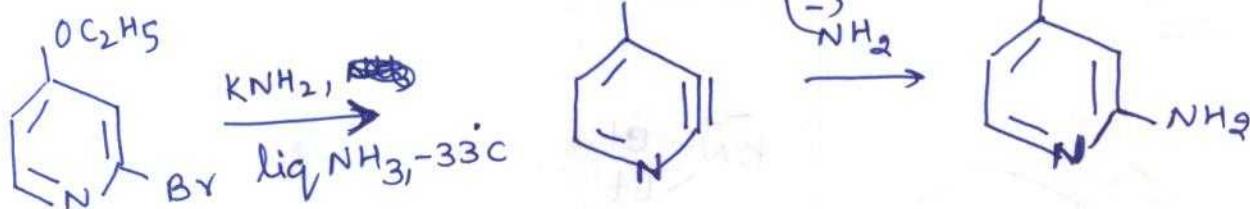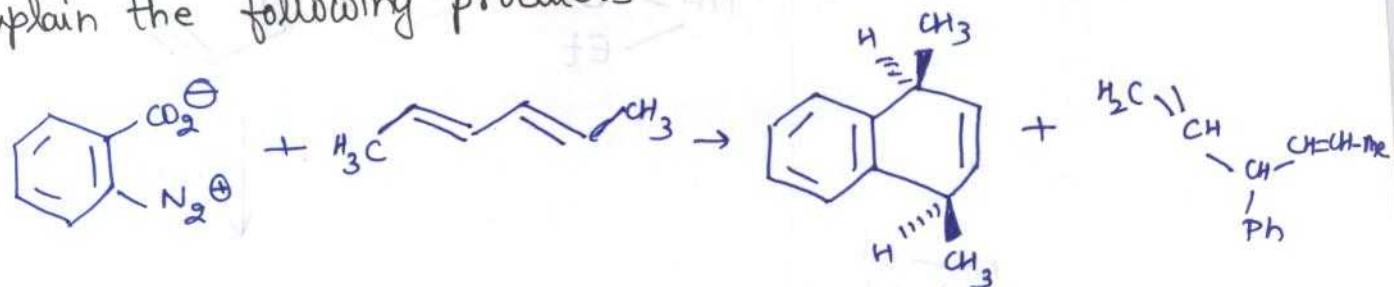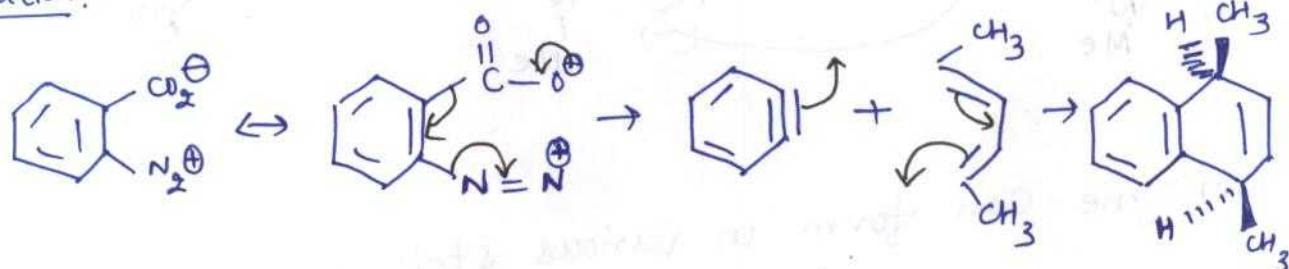
Ex.)
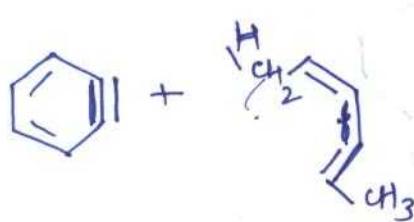
Ex.) explain the following products
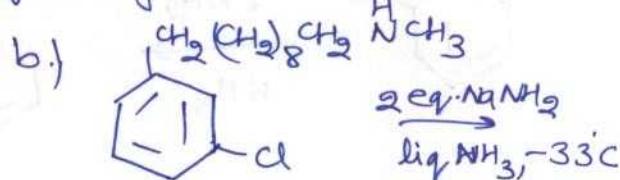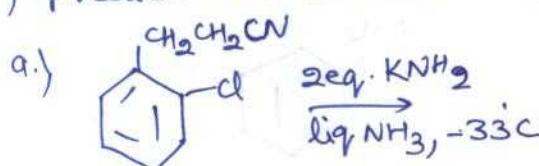
explaination:-


also,
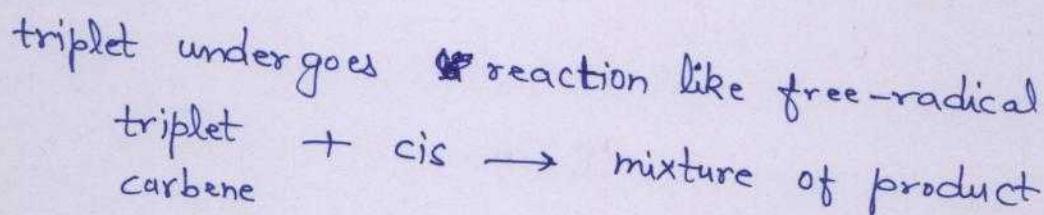
Ex.) predict the outcome of the following reactions:

a.)

2eq. KNH₂
liq NH₃, -33°C

b.)

2 eq. NaNH₂
liq NH₃, -33°C
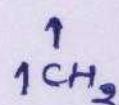
<u>Carbene</u> : Generally they are electrophilic in nature.

- In solution generally <u>singlet</u> carbene is obtained.
- When heat or light ($h\nu$) is used then generally <u>triplet</u> carbene is obtained.
- Electron rich substituents (like cl, Br, ome) stabilize the <u>singlet</u> carbene by delocalization.
- <u>All</u> carbenes which have <u>all electron-rich substituents</u> carrying lone pair adjacent to the carbon centre will be <u>essentially</u> <u>singlet</u> carbene and these are <u>less electrophilic</u> than normal carbene.
- Singlets are less stable than triplet by 40 KJ/mole energy.
- Singlets undergo stereospecific reaction (It undergoes concerted reaction)

$$\text{singlet + cis} \longrightarrow \text{cis - product}$$
carbene

where as

triplet undergoes reaction like free-radical

$$\text{triplet + cis} \longrightarrow \text{mixture of product}$$
carbene

- $\overset{..}{C}H_2$ obtained for CH_2N_2 are generally singlet and they undergo stereospecific reaction with double bond.

always show triplet like

$$\uparrow CH_2$$
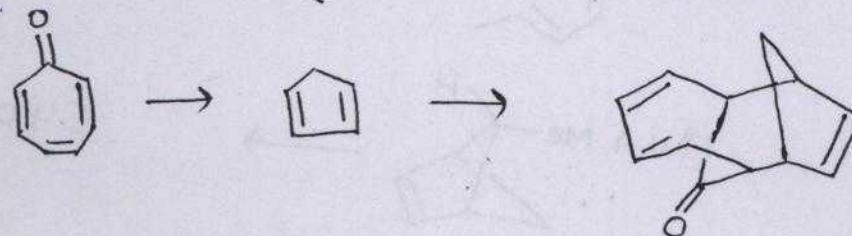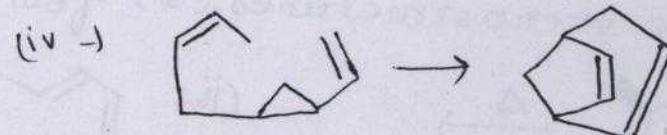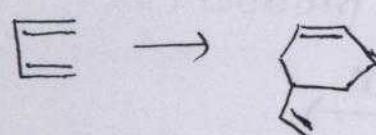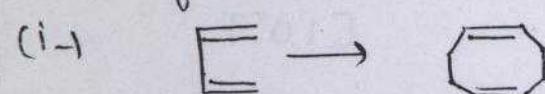
2005:

(1–) Draw HOMO & LUMO for 1,3-butadiene π orbitals under thermal condition. Draw LUMO (SUMO) of the same species under hv condition. Explain why this SOMO can act as both HOMO & LUMO.   [10]

(2–) Indicate condition (thermal/photochemical) as well as feasibility for the accomplishment of the five, (i)–(v), transformations. Justify your answer!

