

[This question paper contains 7 printed pages]

Your Roll No. :

Sl. No. of Q. Paper : **2199** **IC**

Unique Paper Code : 32171201

Name of the Course : **B.Sc. (Hons.) Chemistry**

Name of the Paper : Organic Chemistry - I

Semester : II

Time : 3 Hours

Maximum Marks : 75

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
- (b) Attempt any **six** questions in **all**.
- (c) Question **No.1** is compulsory.

1. Attempt any five questions : 3×5=15

(a) *cis*-but-2-ene on treating with carbene gives 100% *cis*-1,2-dimethylcyclopropane, sometimes it gives mixture of 50% *cis* and 50% *trans*-1,2-dimethylcyclopropane. Explain this observation.

(b) Discuss the stereochemical implications of S_{N1} and S_{N2} reaction.

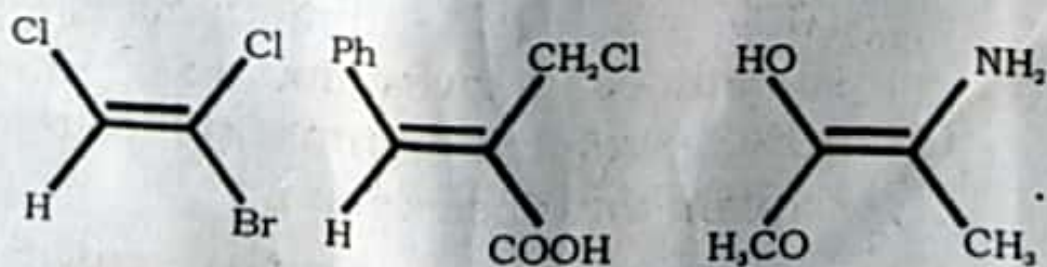
P.T.O.

- (c) Phenol is more acidic than an alkyl alcohol. Explain.
- (d) Write down all the possible conformational isomer of Ethylene glycol. Which conformation is most stable and why ?
- (e) Write the structure formula of (S) (E)-2-Bromo-3-heptene.
- (f) Explain the order of stability of the following carbocations :
 $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$
2. (a) Write down all the possible stereoisomer of 1,3-dibromo-2-methylbutane. Assign R/S configuration to each and every chiral center present in each possible stereoisomer.

6

- (b) Assign priorities and give E/Z notations to following :

6



3. (a) How many products we will get on dehydration of 3,3-Dimethylbutan-2-ol? Explain with mechanism. 4

(b) 1,3-butadiene on treating with HBr gives 3-Bromobut-1-ene at low temperature whereas at high temperature gives 1-Bromobut-2-ene. Explain this observation. 4

(c) (i) Convert Propane to 2,3-Dimethylbutane.

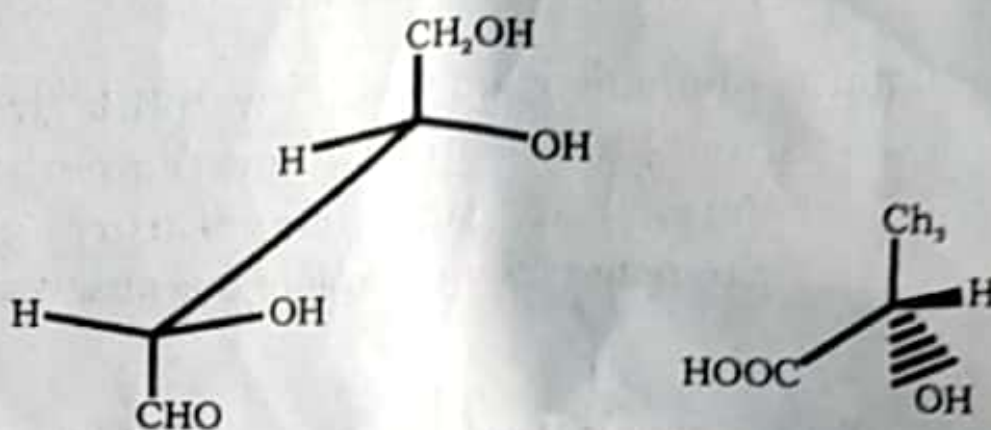
(ii) How is it proved that the chlorination of methane occurs via free radical mechanism? 4

4. (a) Friedel Craft Alkylation of benzene with 1-chlorobutane gives mixture of product. Explain with mechanism. 3

(b) Convert Benzene to 1-chloro-1-phenylethane. 3

(c) Define Huckel's rule and give one example of each with explanation for : Aromatic, Anti-aromatic and Alicyclic compounds. 3

- (d) Write down the standard Fischer Projection for the following : 3



5. (a) Write down all the possible conformational isomers of 1-methylcyclohexane. Which conformer is more stable and why ?

3

- (b) *cis*-1,4-but-2-ene-dioic acid (maleic acid) on treatment with KMnO_4 (cold) gives a product. Explain the reaction with mechanism. Also give the stereochemistry of the product.

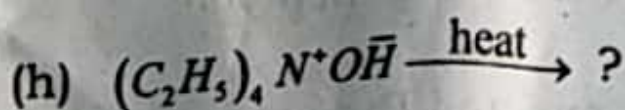
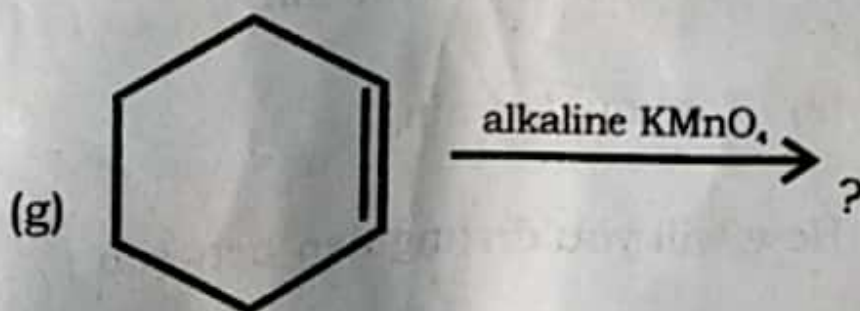
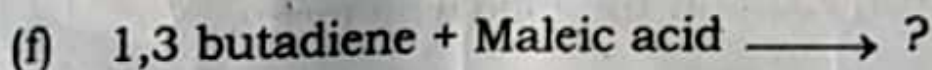
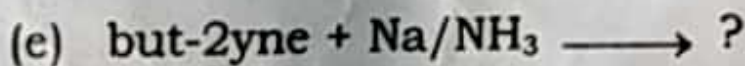
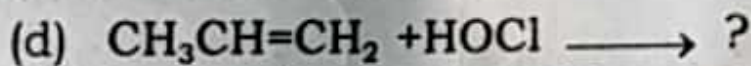
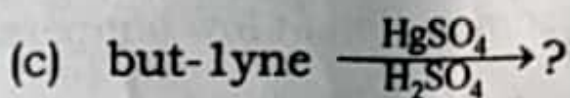
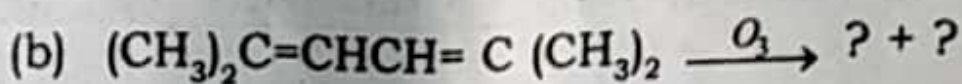
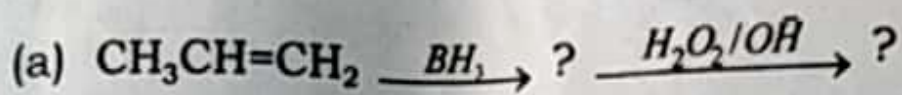
3

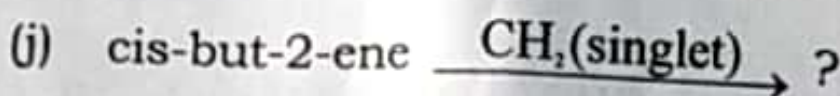
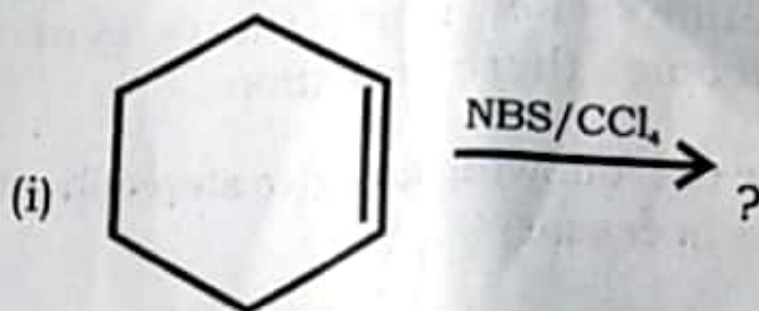
- (c) Convert benzene into *m*-nitrobenzoic acid.