(i–) E → ⬡   (ii–) E → (cyclobutene with vinyl)

(iii–) E → (cyclohexene)   (iv –) (diene) → (bicyclic)

(v–) (cycloheptadienone) → (cyclopentadiene) → (bicyclic ketone)   [20]
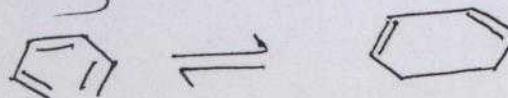
(3 –) Write short accounts on significance of the abbreviated general form of pericyclic selection rules
$[(4q+2)_s + (4r)_a = odd]$ in predicting the feasibility of these reactions under thermal condition.   [10]

2004:

(4–) Thermal interconversion of 1,3,5 hexatriene to cyclohexadiene under thermal takes place by distortion. Explain showing M.O diagram.   [10]
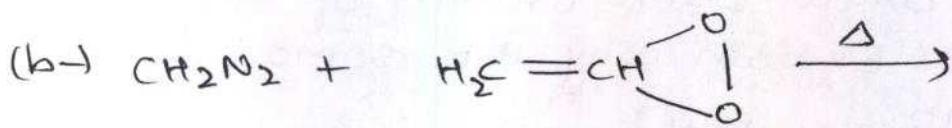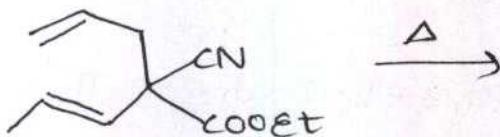
(5–) Illustrate the mechanism involved in [1,3] sigmatropic rearrangement with one suitable example under thermal and photochemical conditions by FMO.   [10]

(6 –) Explain the following interconversion by correlation diagram method:

(bicyclic) ⇌ (benzene)   [10]

7-) (a)

$\xrightarrow{\Delta}$

(b-) CH_2N_2 + $H_2C = CH$ $\xrightarrow{\Delta}$
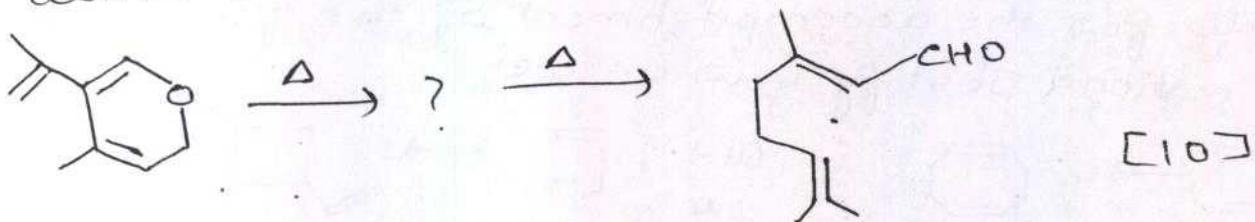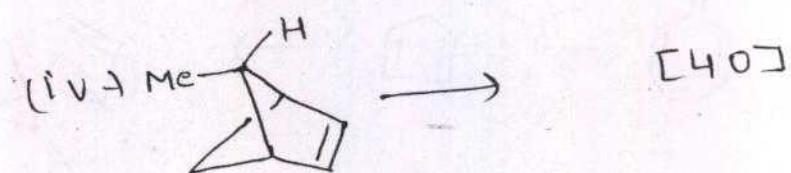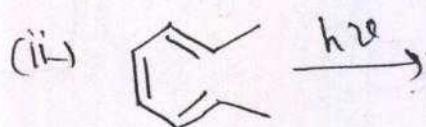
2003:

8-) write the mechanism:

 $\xrightarrow{\Delta}$? $\xrightarrow{\Delta}$

[10]
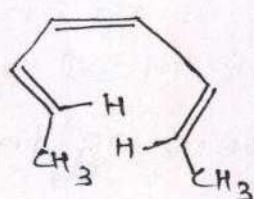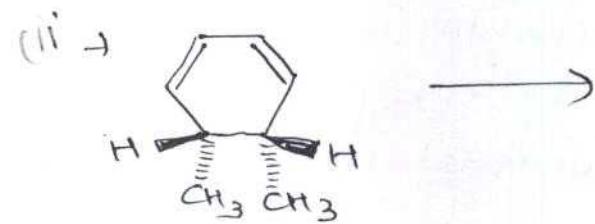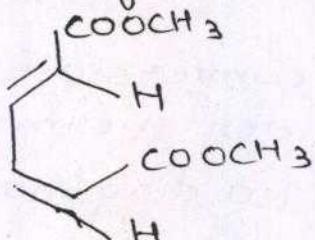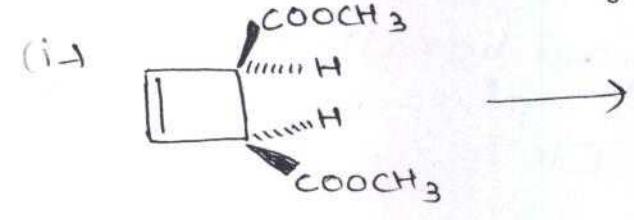
9-) Draw sterostructures (s) for the product (s):

(i -) $\xrightarrow{\Delta}$

(ii-) $\xrightarrow{h\nu}$

(iii -) $\xrightarrow{\Delta}$

(iv-) Me $\longrightarrow$

[40]
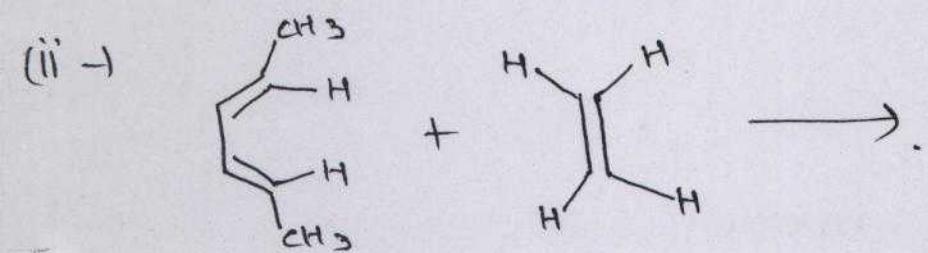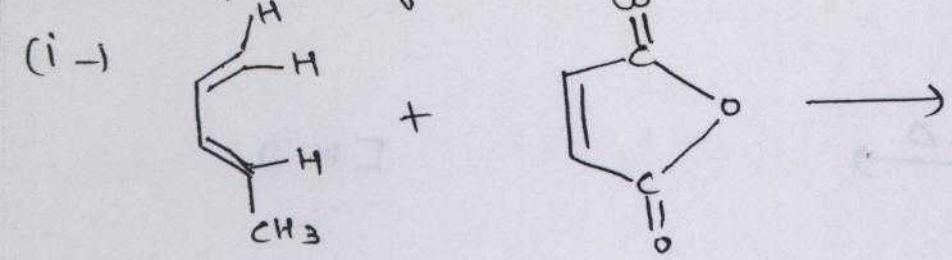
2002:

10-) state whether conrotatory or disrotatory mode of rotation is involved in each of the following reactions. Also state whether you would expect the reaction to occur under the influence of heat or light.

(i-) $\longrightarrow$

(ii -) $\longrightarrow$

[10]

(11-) Diels alder rxn. is a sterospecific reaction. Comment on this. Write the structures of the products expected from each of the following reactions:

(i-)

(ii-)

[10]

(12-) Construct a correlation diagram for conrotatory interconversion of cyclohexadiene - Hexatriene system.

[10]

2001:

(13-) Apply FMO method to predict the reaction conditions for $\pi^4 s + \pi^2 s$' and '$\pi^2 s + \pi^2 s$' cycloadditions. [10]

(14-) Hexatriene cyclohexadiene electrocyclic interconversions can be carried out thermally as well as photochemically. Predict the stereochemistry of these interconversio

[10]

(15-) Predict reaction conditions for 1,3-antrafacial and suprafacial sigmatropic shifts. [10]
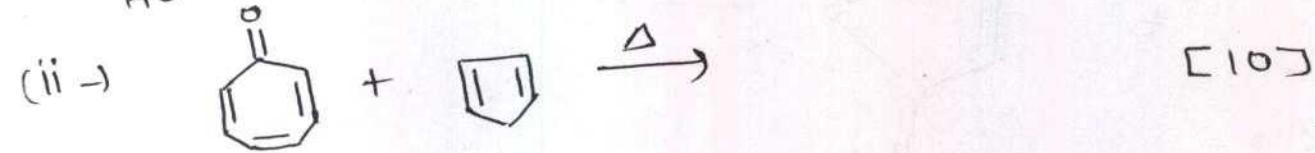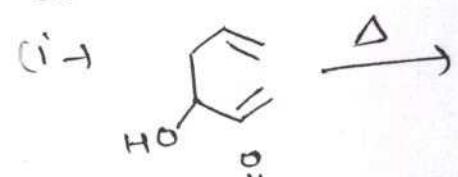
2000:

(16-) Analyse the following rxn:

and show that this is a conrotatory thermally allowed and disrotatory thermally forbidden process. Justify your answer by the construction of correlation for both processes.

[20]

(17-) what products are formed in the following reaction and how:

(i)

(ii)

[10]

Imp topics for 2009

1.) IFS 2008 question – Schottky defect conch

2.) Structure of CaF_2, Zns, cscl, Nacl.

3.) radius ratio rules → IFS 2007 Question

4.) X-ray diffraction & density calculation

5.) Non stoichiometric compounds (IAS 1995 question)

6.) old CSE Questions:– 3, 11, 14, 15, 17, 22, 27, 31 (2005)

3.) Solid State:~

1.) Discuss :- Non-stoichiometric compounds. [15 marks] [1974]

2.) Write short note on Interstitial compounds [15 marks] [1975]

3.) What is defect structure? Discuss existence of non-stoichiometric compounds in the light of this phenomenon? [16 marks] [1978]

4.) Enumerate and illustrate, giving one example of each, the seven systems in which crystalline substances have been classified. [20 marks] [1975]

5.) What is a face-centered cubic lattice? Give the experimental evidence to show that sodium chlorine has got this type of lattice. [20 marks] [1976]

6.) Explain and illustrate: i) Space lattice ii) unit cell iii) Miller indices iv) ionic crystal. [20 marks] [1977]

7.) What are the distinguishing features of the crystal systems: cubic, triclinic, tetragonal and orthorhombic in terms of shapes of the unit cell (length of axes a, b, c and angles α, β, γ)? [16 marks] [1978]

8.) For a primitive cubic unit cell, express the interplannar spacing d_{100} & d_{111} in terms of d_{100}. [4 marks] [1978]

9.) Deduce the Bragg equation for the diffraction of X-rays. [20 marks] [1979]

10.) Explain how X-rays diffraction studies have helped in structural analysis. [20 marks] [1979]

11.) Indicate the principles involved in electron diffraction and mention the advantages of this technique over x-ray diffraction. [20 marks] [1979]

12.) Why are x-rays used to determine the crystal structure? [10 marks] [1980]

13.) Sodium Chloride forms a face-centered cubic crystal. The length of the side of the unit cell

and the molar mass is 0.0585 kg/mol. Find out the density of the salt. [20 marks] [1980]

14.) Describe the method of measuring bond angles and bond distances in diatomic molecules by electron diffraction studies in gases and liquids. [20 marks] [1982]

15.) Give an account of the principles involved in electron diffraction method for the measurement of bond distances and bond angles in simple molecules. How far and in what respects is this method superior to x-ray diffraction method for the same purpose? [60 marks] [1982]

16.) Describe briefly Bragg's x-ray diffraction method for the study of the structures of sodium chloride. [20 marks] [1986]

17.) Describe briefly how x-ray diffraction is used for structure determination. [10 marks] [1987]

18.) Interplanar distance for NaCl crystal is 2.8×10^{-8} cm. In a Bragg scattering experiment using NaCl crystal grating, what would be the wavelength of x-rays which show a first order 'reflection' angle of $8.4°$. [$\sin 8.4° = 0.145$] [15 marks] [1988]

19.) Explain the law of rationality of indices, obtain the ratio $d_{100} : d_{110} : d_{111}$ for a cubic lattice. [10 marks] [1989]

20.) Discuss the characteristics and applications of liquid crystals. [15 marks] [1989]

21.) An orthorhombic crystal has the following unit cell dimensions: $a = 0.542$ nm, $b = 0.917$ nm, $c = 0.645$ nm. Calculate the diffraction angle for first order reflection from (010) plane using x-ray of 0.154 nm. [25 marks] [1990]

22.) Name the important defect in crystals. How are they caused? What is the effect of these defect on the stability of the crystal. [15 marks] [1990]

23.) In sodium chloride crystal, what is the coordination number of the Na^+ ion? How many Na^+ ions occupy second nearest neighbours of Na^+ ion? Show clearly (1 10) planes in a cubic crystal. [15 marks] [1991]

24.) What are liquid crystals? Discuss the arrangements of molecules in smectic and nematic phases of liquid crystals. [15 marks] [1991]

25.) What do you understand by 'Miller Indices' of a set of planes? A plane intercepts the three axes a, b, and c of the unit cell at $\frac{a}{2}$, $-\frac{b}{2}$ and ∞ respectively. What are its Miller indices? If the cell is ortho rhombic, what is the distance between two such adjacent planes if a, b and c are 0.22, 0.30 and 0.35 mm respectively. [15 marks] [1992]

26.) Distinguish intrinsic defects from extrinsic defects and give an example of each. [15 marks] [1992]

27.) Define a cubic crystal in terms of unit cell dimensions and Eulerian angles. What are the Bravais lattices associated with the cubic crystal? For a cubic cell, what is the spacing between planes specified by the Miller indices h, k, and l? What are the numbers of atoms per unit cell for metals crystallizing in simple orthorhombic and body-centered orthorhombic lattices? [20 marks] [1993]

28.) Explain how many ions of each kind are present in the unit cell of i) CaF_2 ii) TiO_2 and iii) Diamond. [15 marks] [1994]

Imp topic for 2009

i) Intermolecular Interactions
      ↳ Ion-dipole forces

ii) Effusion of gases → derivation
             ↳ Pressure dependence

iii) Thermal Conductivity & viscosity

iv) Law of Corresponding States

4.) Gaseous State:-

1.) Derive the Maxwell-Boltzman distribution Law. [20 marks] [1977]

2.) ~~Show~~ What is meant by the equation of state of a gas, state and explain Van der Waals' equation and use it to

   a.) Discuss the isotherms of a real gas near the critical point and b.) obtain a reduced equation of state [20 marks] [1970]

3.) State and Explain Van der Waal's equation and show how it can be used to determine molecular weight through limiting density. [20 marks] [1972]

4.) Discuss the physio chemical principles underlying the liquifaction of ~~gass~~ gases. [20 marks] [1973]

5.) Derive the equation denoting the Law of Corresponding States from van der Waals' equation of state.
   Explain clearly the terms: Critical pressure (P_c); critical temperature (T_c), and critical volume (V_c). Derive expression correlating these values with constants 'a' and 'b' of the van der Waal's equation $\left(P + \frac{a}{V^2}\right)(V-b) = RT$. [50 marks] [1974]

6.) Explain the term root mean square velocity. How is it related to the molecular weight of a gas. [20 marks] [1976]

7.) Explain the Law of Corresponding states. [8 marks] [1977]

8.) Starting with van der Waals' equation obtain expressions for critical Constants (P_c, V_c, T_c) of a gas. Show that for all gases obeying Van der Waals' equation $RT_c / P_c V_c = 2.66$.

9.) Calculate the pressure exerted by 2 moles of nitrogen confined to 5-litre flask at 27°C using:
   i) ideal gas equation ii) Van der Waals' equation.
   [$a = 1.39$ atm lit^2 mol^{-2}; $b = 0.0391$ lit mol^{-1}, $R = 0.082$ lit. atm deg^{-1}]

10.) State and explain the law of corresponding states. For large no. of substances, the quantity $R\tilde{T}_c/P_cV_c$ lies between 3.4 and 3.7. Comment on the fact

[2000] [20 marks]

11.) What do you understand by liquification of gases? Explain critical temperature and critical pressure. Draw schematic diagram for liquification of air.

[15 marks] [2006]

12.) Derive the Van der Waal's equation of state for real gases. What are the units of Van der Waal's constants.

[20 marks] [2007]

13) Define the terms: critical temperature, critical pressure and critical volume. How are these constants determined experimentally?

[20 marks] [2007.]

14.) State and explain Maxwell's law of distribution of velocities of molecules of a gas at a definite temperature. What is meant by most probable velocity.

[20 marks] [2008]

2000

1.) Calculate the rms velocity and the most probable velocity for hydrogen gas at $0°C$

2) 2001

1.) Calculate the avg and rms speeds of N_2 at $500°C$.

2.) Define Boyle Temperature. What is its significance? Estimate the Boyle temperature of N_2 from Van der Waal's constants. Given: $a = 1.39 \ dm^6.atm$; $b = 0.039 \ dm^3$, $R = 0.082 \ dm^3 \ atm.K^{-1}$

3) 2002

1.) Calculate the rms velocity of the molecule of a gas whose density is $1.4 \ gm/litre$ at a pressure of 76 mm Hg.

2.) Write a note on Maxwell's law of distribution of velocities. Derive relation for most probable, avg and mean square velocities.

2003

1.) Write a note on Liquification of gases.

[10 marks] [C]

2006

1.) Write a short note on liquification of gases. Discuss

i) Ion dipole and ii) London Dispersion forces. [10 marks] [C]
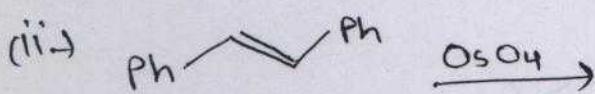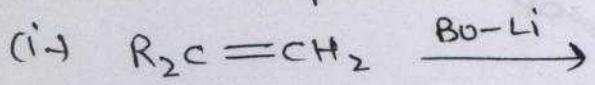
2007

1) Explain and illustrate the terms, dipole-dipole attraction and ion-dipole attraction, which of these a comparatively stronger.

[10 marks] [C]

2.) Suggest explaination/s for the fact that gases diffuse through all the space available to them. [10 marks] [C]
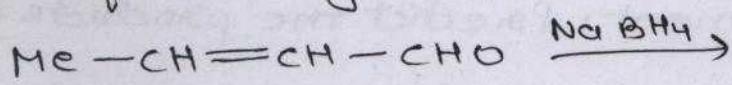
Chemistry (Paper II) (Reagents) (IFS)
2004:

(1) Explain the formation of the products including stereo-chemical aspects with possible mechanism:

(i) $R_2C = CH_2 \xrightarrow{Bu-Li}$
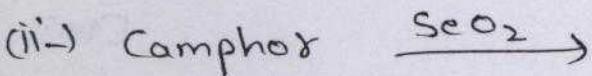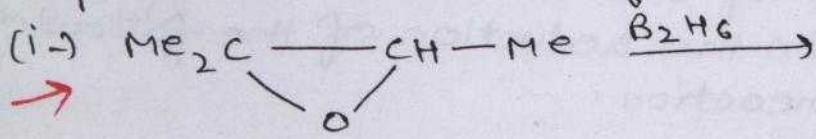
(ii) $Ph \diagup \diagdown Ph \xrightarrow{OsO_4}$ [10]

(2) Explain the important applications of sodium borohydride as a reducing agent. Explain with mechanism the reaction of the following compound: [10]