3

(d) What are the limitations of Wurtz's reaction? How Corey-House synthesis overcomes these limitations. 3

6. Complete the following and give stereochemistry wherever necessary : 12





7. (a) Propene on bromination at low temperature gives different product than reacting at 500°C . Explain. 4

(b) Explain the following terms : 4

(i) 1,3 diaxial interaction

(ii) Torsional strain

(c) How will you distinguish between : 4

(i) 1-heptyne and 2-heptyne

(ii) But-1-ene and Butane

2199

8. Write a short note on any **three** :

4×3=12

- (a) Saytzeff elimination Vs. Hoffmann elimination
- (b) Hydrogen Bonding
- (c) Types of Elimination reactions
- (d) *Oxymercuration*-Demercuration reaction

[This question paper contains 7 printed pages]

Your Roll No. :

Sl. No. of Q. Paper : **2200** **IC**

Unique Paper Code : 32171202

Name of the Course : **B.Sc. (Hons.) Chemistry**

Name of the Paper : Physical Chemistry - II

Semester : II

Time : 3 Hours **Maximum Marks : 75**

Instructions for Candidates :

- Write your Roll No. on the top immediately on receipt of this question paper.
- Answer any **six** questions.
- Question No. **1** is compulsory.
- Use of scientific calculator is allowed.

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}, N = 6.0231023 \text{ mol}^{-1}$$

1. Attempt any five : **5×3**

- The magnitude of the boiling point elevation is less than that of the freezing point depression for a solution of the same concentration : Explain the statement in terms of chemical potential along with diagram.

P.T.O.

- (b) Equilibrium constant K_p is a dimensionless quantity. Explain.
- (c) Is the Joule Thomson experiment reversible? Explain by describing how one could or could not, restore the gas to its initial state by the same path.
- (d) Reversible processes are ideal process and cannot be carried out in practice. Comment.
- (e) Why standard solutions are prepared in volumetric flask rather than a beaker?
- (f) Why ΔG is used more compared to ΔA to express the condition of spontaneity of the reaction?
2. (a) An imaginary gas has the equation of state $PV^2 = n^2KT$ (where K is a constant) and its heat capacity C_v is independent of temperature and pressure. For this gas U depends only on T , as for an ideal gas.
- (i) Obtain an equation that relate the initial and final pressure to the initial and final temperature in a reversible adiabatic expansion of the gas.
- (ii) Find $\overline{C_p} - \overline{C_v}$ for this gas in terms of P , T and K .

- (b) 0.1 M solution of NaCl is found to be isotonic with 1.1% solution of urea. Calculate the apparent degree of dissociation of NaCl . 4
- (c) A useful reaction has a positive value of ΔG . Can the reaction be made to proceed? Explain with example. 2
3. (a) For the solute (2) in dilute solution in a certain solvent the partial molal volume is given by $\bar{V}_2 = a + bm$, where m is the molality of the solution and a, b are constants. Express the partial molal volume \bar{V}_1 in terms of a, b, m and quantities characteristics of the solvent. 5
- (b) The bond dissociation enthalpies of $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$ are $+435.95 \text{ kJmol}^{-1}$ and $+941.8 \text{ kJmol}^{-1}$ and the enthalpy of formation of $\text{NH}_3(\text{g})$ is $-46.024 \text{ kJmol}^{-1}$.
- (i) What is the enthalpy of atomisation of $\text{NH}_3(\text{g})$? 2
- (ii) What is the average bond enthalpy of N-H bond? 2
- (c) Why in the use of entropy as a criterion for spontaneity do we have to consider ΔS_{total} , but in the case of the Gibbs free energy we have to consider only ΔG_{system} not ΔG_{total} ? 3

4. (a) $dU = xy^2dx + x^2y dy$ and $dw = \sin(y) dx + \sin(x) dy$
- (i) Ascertain whether dU and dw are exact or inexact differentials. 3
- (ii) For each differential that is exact find the function of which it is differential by integrating over a suitable path. Show in a diagram the path that you choose. 3
- (b) Calculate the standard enthalpy of formation of ethane at 350 K. Given that its value at 298 K is $-84.68 \text{ kJ mol}^{-1}$ and $\overline{C}_p / (\text{JK}^{-1} \text{ mol}^{-1})$ for $H_2(g)$ is $27.28 + 3.26 \times 10^{-3} T$, $C(s)$ is $16.86 + 4.77 \times 10^{-3} T$ and C_2H_6 is $14.72 + 0.1272 T$. 4
- (c) Distinguish between bond enthalpy and bond dissociation enthalpy. 2
5. (a) One mole of hydrogen and nine moles of nitrogen are mixed at 298 K and 1 atm pressure. Assuming ideal behaviour for the gases, calculate the entropy of mixing per mole of the mixture formed. Would it make any difference if under similar conditions one mole of hydrogen is mixed with nine moles of oxygen? 4

(b) Show that chemical potential μ can also be written as $\left(\frac{\partial U}{\partial n_i}\right)_{v,s,n_j}$. Is this a partial molar quantity? Give reason. 4

(c) Derive a relation between osmotic pressure and elevation in boiling point. 4

6. (a) A 25 g mass of ice at 273 K is added to 150 g of liquid water at 360 K at constant P . What is the final state of system? Calculate ΔS for the process. Given : $\Delta H_{\text{fus}}(\text{H}_2\text{O}) = 6.0095 \text{ kJ mol}^{-1}$, $\overline{C}_p(\text{H}_2\text{O}, \text{l}) = 75.29 \text{ JK}^{-1} \text{ mol}^{-1}$ and $T_m(\text{H}_2\text{O}, \text{s}) = 273\text{K}$. 4

(b) Which of the following processes are spontaneous? Give reason. 4

(i) Reversible isothermal expansion of an ideal gas

(ii) Vaporization of superheated water at 102 °C and 1 bar.

(iii) The constant P melting of ice at its normal freezing point by addition of infinitesimal amount of heat.

(iv) Adiabatic expansion of a gas into vacuum.

(c) Derive the relation $\left(\frac{\partial V}{\partial S}\right)_T = \left(\frac{\partial T}{\partial P}\right)_V$ 4

7. (a) Starting from the definition of G and using thermal equation of state $dG = -SdT + VdP$. Derive the following relation

$$\left(\frac{\partial(\Delta G/T)}{\partial(1/T)} \right)_P = \Delta H \quad 4$$

- (b) 1 mole of an ideal gas at 25 °C and 1 atm is subjected to following changes successively
- (i) Heated to 50 °C at constant volume
 - (ii) Expanded isothermally reversibly till P is 0.5 atm.
 - (iii) Cooled to 25 °C at constant P .

Calculate q , w , ΔU and ΔH if $C_v = \frac{3}{2}R$.

6

- (c) Van't Hoff factor, i , for aqueous solution of both $NaCl$ and CH_3COOH depends on the concentration of the solution. Explain.

2

8. (a) Heat capacity of metal X is $3.053 \text{ J}^\circ\text{C}^{-1}\text{mol}^{-1}$ at 20 K. Calculate the standard absolute entropy of this substance in $\text{JK}^{-1} \text{mol}^{-1}$ at 20 K.

4

(b) Derive the relation $\Delta S = C_p I_n \frac{T_f}{T_i} - \alpha V (P_f - P_i)$

starting from $dH = TdS + VdP$. 4

(c) At 480 K and a total pressure of 1 atm, a mixture consisting of nitrogen and hydrogen in the mole ratio of 1:3 contains 16% ammonia at equilibrium. Calculate K_p for the reaction. 4

This question paper contains 8 printed pages]

Roll No.