$Me - CH = CH - CHO \xrightarrow{NaBH_4}$
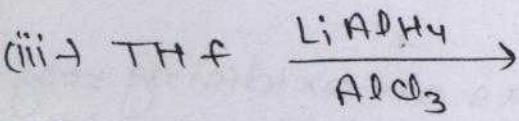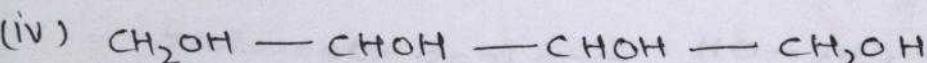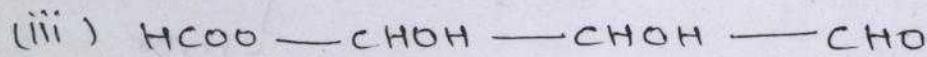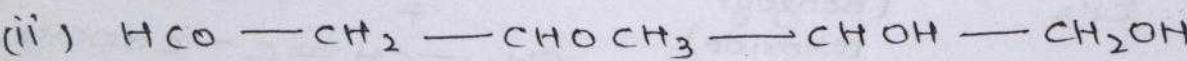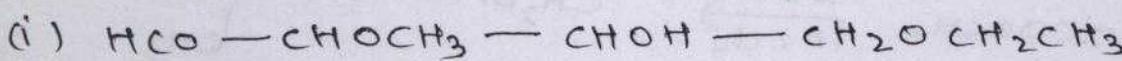
(3) Explain the formation of products, stereochemical aspects & mechanism for the following reactions:

(i) $Me_2C \overset{}{\underset{O}{\diagdown \diagup}} CH - Me \xrightarrow{B_2H_6}$

(ii) Camphor $\xrightarrow{SeO_2}$

(iii) THf $\xrightarrow[AlCl_3]{LiAlH_4}$ [15]
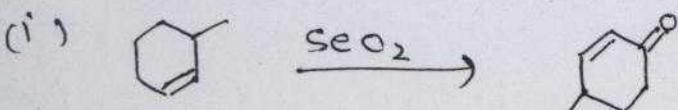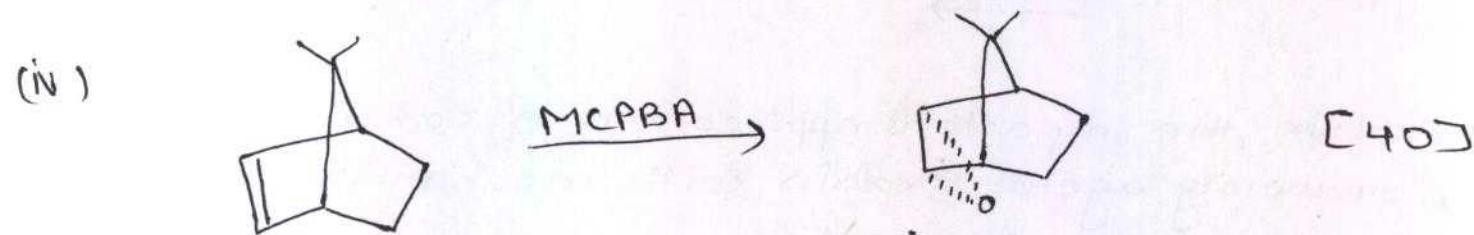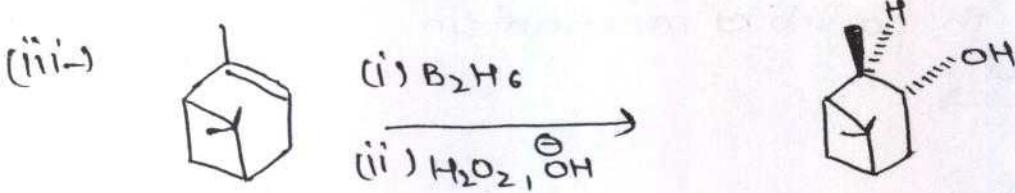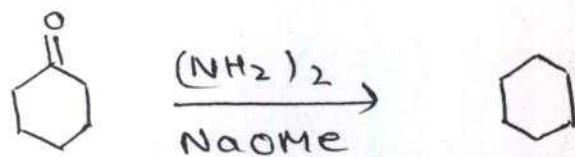
(4) How will you employ reaction with HIO_4 in differentiating the four compounds (1-4)? Indicate the products and HIO_4 consumed in each case:

(i) $HCO - CHOCH_3 - CHOH - CH_2O CH_2 CH_3$

(ii) $HCO - CH_2 - CHOCH_3 - CHOH - CH_2OH$

(iii) $HCOO - CHOH - CHOH - CHO$
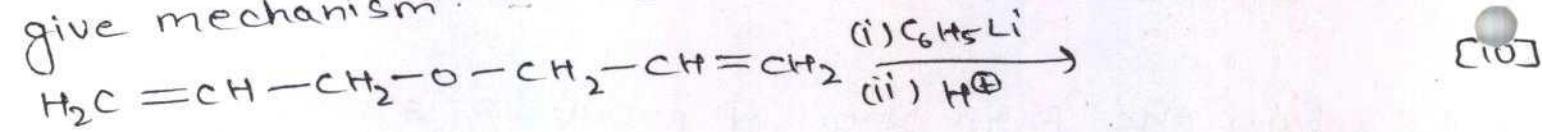
(iv) $CH_2OH - CHOH - CHOH - CH_2OH$ [10]

(5) Explain the formation of the products, Including stereochemical aspects, if any, with mechanism:

(i) $\xrightarrow{SeO_2}$

(ii→)

$$\text{(cyclohexanone)} \xrightarrow[\text{NaOMe}]{(NH_2)_2} \text{(cyclohexane)}$$

(iii→)

$$\xrightarrow[\text{(ii) } H_2O_2,\ \overset{\ominus}{O}H]{\text{(i) } B_2H_6} \text{(product with OH)}$$

(iv)

$$\xrightarrow{MCPBA} \text{(epoxide product)} \qquad [40]$$

(6→) Name the rearrangement. Predict the products & give mechanism:

$$H_2C=CH-CH_2-O-CH_2-CH=CH_2 \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) } C_6H_5Li} \qquad [10]$$
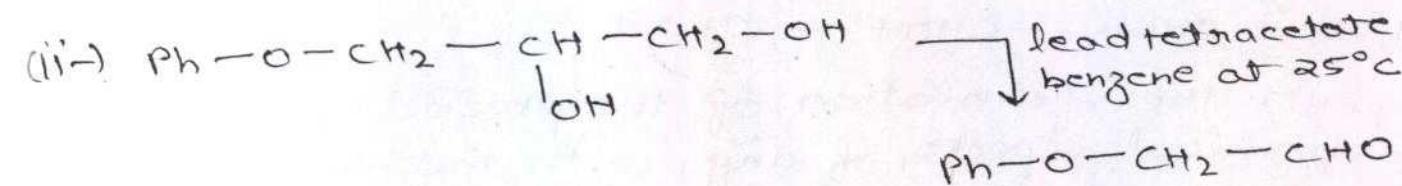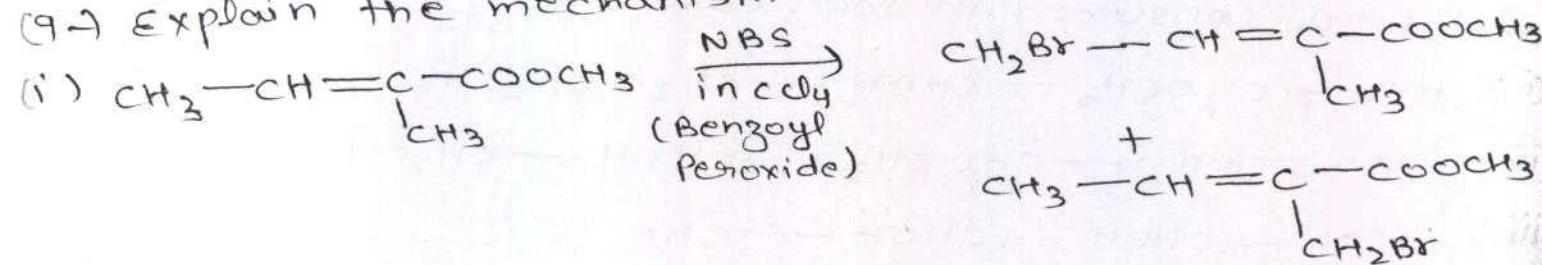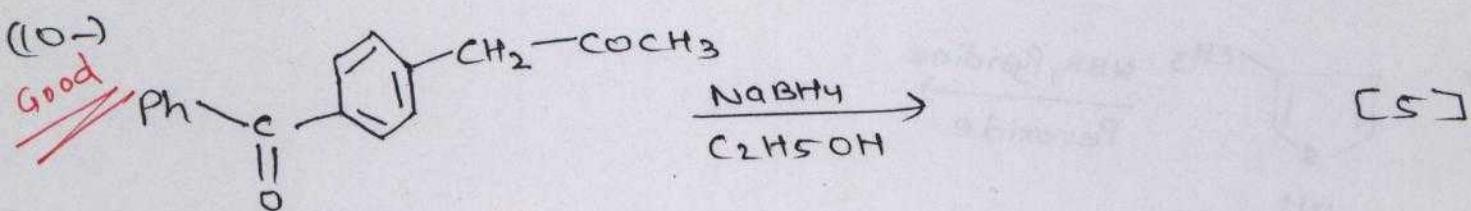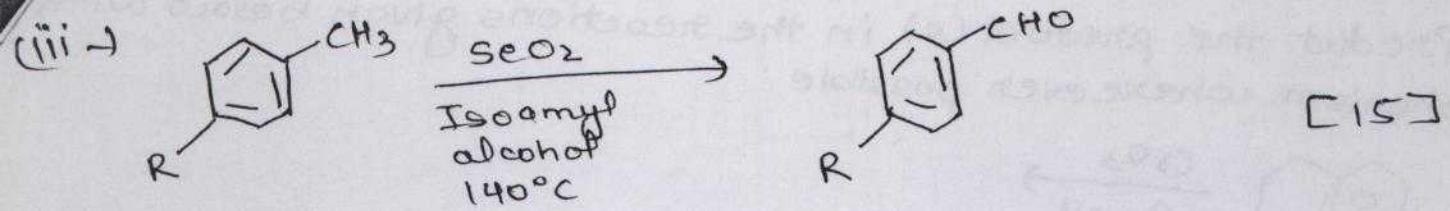
(7→) Explain the application of Lithium aluminium hydride as a reducing agent. Explain the reduction of the following compound. formulate the reaction:

$$\xrightarrow{\underset{(C_2H_5)_2O}{LiAlH_4}} \qquad [10]$$
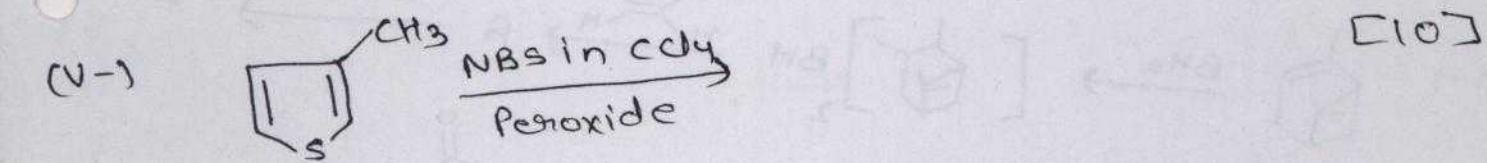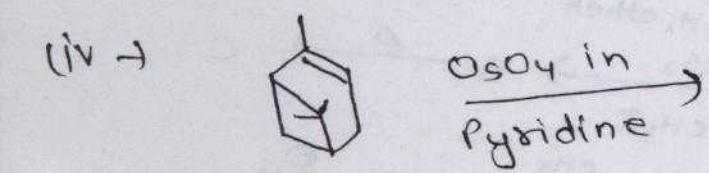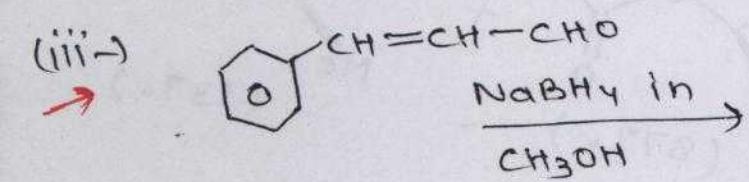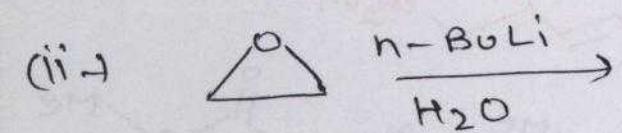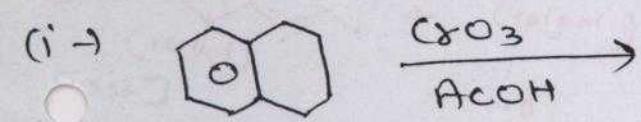
(8→) Describe the application of SeO_2 as an oxidising reagent. Explain the oxidation of phenyl benzyl ketone with this reagent in aqueous acetic acid at 89°C. [10]

(9→) Explain the mechanism:

(i)
$$CH_3-CH=\underset{\underset{CH_3}{|}}{C}-COOCH_3 \xrightarrow[\substack{\text{in } cCl_4 \\ \text{(Benzoyl Peroxide)}}]{NBS} \quad CH_2Br-CH=\underset{\underset{CH_3}{|}}{C}-COOCH_3$$
$$+$$
$$CH_3-CH=\underset{\underset{CH_2Br}{|}}{C}-COOCH_3$$

(ii→)
$$Ph-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-OH \xrightarrow[\text{benzene at 25°C}]{\text{lead tetraacetate}}$$
$$Ph-O-CH_2-CHO$$

②

(iii→) [structure: toluene with R para, CH₃] $\xrightarrow[\substack{\text{Isoamyl}\\\text{alcohol}\\140°C}]{SeO_2}$ [structure: benzaldehyde with R para, CHO] [15]

(0-)
~~Good~~ Ph—C(=O)—[benzene]—CH₂—COCH₃ $\xrightarrow[C_2H_5OH]{NaBH_4}$ [5]

(II→) Predict the products in the reactions given below:

(i→) [bicyclic structure with O] $\xrightarrow[ACOH]{CrO_3}$

(ii→) [epoxide/oxirane structure] $\xrightarrow[H_2O]{n-BuLi}$

(iii→) [benzene with O and CH=CH—CHO] $\xrightarrow[CH_3OH]{NaBH_4 \text{ in}}$

(iv→) [α-pinene structure] $\xrightarrow[Pyridine]{OsO_4 \text{ in}}$

(V-) [thiophene with CH₃] $\xrightarrow[Peroxide]{NBS \text{ in } CCl_4}$ [10]

(1) Predict the product(s) in the reactions given below with mechanism where ever possible:

(i)

(structure: bicyclic with O) $\xrightarrow[\text{AcOH}]{CrO_3}$

(ii)

(thiophene ring with CH_3) $\xrightarrow[\text{Peroxide}]{\text{NBS, Pyridine}}$

(iii)

(cyclohexadiene with OH) $\xrightarrow[\text{THF}]{OsO_4, \text{Pyridine}}$

(iv)

(structure with C=O and $COOCH_3$) $\xrightarrow{\text{NaBH}_4, CH_3OH}$

$\xrightarrow[\text{ether}]{\text{LiAlH}_4}$

(major) + (minor) — with OH, $COOCH_3$, CH_2OH products

[20]

(2) Ph—C(Me)—C(=O) $\xrightarrow{\text{Per acid}}$

Ph—O—C(=O)—Me (Me) (87%) + Ph—C(Me)—C(=O)—O—Me (Me) (13%)

(3) (i) (cyclooctanone) $\xrightarrow[\text{(ii) } H_3O^\oplus]{\text{(i) LiAlH}_4}$ A $\xrightarrow[\text{(iii) } CH_3I]{\text{(i) NaH, ether} \quad \text{(ii) } CS_2}$ B $\xrightarrow{\Delta}$ C

(ii) (structure) $\xrightarrow{\text{BH}_3}$ [ ]BH_2 $\xrightarrow[\text{CH}_3 \quad H \quad CH_3 \quad H]{}$ A $\xrightarrow{H_2O_2, \; \overset{\ominus}{O}H}$ B

(iii) (di-Ph C=O) + CH_2— (cyclopentadienyl) $\xrightarrow[\text{(ii) } n\text{-BuLi}]{\text{(i) Ph}_3P}$ A $\xrightarrow{\text{(N–Br succinimide)}}$ B

(iv) (cyclohexanone) $\xrightarrow{\text{NaBH}_4}$ A $\xrightarrow{H_2SO_4}$ B $\xrightarrow{Pb(OAc)_4}$ C + D + E [3]

(4) Explain: o-deuterio-fluorobenzene reacts with sodium amide in liq. ammonia to yield aniline more slowly than does o-deuteriobromobenzene, when the reaction of

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Thermodynamics

1. Prove that entropy is a state function.

(10, 2005)

2. Derive Clausius –Clapeyron equation for the variation of vapour pressure with temperature. Calculate the equilibrium pressure for the conversion of graphic to diamond at 25°C assuming their densities to be 2.25 and 3.51 gm cm^{-3} and $\Delta G° =$ 2900 Jule per mole.

(25, 2005)

3. Define molar partition function and explain its importance. Show that heat capacity of ideal gas is $\frac{3}{2}$ R.

(20, 2005)

4. Derive an expression for the entropy of mixing of two ideal gases at the same temperature and pressure.

(20, 2005)

5. Mention the temperature and pressure at which water has a triple point where it can exist as solid ice liquid and vapour. Apply phase rule to this triple point.

(20, 2005)

6. Derive the equation for calculating the entropy change for isothermal pension of a perfect gas.

(20, 2004)

7. Discuss upper and lower critical solution temperatures with examples. Explain thermodynamic interpretations of the upper critical solution temperature.

(2004)

8. Derive the nearest heat theorem

(20, 2004)

9. Derive Clausius – Clapeyron equation for the variation of vapour pressure with temperature.

(20, 2004)

10. Define molecular partition function. What is its importance? Calculate the translational contribution to the internal energy of an ideal gas and show that its heat capacity is $\frac{3}{2} R$.

(20, 2003)

11. Obtain the expression for the entropy of mixing of two ideal gases with n$_1$ and n$_2$ moles respectively at the same temperature and pressure.