--	--	--	--	--	--	--	--	--	--	--

S. No. of Question Paper : 6490

Unique Paper Code : 32171201

HC

Name of the Paper : Organic Chemistry-I

Name of the Course : B.Sc. (H) Chemistry

Semester : II

Duration : 3 Hours

Maximum Marks : 75

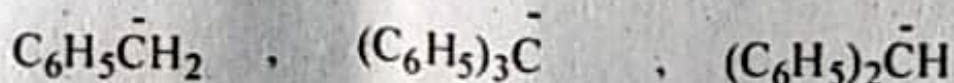
(Write your Roll No. on the top-immediately on receipt of this question paper.)

Answer six questions in all.

Question No. 1 is compulsory.

1. Attempt any five :

(a) Giving reasons, arrange the following carbanions in increasing order of stability :



(I)

(II)

(III)

P.T.O.

(b) Explain the following :

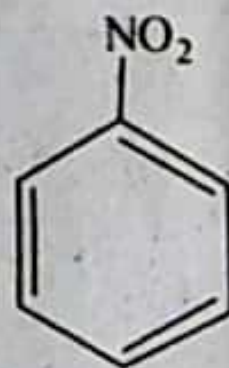
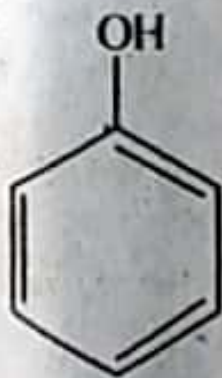
- (i) Benzylamine is more basic than aniline.
- (ii) α -bromobutanoic acid is stronger acid than β -bromobutanoic acid.

(c) Define the terms enantiomers and diastereoisomers.

Explain with suitable examples.

(d) Explain why 1, 3-pentadiene is more stable than 1, 4-pentadiene.

(e) Giving reasons, arrange the following in increasing order of reactivity towards ring bromination :



(f) How would you distinguish 1-butyne from 1-butene chemically?

(g) Draw all conformations of 1, 2-dimethylcyclohexane.

Which conformer is most stable and why ?

(h) Why is nitration of toluene faster than nitration of nitrobenzene ? 5×3=15

2. (a) Carry out the following conversions (any *three*) :

(i) 2-Pentanone from 1-pentene

(ii) Chloroprene from acetylene

(iii) 2, 3-Dimethylbutane from propane

(iv) 1-Phenylethane from bromobenzene

(v) Propyne to tert.-butylalcohol.

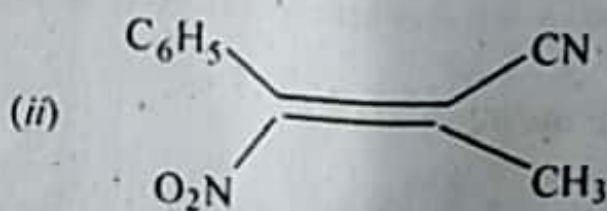
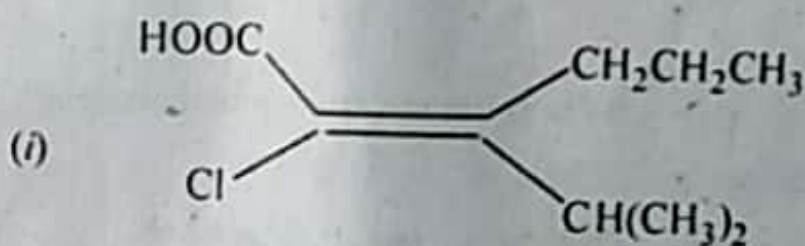
(b) Write down the mechanism involved in bromination of aromatic hydrocarbons.

(c) Giving reasons, arrange the following in increasing order of boiling points :

Neopentane, *n*-hexane, 2-methylpentane, 2, 3-dimethylbutane. 6,3,3

P.T.O.

3. (a) Draw the Fischer projections for all possible stereoisomers of butane-2, 3-diol. What is the correlation among these stereoisomers? Comment on the optical activity of these isomers.
- (b) Explain why the chair conformation of cyclohexane is more stable than the boat conformation.
- (c) Assigning priority order, explain how you will designate E/Z to the following :

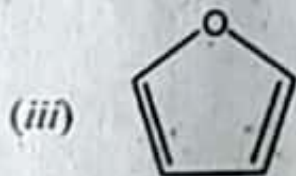
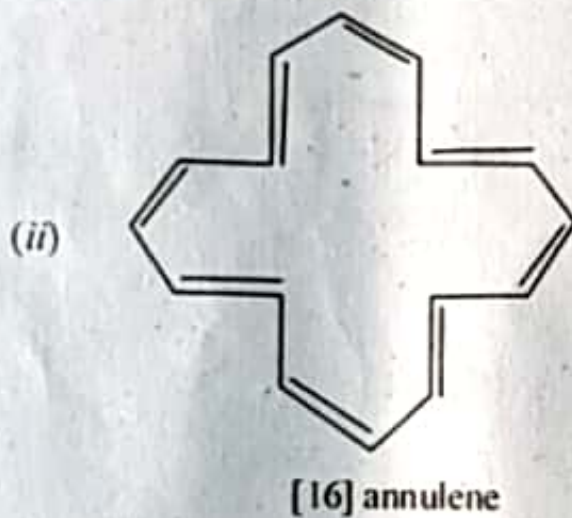
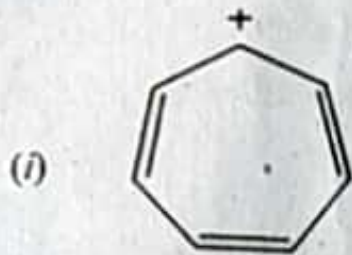


4.4.4

4. (a) Discuss the stereochemistry of addition of bromine to cis-2-butene.
- (b) Chlorine is more reactive but bromine is more selective in halogenation of alkanes. Explain.

(c) Which of the following compound/s is/are aromatic ?

Give reasons (any two) :

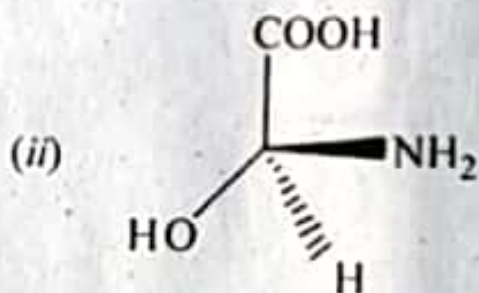
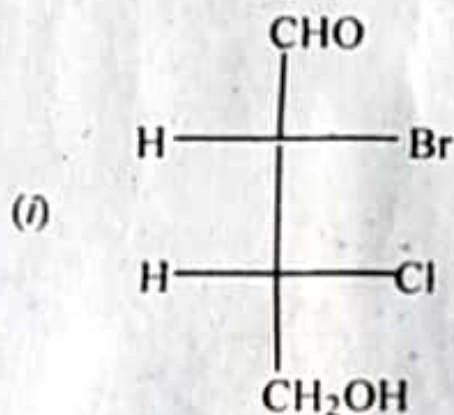


4,4,4

5. (a) Calculate the percentage of isomers formed on monochlorination of *n*-butane. Relative rates of hydrogens $3^\circ : 2^\circ : 1^\circ$ towards chlorination at room temperature are 5.0 : 3.8 : 1.

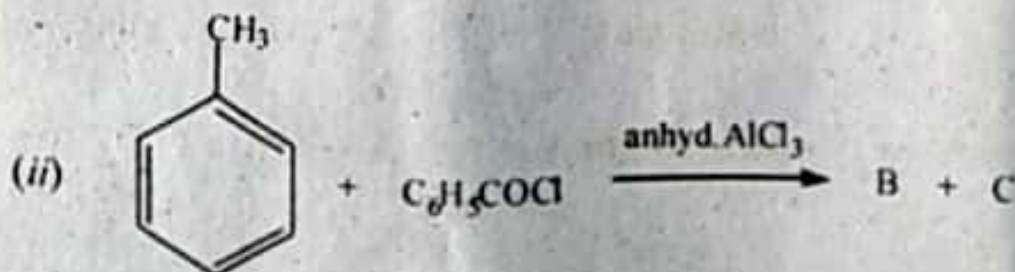
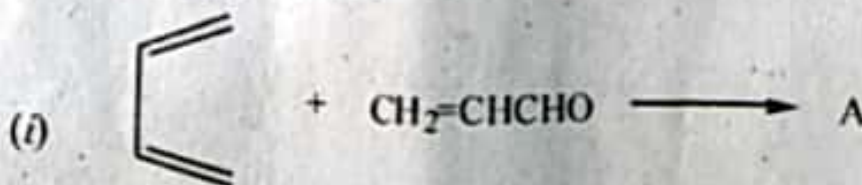
P.T.O.