(10, 2003)

12. What is the entropy of mixing of one mole of oxygen with one mole of nitrogen at 25°C assuming they are ideal gases?

(10, 2003)

13. The vapour of water is 23.75 torr at 25°C and 760 torr at 100°C. What will be the heat of vaporization? (30, 2003)

14. Prove that entropy is a state function.

(30, 2002)

15. Discuss the entropy of phase transition at the transition temperature and the variation of entropy with temperature.

(30, 2002)

16. Derive clapeyron equation and show that it can be represented by the equation

$$P = P^* \, e^{-\frac{\Delta H_V}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)}$$

for liquid vapour boundary assuming ideal gas behaviour and making certain approximation.

(30, 2001)

17. Show that the total differential of entropy in terms of temperature and volume can be expressed by the equation

$$ds = \frac{C_V}{T}dT + \frac{\alpha}{K}dv$$

(30 2001)

2008 :

(1-) Explain the criteria of equilibrium & spontaneity in terms of U, S, A & G. [20]

(2-) "The third law of thermodynamics states an impossibility." Justify this statement. [10]

(3-) Explain why the molar entropy of ice crystals approaches 3.35 J/k/mol, as the temperature zero Kelvin is approached. [10]

(4-) Define chemical potential. Explain its significance. Deduce equations for the variation of chemical potential with temperature & pressure. [20]

(5-) For the reaction
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$K_p = 1.64 \times 10^{-4}$ at 670 K. Calculate ΔG°. [10]
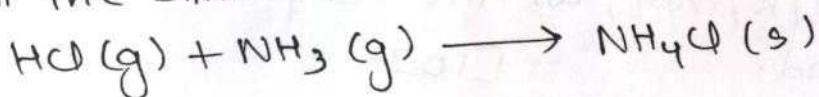
2009 :

2006:
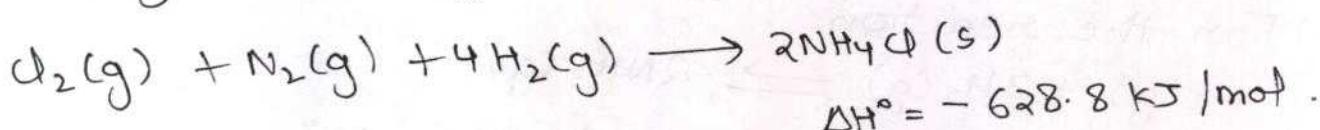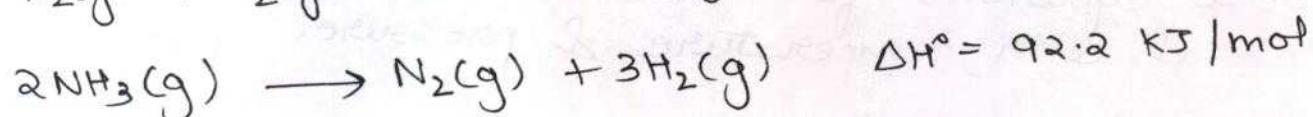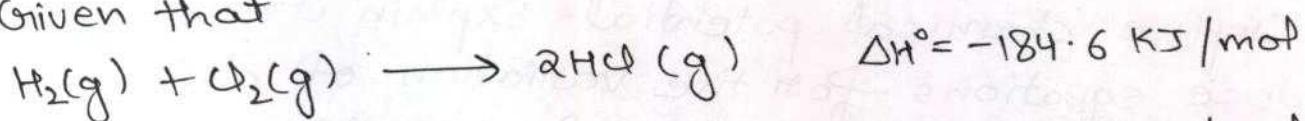
(1) What do you understand by entropy of a system? How it increases with increasing temperature & Δs becomes zero at absolute temperature?

[20] [c]

(2) Explain Hess's law. calculate the enthalpy change for the rxn.

$$HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$$

Given that

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H° = -184.6 \text{ KJ/mol}$$

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g) \qquad \Delta H° = 92.2 \text{ KJ/mol}$$

$$Cl_2(g) + N_2(g) + 4H_2(g) \longrightarrow 2NH_4Cl(s)$$
$$\Delta H° = -628.8 \text{ KJ/mol}.$$

[20]

2007:

(1) The enthalpy of neutralization of NH_4OH & HCl is -51.46 KJ/mole. calculate the enthalpy of ionisation of NH_4OH. Assume that the enthalpy of neutralization of a strong acid with a strong base is -55.9 KJ/mole.

[20]

(2) Discuss the entropy change in reversible & irreversible processes. comment on the statement: "Entropy of the universe is always increasing". [20]

(3) Explain nernst heat-theorem. How does it lead to the enunciation of the 3rd law of thermodynamics. How can the latter be verified experimentally.

[20]

1.) Give a critical account · of the factors which affect the stability of complex ions and discuss the principle of any one method employed for determining the stability constant of complex ions in solution. [1973]

2.) Why is the colour of $[Cu(NH_3)_4]^{2+}$ different from that of $[Cu(H_2O)_6]^{2+}$ or $[Cu(NH_4)]^{3-}$? [1975]

3.) Mention the causes for splitting of d orbitals. [1976, 8 marks]

4.) What is 'stability constant' of a complex? Discuss the the principle involved in the determination of the stability constant of a complex by either p^H metric or polarographic method. [1976, 16 marks]

5.) How do you explain the magnetic properties of complexes in the light of electrostatic crystal field theory? [1976, 16 marks]

6.) What is crystal field splitting? Discuss its importance. [1977, 16 marks]

7.) What is stability constant of a complex? Enumerate the different methods used to determine it and describe one of them. [1977, 16 marks]

8.) Give a brief account of the Ligand field theory of co-ordination compounds and illustrate its applications in elucidating the spectral and magnetic properties of such compounds. [1978]

9.) Discuss how the Crystal Field Theory and the ligand field theory account for the bonding in metal complexes.

[1979, 20 marks]

10.) Draw d-orbital splitting diagrams for the high and low-spin octahedral complexes of Fe^{3+}. [1979, 30 marks]

11.) Explain why cyanocomplexes generally have low-spin configuration.

[1979, 10 marks]

12.) By using d-orbital splitting show which d^n configurations in transition metals are capable of both high spin and low spin configurations in an octahedral field.

[1980, 20 marks]

13) ~~Why do the electronic absorption spectra~~ The complex $[NiCl_4]^{2-}$ is paramagnetic with two unpaired electrons, while $[Ni(CN)_4]^{2-}$ is diamagnetic. By using Ligand Field theory explain these observations in terms of the structure of these complexes.

[1980, 20 marks]

14.) What are transition elements? Explain the basis of colour and variable valency of transition metal complexes.

[1980, 20 marks]

15.) Diamagnetic complexes of Co(III) like $[Co(NH_3)_6]^{3+}$ and $[Co(NO_2)_6]^{3-}$ are orange-yellow while paramagnetic complexes like $[CoF_6]^{3-}$ and $[Co(H_2O)_3F_3]$ are blue. Explain qualitatively the difference in colour.

[1981, 20 marks]
[1983, 20 marks]

16.) $[Ni(CN)_4]^{2-}$ is diamagnetic while $[NiCl_4]^{2-}$ is paramagnetic with two unpaired electrons. Similarly $[Fe(CN)_6]^{3-}$ has only one unpaired electron, but $[Fe(H_2O)_6]^{3+}$ has five. Explain these on the basis of

17.) Give an account of the Crystal Field Theory in relation to the studies of metal complexes. What are the salient features of the Adjusted Crystal Field Theory (Ligand Field Theory)?   [1982, 20 marks]

18.) Give an account of the importance of pi-bonding in metal complexes. What are the experimental methods of evaluation of pi-bonds?   [1982, 20 marks]

19.) Write a note on the nature and significance of Charge transfer spectra.   [1983, 20 marks]

20.) ~~In~~ Give an account of relation of pairing energies of d^6 complexes to the crystal field stabilization energy.
                              [1983, 30 marks]

21.) Draw the d-orbital splitting pattern for a transition metal ion in a tetrahedral complex.   [1983, 20 marks]

22.) Coordination number 7 cannot be considered at all common and coordination number 8 cannot be considered to be common; yet the number of their known compounds has increased rapidly in recent years and is exceeded by 4 and 6 coordination only; while there are few structures known with co-ordination number more than 8. Taking one example of each type. Explain this [1983, 20 marks]

23.) What is Ligand Field Stabilization energy? Discuss its influence on the thermodynamic properties of transition metal complexes.   [1984, 20 marks)

24.) Calculate the spin-only magnetic moment for Co(II) ion in
i) a weak octahedral crystal field and ii) a strong octahedral crystal field.
                              [1984, ...]