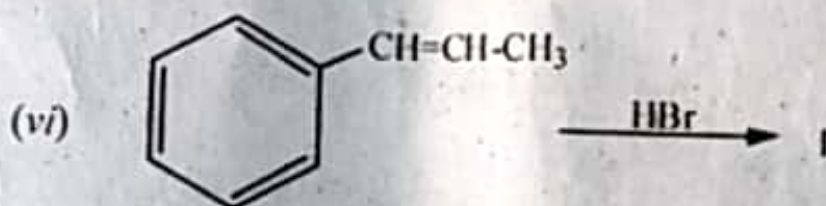
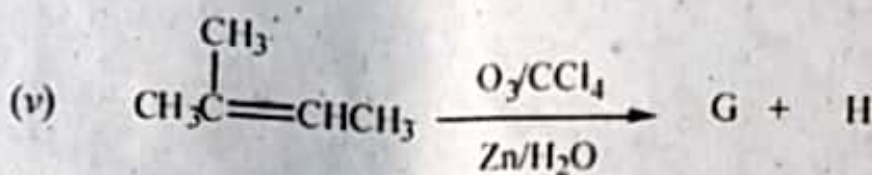
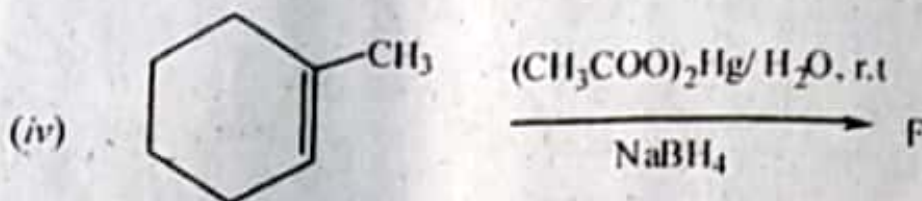
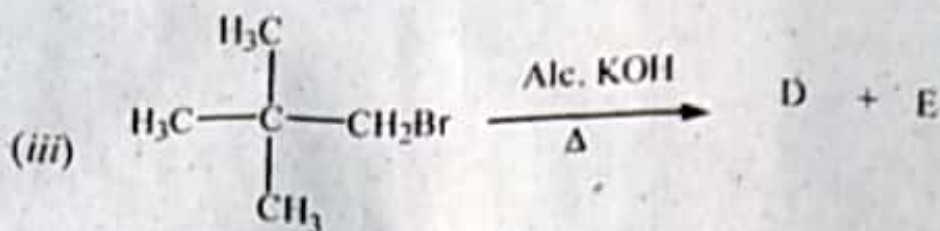
- (b) What happens when isobutylene is heated with Conc. H_2SO_4 ? Explain giving the mechanism.
- (c) Assigning priority order, explain how you will designate R/S configuration to the following :



4,4,4

6. (a) Complete the following reactions :





- (b) An optically active compound "A" with molecular formula C_6H_{10} decolorizes bromine solution and gives white precipitate with ammonical solution of silver nitrate. Compound "A" on ozonolysis gives two compounds "B" and resolvable "C". Identify A, B and C.
- (c) Define resolution. How would you resolve a racemic mixture of lactic acid ?

6,3,3

P.T.O.

This question paper contains 7 printed pages]

(4)

N

Roll No.

--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

S. No. of Question Paper : 6491

Unique Paper Code : 32171202

HC

Name of the Paper : Physical Chemistry-II

Name of the Course : B.Sc. (Hons.) Chemistry

Semester : II

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Answer six questions in all. Question No. 1 is compulsory.

Use of scientific calculators is allowed.

Logarithmic tables can be provided, if required.

1. Explain, giving reasons, any *five* of the following :

(a) An ideal gas does not heat or cool on expansion or compression. Explain.

(b) The limiting partial molar volume of MgSO_4 in water is $-1.4 \text{ cm}^3\text{mol}^{-1}$. Explain.

P.T.O.

- (c) What are the shortcomings of Joule's experiment?
- (d) While stating the enthalpy change of a chemical reaction, the temperature and pressure of both the reactants and products are considered identical. Explain
- (e) Crystallization process is attended by a decrease in entropy of the system yet it occurs spontaneously. Comment.
- (f) It is not necessary to specify the pressure in third law. Explain.
- (g) Integral enthalpy of solution is positive for NaCl and negative for KCl. Explain.
- (h) Why is the value of C_p always greater than C_v ? 5×3
2. (a) Two moles of an ideal monatomic gas ($C_{v,m} = 12.55 \text{ JK}^{-1}\text{mol}^{-1}$) expands irreversibly and adiabatically from an initial pressure of 1.013 MPa against a constant external pressure of 0.1013 MPa, until the temperature drops from the initial value of 325 K to a final value of 275 K. Determine the final volume of the gases system and the work involved in the expansion process.

(b) Derive the relation $C_p - C_v = TV \frac{\alpha^2}{\beta}$.

(c) Show that the magnitude of work involved in a reversible adiabatic expansion of an ideal gas is less than that of the isothermal one, when the expansion is carried out between the same initial and final pressures 4, 4, 4

3. (a) The Joule-Thompson coefficient of a gas can be positive, negative or zero. Comment.

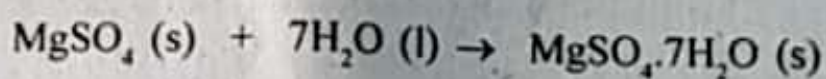
(b) Show that the expression for expansion work for expansion of a van der Waals gas is given by :

$$w = -nRT \ln \frac{V_2 - nb}{V_1 - nb} - n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right).$$

(c) 20 g of N_2 at 300 K is compressed reversibly and adiabatically from 20 dm³ to 10 dm³. Calculate the final temperature, q, w, ΔU and ΔH . 4,4,4

4. (a) Show, with suitable example, that the standard enthalpy of formation of an element in its most stable state of aggregation is immaterial in calculation of enthalpy of a reaction.

- (b) 91 kJ of heat was evolved when one mole of MgSO_4 was dissolved in a specified amount of water. When the solution of the same composition was formed by dissolution of one mole of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in suitable quantity of water, 13 kJ of heat was absorbed. Determine the enthalpy of hydration for the reaction



- (c) Derive the Kirchhoff equation for the enthalpy change of a reaction when :

(i) C_p independent of temperature

(ii) C_p depends on temperature.

3,4,5

5. (a) To predict the spontaneity of a process both ΔS_{sys} and ΔS_{surr} are considered but ΔG alone is sufficient for the same. Explain.

- (b) One mole of an ideal monatomic gas at 298 K, occupying a volume of 3 dm^3 , is expanded adiabatically and reversibly to a pressure of 101.325 kPa. Calculate q , w , ΔU , ΔH , and ΔS .

(5)

(c) Show that $dS = \frac{C_v}{T} dT + \frac{\alpha}{\beta} dV$,

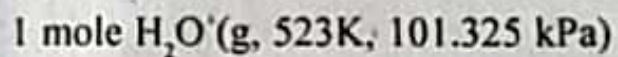
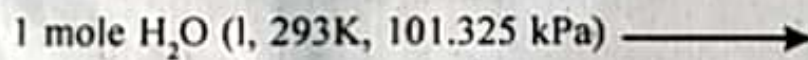
where α and β are the coefficient of thermal expansion and compressibility factor respectively. 3,4,5

6. (a) Show that for an ideal gas undergoing reversible isothermal expansion; $\Delta G = \Delta A$.

(b) Derive the following relations :

$$\left[\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right]_p = \Delta H$$

(c) Calculate $\Delta_r S$ for the process



Given the following data :

$$C_{p,m}(\text{l}) = 75.312 \text{ JK}^{-1}\text{mol}^{-1}; C_{p,m}(\text{g}) = 35.982 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta_{\text{vap}} H \text{ at } 373 \text{ K, } 101.325 \text{ kPa} = 40.668 \text{ kJ mol}^{-1} \quad 3,4,5$$

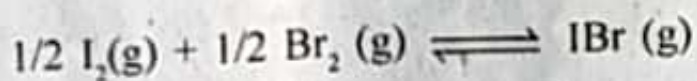
7. (a) Derive the relation $\left(\frac{\partial \mu_i}{\partial p} \right)_{T, n_j, s} = -V_{i, pm}$

(b) Show that the chemical potential of an ideal gas in a mixture of ideal gases is lesser than the chemical potential of the pure ideal gas maintained at the same temperature and total pressure.

P.T.O.

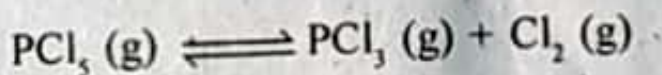
(c) Calculate the $\Delta_{\text{mix}} G$, $\Delta_{\text{mix}} S$ and $\Delta_{\text{mix}} H$ when 20 mol of gas A is mixed in a gases mixture formed by mixing 20 mol of gas A and 20 mol of gas B, at 298 K and 1 atm pressure. 3,4,5

8. (a) For the following reaction, predict and explain the change in extent of reaction upon an increase in pressure :



(b) Show that for an endothermic reaction, an increase in extent of reaction increases the equilibrium extent of reaction at equilibrium.

(c) $\text{PCl}_5(\text{g})$ dissociates according to the reaction,



At 523 K, the equilibrium constant K_p^0 for the reaction is 1.80. Determine the degree of dissociation of PCl_5 . 3,4, 5

9. (a) When 0.1 M aqueous solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ is separated from 0.1 M FeCl_3 solution by a semipermeable membrane, predict whether the blue color will appear in either of the compartments as a result of the reaction between $\text{K}_4[\text{Fe}(\text{CN})_6]$ and FeCl_3 due to osmosis. Give reasons in support of your answer.

- (b) Calculate the depression in freezing point of CCl_4 upon dissolution of a non-volatile substance in it, if the relative vapor pressure lowering is recorded as 0.04. The molar mass and freezing point depression constant for CCl_4 is 342 gmol^{-1} and $31.8 \text{ K kgmol}^{-1}$, respectively.

- (c) Derive thermodynamically :

$$\Delta T_f = \frac{RT_0^2 M_1}{\Delta H_{fus}} \times m \quad 3,4,5$$

(2)
[This question paper contains 8 printed pages]

Your Roll No. :

Sl. No. of Q. Paper : **2201** **IC**

Unique Paper Code : 32171401

Name of the Course : **B.Sc. (Hons.) Chemistry**

Name of the Paper : Inorganic Chemistry- III,
Coordination Chemistry

Semester : IV

Time : 3 Hours

Maximum Marks : 75

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
- (b) Attempt **Six** questions in **all**.
- (c) Question **No.1** is compulsory.

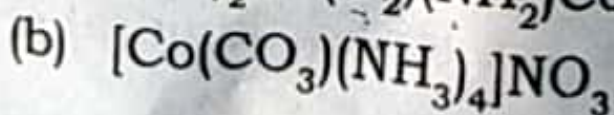
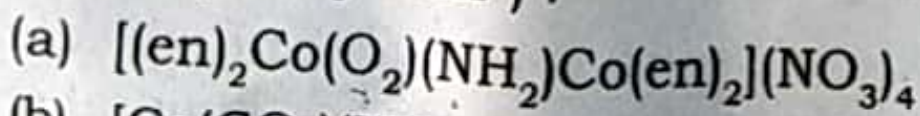
1. Attempt any **five** of the following : $5 \times 3 = 15$

- (i) In comparison to lanthanoids, actinoids have greater tendency to form complexes. Explain.
- (ii) Metal ions with d^3 and d^8 electronic configuration, prefers octahedral geometry. Justify.

P.T.O.

- (iii) Explain the variation of lattice energy of the divalent 3d transition metal halides.
- (iv) When hydrogen peroxide is added to the solution of potassium dichromate in dilute sulphuric acid and the resultant solution is shaken with ether, a blue coloured solution is obtained. Give the relevant chemical equation and the structure of the compound responsible for imparting blue colour in ether.
- (v) What is nephelauxetic effect? How does this effect explain the covalent nature of metal-ligand bonds?
- (vi) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is square planar, while CuCl_4^{2-} is tetrahedral. Give reason.
- (vii) Why do transition metals act as good catalysts?

2. (i) Name the following complexes according to the IUPAC system of nomenclature (attempt any **four**):



- (c) $K_2[OsCl_5N]$
 (d) $Na[Pt Br Cl(NH_3)(NO_2)]$
 (e) $[Pt(py)_4][PtCl_4]$

(ii) Write the formulae of the following complexes (attempt any **four**) : 4

(a) Tris(ethylenediamine)cobalt(III) hexacyanidochromate(III).

(b) Tetraamminechloridonitrit-N-cobalt(III)ion

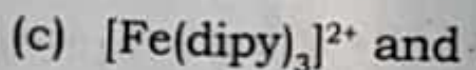
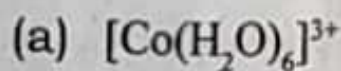
(c) Tetrakis(triphenylphosphane)platinum (0)

(d) Pentaamminethiocyanato-N-chromium (III)tetrachloridozincate(II)

(e) Potassium tetraazidocobaltate(II)

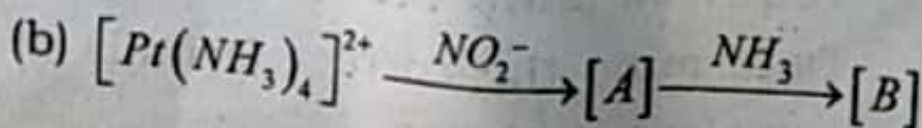
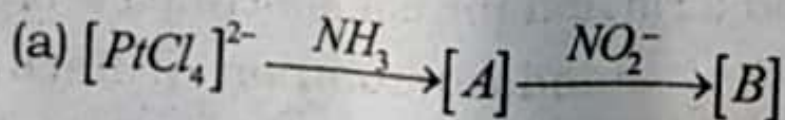
(iii) A solution containing 0.319 g of $CrCl_3 \cdot 6H_2O$ was passed through cation exchange resin in the acid form and the acid liberated was titrated with a standard solution of NaOH. This required 28.5 mL of 0.125 M NaOH. Determine the correct formula of Cr(III) complex. 4

3. (i) Why Charge transfer transitions give rise to more intense absorptions? State the nature of transitions responsible for colour in the following species : 4



(ii) The complex $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ exists in two isomeric forms α and β . The α -form reacts with oxalic acid to form $[\text{Pt}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$ whereas β -form gives $[\text{Pt}(\text{NH}_3)_2(\text{C}_2\text{O}_4\text{H})_2]$. Give the structures of α and β forms. Explain what physical method can be used to differentiate between the two forms. 4

(iii) Based on **Trans effect**, write the products of the following reactions : 4



4. (i) Using the valence bond theory, predict the type of hybridization involved, along with the geometry and the magnetic moment (in Bohr magnetons) for $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{MnF}_6]^{3-}$.
- (ii) Coordinated water molecules in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ can be successively replaced by 2,2'-dipyridyl, finally resulting in the formation of $[\text{Fe}(\text{dipy})_3]^{2+}$. In this process , the third equilibrium constant is observed to be greater than the second one. Explain.

4

- (iii) The magnitude of the crystal field splitting in tetrahedral complexes is considerably less than in octahedral fields. Explain.

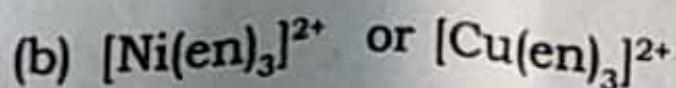
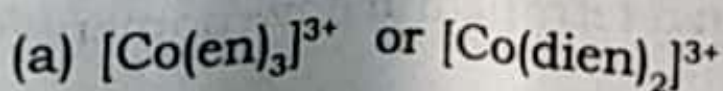
4

5. Explain the following :

- (i) Show by means of a diagram, how the pattern of d-orbital splitting changes as an octahedral complex undergoes tetragonal distortion and eventually becomes a square planar complexes.
- (ii) Why are chelated complexes more stable in comparison to non-chelated complexes ? Which one of the following is more stable ? Justify your answer :

4

4



5

P.T.O.