25.) Discuss the factors which determine the nature of electronic absorption spectra of transition metal complexes
[1985, 30 marks]

26.) Predict giving reasons the spin only magnetic moments of the following ions: [1985, 20 marks]

$[Ni F_6]^{4-}$, $[Cr(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{4-}$, $[Ti(H_2O)_6]^{3+}$, and $[VCl_4]^{-}$

27.) Explain, giving examples, charge transfer transitions.
[1986, 10 marks]
[1987, 10 marks]
[1988, 5 marks]

28.) Calculate the spin-only magnetic moment of Co^{3+} ion
i) in a weak octahedral crystal field ii) a strong octahedral crystal field. [1987, 20 marks]

29.) Use Crystal field theory to discuss the ligand field stabilization energies of M^{2+} ions in $[M(H_2O)_6]^{2+}$ complexes where M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn
[1987, 30 marks]

30.) Give examples and explain the formation of compounds with i) two centre metal–metal bonds
ii) metal atom clusters. [1988, 20 marks]

31.) Explain the bonding in ferrocene. [1988, 20 marks]

32.) Explain the John–Teller Effect. [1988, 20 marks]

33.) Discuss the selection rules as applicable in the electronic spectra of transition metal complexes. [1988, 10 marks]

34) Calculate the spin only magnetic moment (in B.M.) of Sc^{3+}, V^{3+}, Mn^{2+}, Fe^{2+} and Cr^{3+} [1988, 20 marks]

35.) Give the electronic configuration and the number of unpaired electrons in Cr^{3+}, Cr^{2+}, Mn^{2+}, Co^{3+} and Co^{2+} in strong and weak octahedral fields. [1989, 20 marks]

36.) Using VB approach, explain the bonding in $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, $[Fe(H_2O)_6]^{2+}$, $[CoF_6]^{3-}$, and $Ni(CO)_4$. Also comment on their geometry [1989, 15 marks]

37.) Explain John-Teller Effect. [1989, 15 marks]

38.) Represent systematically the splitting of d-orbitals for tetrahedral and octahedral geometric arrangement of ligands. [1989, 10 marks]

39) Why is d^4 the most easily spin paired configuration in tetrahedral complexes? [1990, 10 marks]

40.) Write the d-electron configuration for d^n species (n = 3-8) in a weak octahedral field. Give the number of unpaired electrons in each case. [1990, 15 marks]

41.) Octahedral Co(III) complexes are pale pink while tetrahedral Co(II) complexes are usually intensely blue. Give reasons [1990, 10 marks]

42.) Octahedral and tetrahedral Ni(II) complexes are paramagnetic while square planar- are diamagnetic. [1990, 10 marks] Give reasons.

43.) What do you understand by Jahn-Teller effect? Explain with two suitable examples. [1991, 20 marks]

44.) An approximately octahedral complex of Co(III) with ammonia and chloride ligands give 2 bands with (ϵ_{max}) between 60 and 80 $m^{-1} cm^{-1}$, one weak peak with ϵ_{max} 2 $M^{-1} cm^{-1}$ and

a strong band with $\epsilon_{max} = 2 \times 10^4$ m$^-$ cm$^-$. Discuss the origin of the bands.   [1991, 30 marks]

from shriver & Atkins

45.) For what d^n configuration could maximum values of ligand field stabilization energy can be achieved for octahedral and for tetrahedral complexes? Are these situations actually encountered? [1992, 15 marks]

46.) What kind of Jahn-Teller distortion of a tetrahedral ML_4 complex would be expected for a d^9 ion? Explain your answer.   [1992, 20 marks]

47.) Discuss the magnetic properties of the octahedral complexes of Cr^{3+}, Cr^{2+}, Co^{3+} and Co^{2+}. [1992, 15 marks]

48.) What are the basic assumptions of crystal field theory? What are the electronic configurations for a d^6-complex in the presence of weak and strong octahedral crystal fields? How can magnetic studies verify your conclusions? What is spin-orbit coupling and what are its implications for magnetic and electronic spectral properties of inorganic complexes?   [1993, 20 marks]

49.) For transition-metal complexes, give a comparison between crystal-field, molecular orbital and valence-bond theories of bonding. Draw a picture of metal-ligand $d\pi - p\pi$ overlap.   [1993, 20 marks]
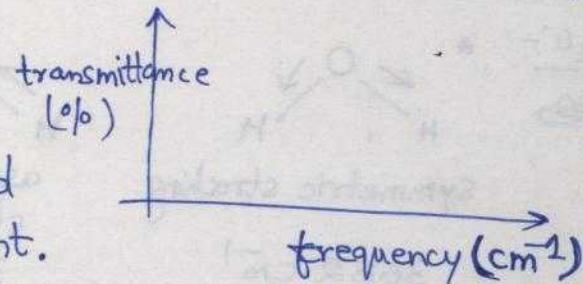
50.) How will the electronic spectra of cis and trans $[Co(en)_2 Cl_2]^+$ differ from each other? Give plausible explaination for the differences in their spectra.   [1994, 15 marks]

Infra red Spectroscopy :→

- Infra red region is beth $4000 - 650$ cm^{-1}.
- Functional groups in organic compounds have absorptions which are characteristic not only in position but also in intensity.
- In an infra red spectrometer, infrared radiation of successively increasing wavelength is passed through the sample of the compound and percent transmittance measured.
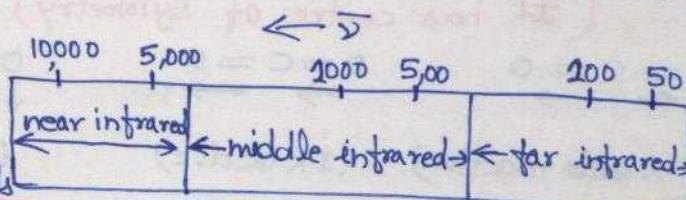
→ A 100% transmittance means no absorption and if all the radiation is absorbed the transmittance is 0 percent.

[graph: transmittance (%) on vertical axis vs frequency (cm^{-1}) on horizontal axis]

* It is impossible for any two different compounds (except enatiomers) to have precisely the same infrared spectrum.

* Finger print region :- (1500 to 600 cm^{-1}) because the pattern of absorption in this region are unique to any particular compound, so this region is called "finger print region".

* Infrared regions :-
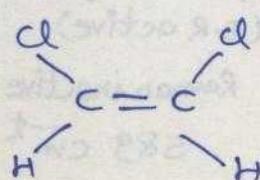
→ radiations in middle infrared regions corresponds to transition beth vibrational states.

[diagram: scale showing 10000 5,000 | near infrared | middle infrared | far infrared | with markings 1000 500 100 50, arrow ←$\bar{\nu}$ above, arrow →λ below]
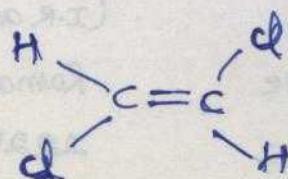
* The absorption of an infrared light quantum can occur only if the molecular vibrations lead to a change in the dipole moment of the molecule. Otherwise, they are said to be infrared inactive.

→ for ex :-

[structure: Cl and Cl on same side, C=C, H and H — for C=C vibration (I.R active)]

[structure: H and Cl, C=C, Cl and H (I.R inactive) becoz $\mu = 0$]