(iii) NiFe_2O_4 is inverse spinel while Mn_3O_4 is a normal spinel. Explain on the basis of CFT.

4

6. (i) Indicate the type of isomerism exhibited by the following pairs of isomers and suggest one method in each set to distinguish them :

4

(a) cis - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and trans - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

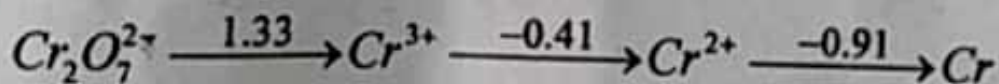
(b) $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$

(ii) On the basis of molecular orbital theory, explain the order of Δ_0 for octahedral complexes having the ligands I^- and CO .

(iii) Calculate in kJmol^{-1} , the crystal field stabilization energy attained by Fe^{2+} ion in an octahedral oxide ion environment. Given, Δ_0 for Fe^{2+} in oxide ion environment is 124 kJmol^{-1} . What will be the value of CFSE in a tetrahedral environment of oxide ion.

4

7. (i) Explain the effect of temperature on magnetic susceptibility of ferromagnetic and antiferromagnetic materials. 4
- (ii) In the electronic spectra of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ single broad peak with maximum at 20300 cm^{-1} is observed. Explain. 4
- (iii) What is lanthanoid contraction? What are the major consequences of lanthanoid contraction? 4
8. (i) Given below are the Latimer diagram for Cr in acidic medium : 6



Answer the following questions :

- (a) Write the half reaction for the conversion of $\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cr}^{3+}$
- (b) Is there any tendency of Cr^{2+} to reduce to Cr? Give reasons.
- (c) Calculate the skip step emf for $\text{Cr}^{3+} \longrightarrow \text{Cr}$ change.

- (ii) A blackish brown coloured solid (A) when fused with alkali metal hydroxides in presence of air produces a dark green compound (B), which on electrolytic oxidation in alkaline medium gives a dark purple coloured solution of compound (C). Acidified aqueous solution of (C) on treatment with oxalic acid gives a colourless species (D). Identify (A), (B), (C) and (D). Also explain the sequence of reactions involved. 6

(1) [This question paper contains 4 printed pages]

Your Roll No. :

Sl. No. of Q. Paper : 2202 IC

Unique Paper Code : 32171402

Name of the Course : B.Sc. (Hons.) Chemistry

Name of the Paper : Organic Chemistry - III

Semester : IV

Time : 3 Hours

Maximum Marks : 75

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
 - (b) Attempt **six** questions in **all**.
 - (c) Question **NO.1** is compulsory and carries **15** marks.
 - (d) **All** other questions are of **12** marks each.
1. (a) Amine 'A' (C_7H_9N) reacts with benzoyl chloride in the presence of sodium hydroxide to give compound 'B' ($C_{14}H_{13}NO$). 'A' reacts with benzene sulphonyl chloride in potassium hydroxide solution to give water insoluble precipitate of compound 'C'. Identify compound A and give equation for its conversion into the compound B and C. Name the reaction involved in the conversion of A to B with mechanism. 6

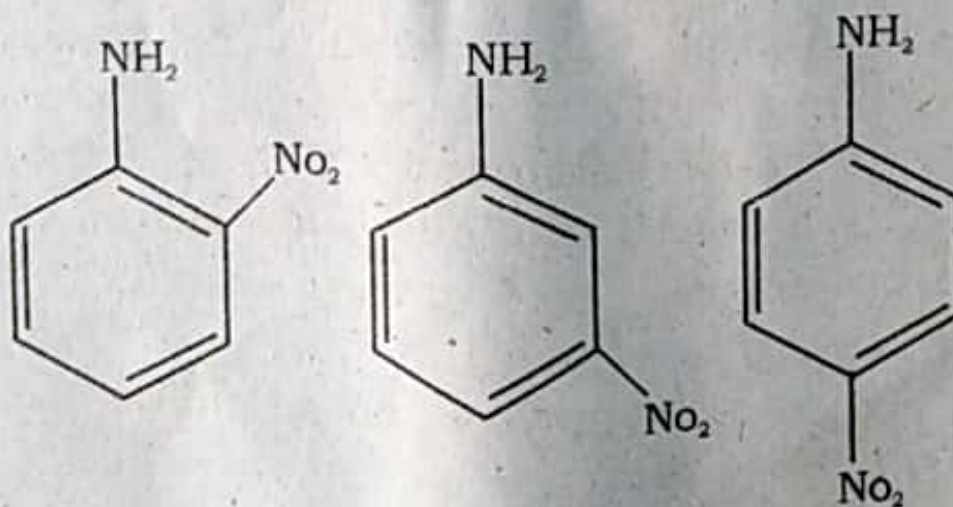
P.T.O.

- (b) Anthracene undergoes electrophilic substitution reactions at 9-position. Explain. 3
- (c) How will you distinguish between 1^o, 2^o and 3^o amines using Hinsberg test. 3
- (d) Suggest a best reagent for the conversion of pyrrole to (i) 2-nitropyrrole, (ii) Pyrrole-2-sulphonic acid, and (iii) Pyrrole-2-aldehyde. 1×3=3

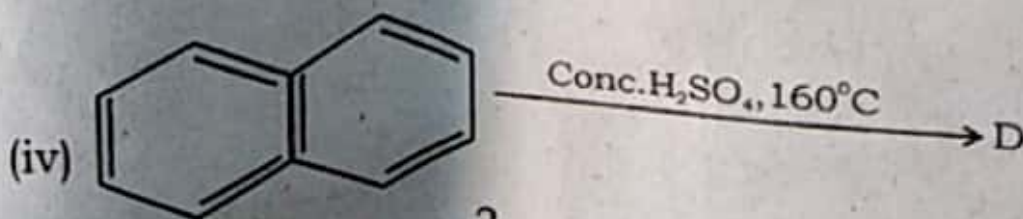
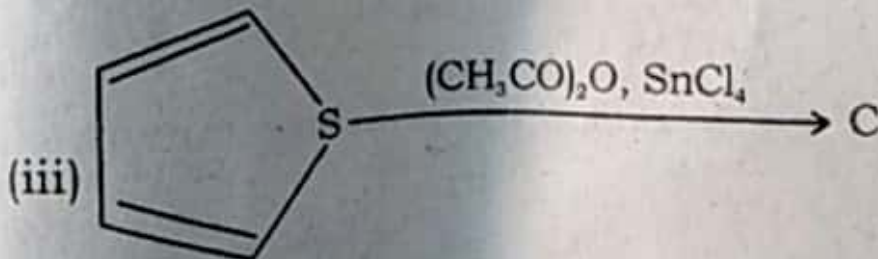
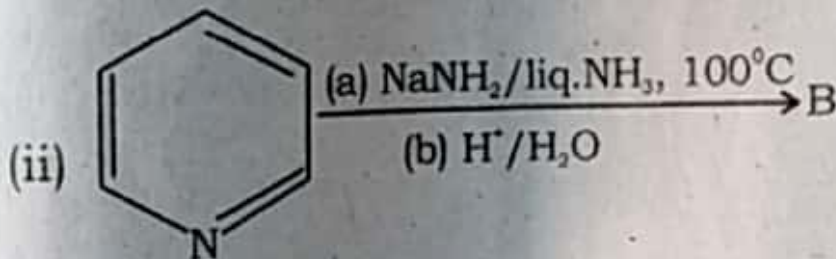
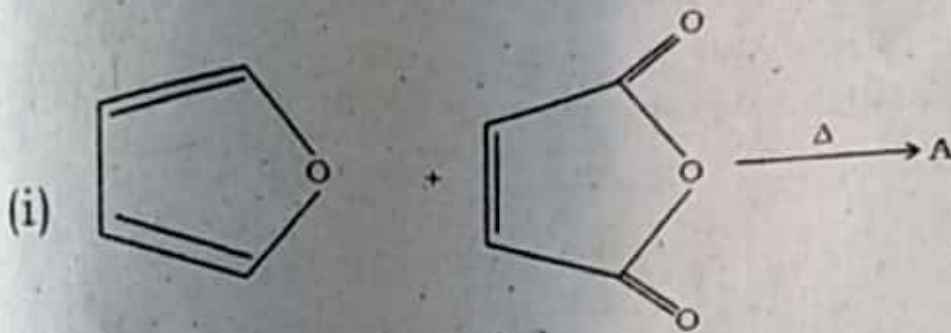
2. Carry out the following conversions using the necessary reagents : 3×4=12

- (i) Nitrobenzene to p-nitrophenol
(ii) Aniline to p-nitrobenzoic acid
(iii) Naphthalene to o-aminobenzoic acid
(iv) Pyridine to 2-pyridylacetic acid

3. (a) Arrange the following nitroanilines in the order of decreasing basicity with suitable explanation : 3

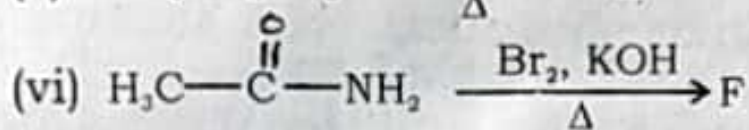
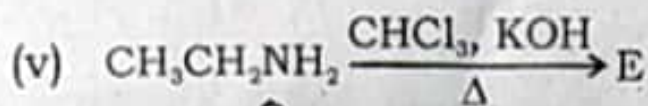


- (b) Give the order of reactivity of 5-membered heteroaromatic compounds with suitable explanation. 3
- (c) Pyridine undergoes nucleophilic substitution mainly at position-2. Explain. 3
- (d) Pyrrole does not undergo Diels-Alder reaction while N-acetyl pyrrole undergoes Diels-Alder reactions. Explain. 3
4. Complete the following and write the name of reaction involved in each case : 2×6=12



3

P.T.O.



5. (a) Explain the reactions which indicate the position of linkage between pyridine and N-methylpyrrolidine in nicotine. 6
- (b) How will you distinguish between nitriles and isonitriles? Explain giving reactions involved. 3
- (c) What is isoprene rule? Indicate the isoprene units in the structure of citral. 3
6. (a) Give the synthesis of nicotine from nicotinonitrile. 6
- (b) What happens when : $2 \times 3 = 6$
- (i) Citral is treated with aq. K_2CO_3
- (ii) Nicotine is treated with $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$
- (iii) Phenanthrene is subjected to ozonolysis.

7. Write short note on the following (any **three**) :

$4 \times 3 = 12$

- (a) Gabriel phthalimide synthesis
- (b) Skraup Quinoline synthesis
- (c) Fischer Indole synthesis
- (d) Hoffmann bromamide degradation

1800

[This question paper contains 8 printed pages]

Your Roll No.

:

Sl. No. of Q. Paper

: **2203** **IC**

Unique Paper Code

: 32171403

Name of the Course

: **B.Sc. (Hons.) Chemistry**

Name of the Paper

: Physical Chemistry-IV

Semester

: IV

Time : 3 Hours

Maximum Marks : 75

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
- (b) Attempt **six** questions in all.
- (c) Question **No.1** is compulsory.
- (d) Attempt at least **one** question from each **Section**.
- (e) Use of scientific calculator is permitted.

1. Explain any **five** of the following : 5×3

- (a) Larger the activation energy, greater is the effect of temperature rise on rate constant.
- (b) The molar conductivity of Li^+ ion is less than that of Cs^+ ion in aqueous medium.

P.T.O.

- (c) Walden's Rule is not applicable to cations of small size.
- (d) Rate of a photochemical reaction is independent of the initial concentration of the reactants.
- (e) Quantum efficiency of fluorescence decreases with the concentration of the solution.
- (f) Beer's law fails in case of aqueous dilute $K_2Cr_2O_7$ solution.
- (g) It is rare for a reaction to have molecularity more than three.

Section - A

2. (a) Discuss the asymmetry effect and electrophoretic effect in Debye Huckel Onsager theory. 4
- (b) Explain using Grotthus mechanism, how H^+ ion and OH^- ions have abnormally high conductance values. 3
- (c) The conductivity of a saturated solution of $[Co_2Fe(CN)_6]$ is $3.00 \times 10^{-6} \Omega^{-1} cm^{-1}$ and that of water used is $4.1 \times 10^{-7} \Omega^{-1} cm^{-1}$. The ionic molar conductivities of Co^{2+} and $Fe(CN)_6^{4-}$ are $87 \Omega^{-1} cm^2 mol^{-1}$ and $444 \Omega^{-1} cm^2 mol^{-1}$ respectively. Calculate the solubility and solubility product of $[Co_2Fe(CN)_6]$ in water at $25^\circ C$. 5

3. (a) What is transference number ?

Derive the expression $t \propto v$ for an ion where t is the transference number and v is the absolute velocity of the ion.

5

(b) Explain Wien effect.

3

(c) A potential of 5.60 V is applied to two electrodes placed 11 cm apart; how far is an ammonium ion expected to move in 2 hours in a dilute solution of ammonium salt at 25°C ?
(Given : $\lambda (\text{NH}_4^+) = 73.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)

4

4. (a) Calculate the transport numbers of H^+ ion and Cl^- ion from the following data obtained from the moving boundary method using cadmium chloride as the indicator electrolyte.

(Given : Atomic mass of Ag = 108 g mol⁻¹)

Concentration of HCl solution = 0.100 N

Mass of silver deposited in the coulometer

= 0.1209 g

Movement of the boundary = 7.50 cm

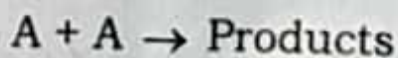
Cross - section of the tube = 1.24 cm²

4

- (b) Discuss the titration curves obtained in the conductometric titrations of : 4
- (i) HCl versus NaOH solutions
 - (ii) CH_3COOH versus NaOH solutions
- (c) Molar conductivity of 0.01 M solution of MgCl_2 is $195 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ at 25°C . A cell with electrodes that are 1.80cm^2 in surface area and 0.50cm apart is filled with 0.01 M MgCl_2 solution. How much current will flow when the potential difference between the two electrodes is 5.0V ? 4

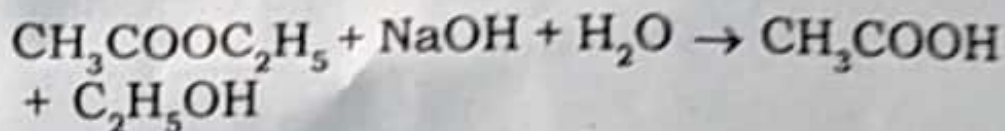
Section - B

5. (a) For the given **second** order reaction



- (i) Write down its differential rate law and deduce the integrated rate law.
 - (ii) Show that the half-life of such a reaction is inversely proportional to the initial concentration of A. 4
- (b) Write down the differences between order and molecularity. 3

- (c) The following results were obtained from the saponification of ethyl acetate

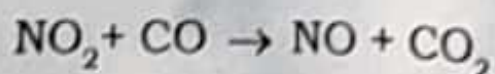


using equal concentrations of ester and alkali.

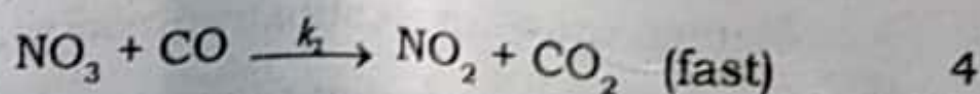
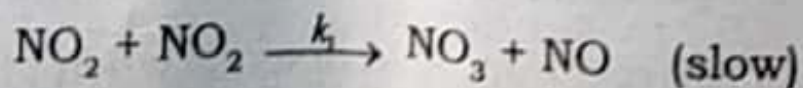
Time/ min	0	4.89	10.07	23.66	∞
Vol. of acid/ml	47.65	38.92	32.63	22.58	11.84

Show that the reaction follows second order kinetics. 5

6. (a) Using Steady State Approximation, derive the differential rate law for the reaction between NO_2 and CO at low temperature.