for C=C, vibration   (I.R active)
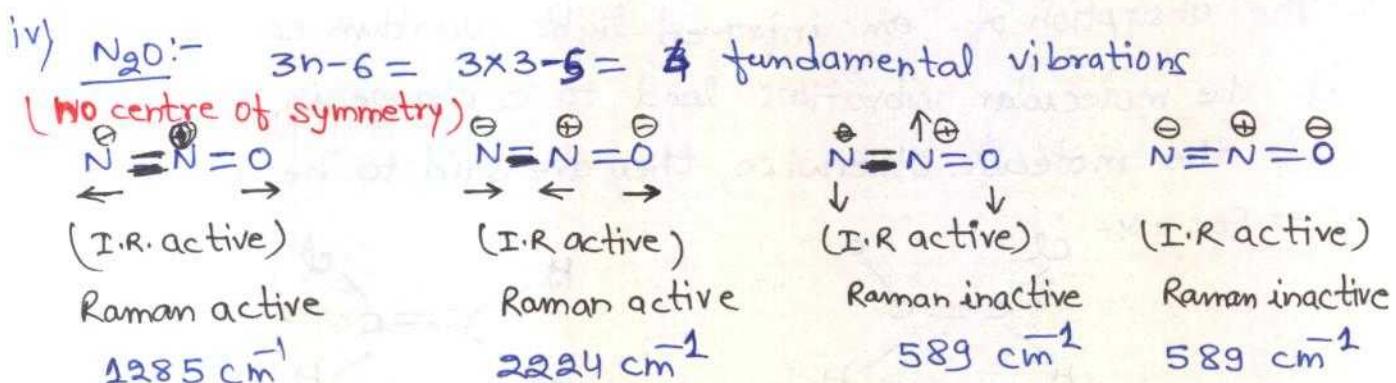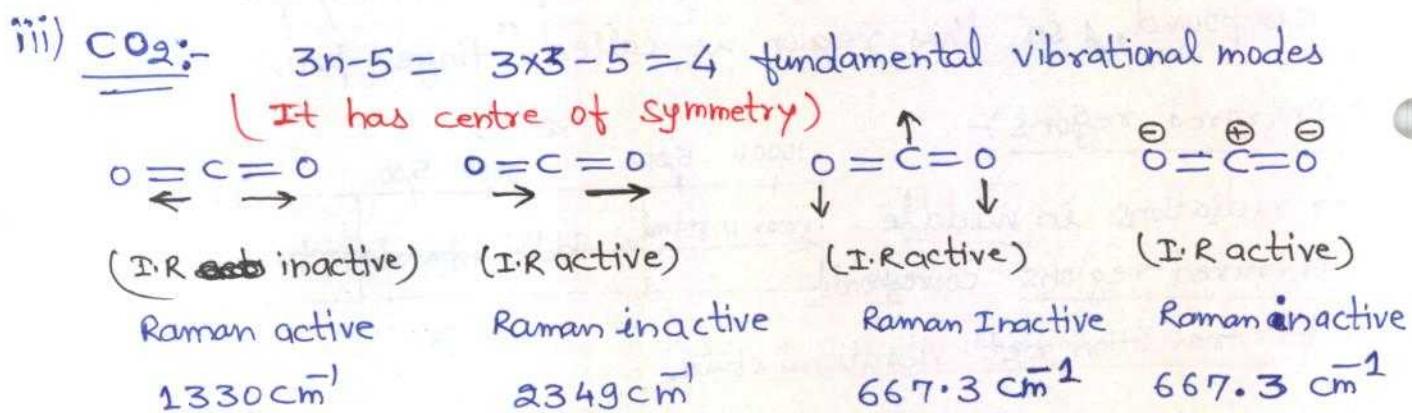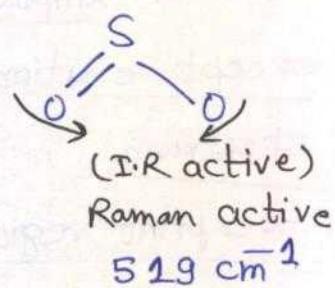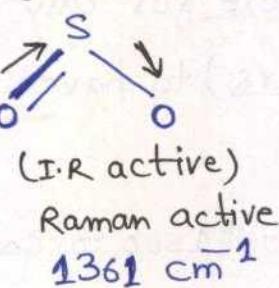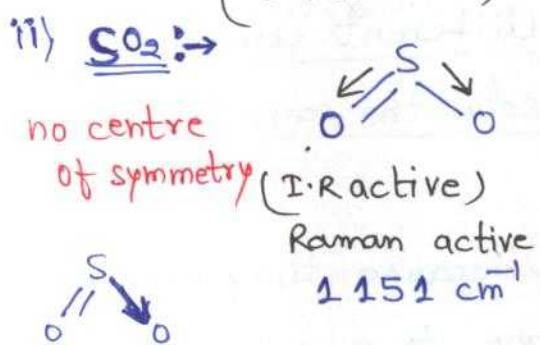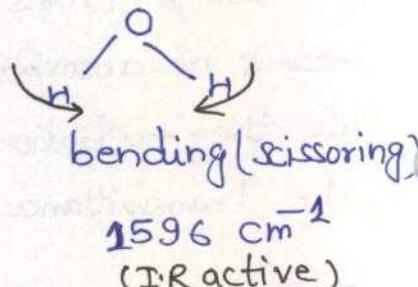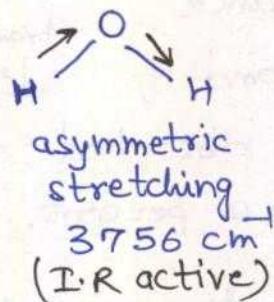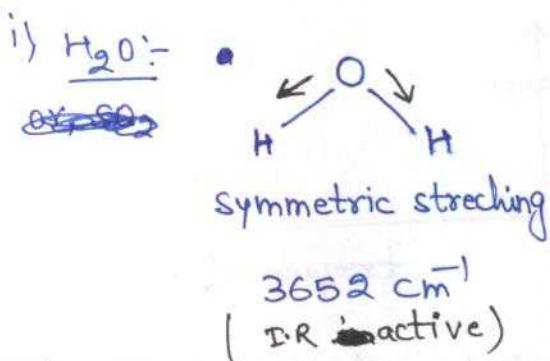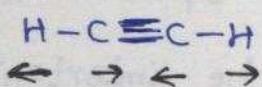
* fundamental Vibrations :-
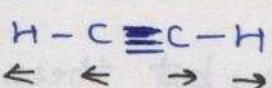
→ A non-linear molecule with n atoms generally has $3n-6$ fundamental vibrational modes

→ A linear molecule has $3n-5$ vibrational modes.

→ many of these vibrations occur at the same frequency and are therefore "degenerate" so all the possible peaks are not seen as independent absorptions.

i) H_2O :-

~~or SO~~

symmetric streching

3652 cm^{-1}

(I.R ~~in~~ active)

asymmetric stretching

3756 cm^{-1}

(I.R active)

bending (scissoring)

1596 cm^{-1}

(I.R active)

ii) SO_2 :→

no centre of symmetry

(I.R active)

Raman active

1151 cm^{-1}

(I.R active)

Raman active

1361 cm^{-1}

(I.R active)

Raman active

519 cm^{-1}

iii) CO_2 :- $3n-5 = 3\times3-5 = 4$ fundamental vibrational modes

(It has centre of symmetry)

$O=C=O$

(I.R ~~and~~ inactive)

Raman active

1330 cm^{-1}

$O=C=O$

(I.R active)

Raman inactive

2349 cm^{-1}

$O=\overset{\uparrow}{C}=O$

(I.R active)

Raman Inactive

667.3 cm^{-1}

$\overset{\ominus}{O}=\overset{\oplus}{C}=\overset{\ominus}{O}$

(I.R active)

Raman inactive

667.3 cm^{-1}

iv) N_2O :- $3n-6 = 3\times3-6 = 4$ fundamental vibrations

(No centre of symmetry)

$\overset{\ominus}{N}=\overset{\oplus}{N}=O$

(I.R. active)

Raman active

1285 cm^{-1}

$N=N=\overset{\ominus}{O}$

(I.R active)

Raman active

2224 cm^{-1}

$\overset{\ominus}{N}=\overset{\oplus}{N}=O$

(I.R active)

Raman inactive

589 cm^{-1}

$\overset{\ominus}{N}=\overset{\oplus}{N}=\overset{\ominus}{O}$

(I.R active)

Raman inactive

589 cm^{-1}

v.) <u>Acetylene</u>:- (C_2H_2) $3 \times 4 - 5 = 7$ fundamental vibrations

H−C≡C−H
← → ← →
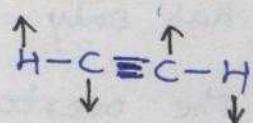
(I.R. inactive)
(Raman active)

3374 cm^{-1}

H−C≡C−H
← ← → →
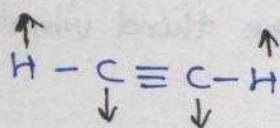
(I.R inactive)
(Raman active)

1974 cm^{-1}

H−C≡C−H
← → → ←
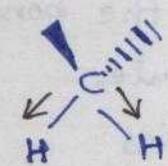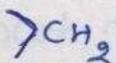
(I.R. active)
(Raman inactive)

3287 cm^{-1}

H−C≡C−H
↑   ↑
↓   ↓
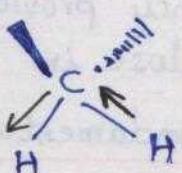
(I.R inactive)
(Raman active)
doubly degenerate
612 cm^{-1}

H−C≡C−H
↓   ↓
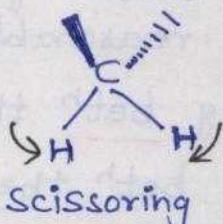
(I.R active)
(Raman inactive)
doubly degenerate

(729 cm^{-1})

VI) <u>Methylene Group</u>:-   >CH_2

H   H

Symmetric
stretching

H   H

asymmetric
stretching

H   H

scissoring

H⊕   H⊖
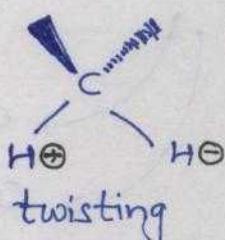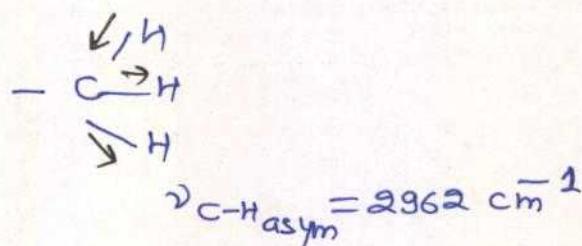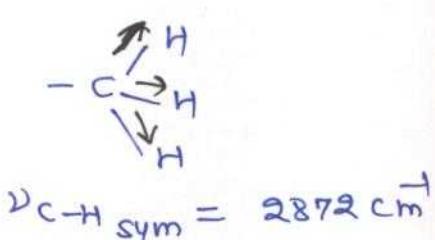
twisting

* Because of its high symmetry Buckminster fullerene (C_{60}) has only four absorption bands in its I.R spectrum.
* The overtone bands are very weak, but these can be important for characterisation of certain class of compounds, particularily benzene derivatives.

overtones may arise $\longrightarrow$ when molecule in lowest or first vib. state is excited to the third vibrational level

$\longrightarrow$ "Combination band" occurs when a single photon has precisely the correct energy to excite two vibrations at once.

* <u>Coupled vibrations:-</u> $\rightarrow$ takes place beth two bonds vibrating with similar frequency provided that the bonds are reasonably close in the molecule.

$\longrightarrow$ coupling beth the <u>fundamental frequencies</u>

$\longrightarrow$ Coupling beth the <u>fundamental vibration</u> and the overtone of some other vibration (This is called Fermi Resonance)

ex:- methyl group

ν_{C-H} sym $= 2872$ cm^{-1}

ν_{C-H} asym $= 2962$ cm^{-1}

$\rightarrow$ other compds showing coupling; $-CH_2$ group, nitro$(-NO_2)$; amino groups $(-NH_2)$.

$\rightarrow$ Generally anti-symmetric streching frequency is of higher frequency

$\rightarrow$ In CO_2, $O=C=O$ $(\nu_{C=O}$ asym $= 2350$ cm$^{-1})$ is due to coupling beth two $C=O$ vibrations

$\checkmark$ Coupling is useful for the detection of $\rightarrow$ primary amines and primary amides via two