The proposed reaction mechanism is :

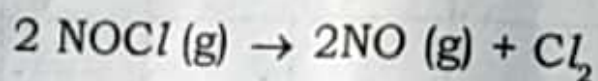


2203

- (b) Compare the rate constants as given by Arrhenius equation and the Collision theory and show that : 4

$$E_a = E_0 + \frac{RT}{2}$$

- (c) For the reaction :



The rate constant is $2.8 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $7.0 \times 10^{-1} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 300 K and 400 K respectively. What is the energy of activation for the reaction ? 4

7. (a) Kinetics of enzyme catalysed reactions is studied by Michaelis - Menten mechanism. Using the Steady State approximation, relate enzyme and substrate concentration to rate of the reaction. Also discuss when Michaelis Menten constant \gg substrate concentration, how the rate variation takes place. 4

- (b) Outline any **two** methods which are employed for determination of order of a reaction. 4
- (c) At 380°C , the half life period for the **first** order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1} . Calculate the time required for 75% decomposition at 450°C . 4

Section - C

8. (a) Derive Stern -Volmer Equation. What is its significance ? 5
- (b) What is Quantum yield or quantum efficiency ? Write down the reasons for high and low quantum yield. 3
- (c) In the photochemical combination of $\text{H}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ a quantum efficiency of about 1×10^6 is obtained with a wavelength of 480 nm . What amount of HCl will be produced under these conditions if one calorie of radiant energy is absorbed ? 4

Your Roll No.....

Sr. No. of Question Paper : 2341 IC

Unique Paper Code : 42171205

Name of the Paper : Chemical Energetics,
Equilibrium & Functional
Organic Chemistry- I

Name of the Course : B.Sc. (Programme)

Semester : II

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Use of Scientific calculator and log table is allowed.
3. Use separate sheets for **Section A** and **Section B**.

SECTION A
(PHYSICAL CHEMISTRY)

Attempt any **three** questions in all and
Question No. 1 is compulsory.

1. Attempt any **five** questions :

(a) What do you understand by buffer? Give an example of basic buffer.

P.T.O.

- (b) What are extensive and intensive variables? Classify the following as extensive and intensive- molar entropy, enthalpy, temperature, heat capacity.
- (c) State Le-Chatelier's principle and explain the effect of change of temperature on equilibrium.
- (d) What is pH? Calculate the pH of 0.001 M NaOH.
- (e) Differentiate between differential enthalpy of solution and integral enthalpy of solution.
- (f) Why salts of strong acid and strong base do not get hydrolysed? (2.5×5)
2. (a) Define enthalpy of neutralization. The enthalpy of neutralization of HCl with NaOH is 57.3 kJmol^{-1} and NH_4OH is -51.3 kJmol^{-1} . Calculate the enthalpy of ionization of NH_4OH .
- (b) Explain the term entropy and give its physical significance. The entropy of the universe is increasing. Explain.
- (c) What is the physical significance of ΔG ? Show that $\Delta G_{\text{sys}} = -T\Delta S_{\text{sys}}$. (4,4,4½)
3. (a) What are the characteristics of chemical equilibrium? Find the relationship between K_p and K_c .

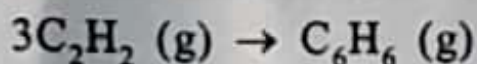
(b) Explain the following :

(i) A Solution of Na_2CO_3 is alkaline.

(ii) A solution of NaCl is neutral.

(c) Define solubility product. At 25°C , a saturated solution of BaSO_4 is $3.9 \times 10^{-5} \text{ M}$. What is its solubility in $0.1 \text{ M Na}_2\text{SO}_4$ solution? (4,4,4½)

4. (a) Calculate the enthalpy change of the reaction



Given that Enthalpy of combustion of $\text{C}_2\text{H}_2 (\text{g})$ and $\text{C}_6\text{H}_6 (\text{g})$ are -1.30 kJmol^{-1} , $-3.302 \text{ kJmol}^{-1}$ respectively.

(b) Calculate the hydrolysis constant and degree of hydrolysis of 10^{-2} M solution of NH_4Cl . Given that K_b of NH_4OH is $1.8 \times 10^{-5} \text{ M}$.

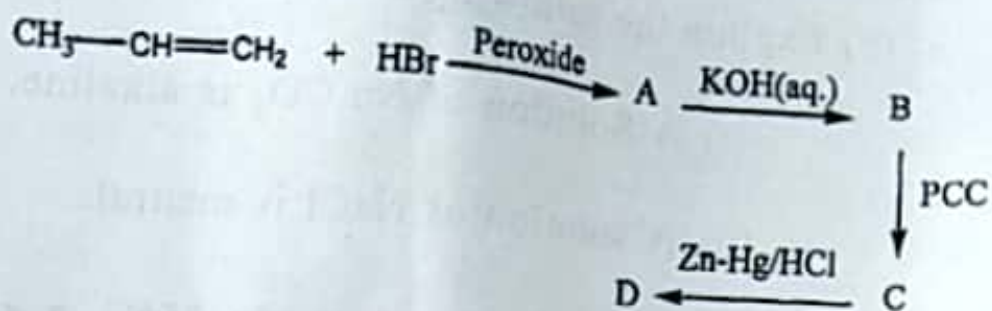
(c) What is C_v and C_p . Show that $C_p - C_v = R$. (4,4,4½)

SECTION B
(ORGANIC CHEMISTRY)

Attempt any three questions in all.

5. (a) Complete the following reaction and draw the structure of (A), (B), (C) and (D).

P.T.O.



(b) Discuss how benzene is converted into chlorobenzene. Explain its mechanism.

(c) What do you understand by $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions? Discuss the stereochemistry of $\text{S}_{\text{N}}1$ reaction. (4,4,4½)

6. (a) Give reason for the following:

(i) p-Nitrochlorobenzene undergoes nucleophilic substitution reaction faster than chlorobenzene.

(ii) Phenol is more acidic than alcohols.

(b) Why do aldehydes and ketones undergo nucleophilic addition reaction? Give chemical reaction for the formation of oxime.

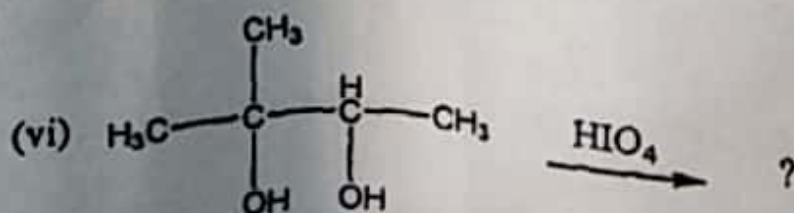
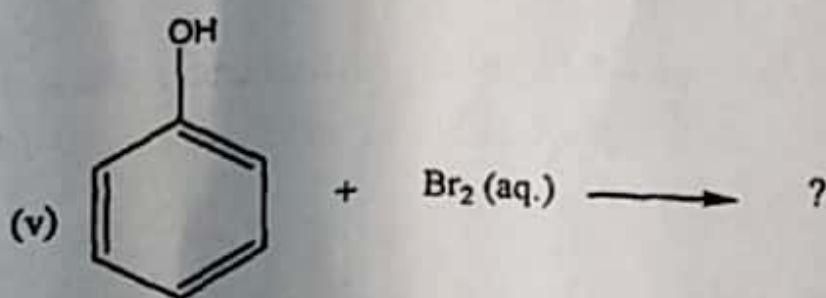
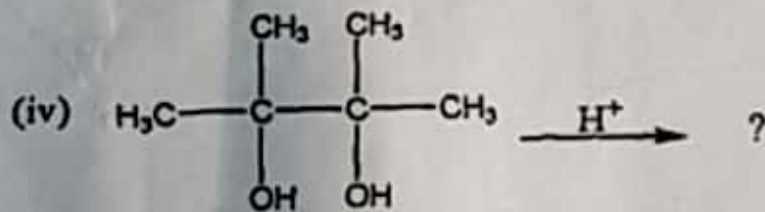
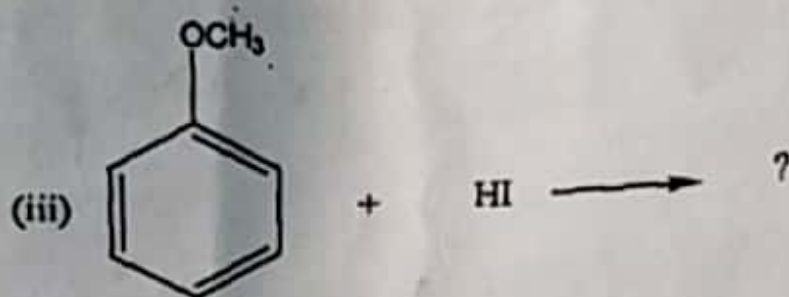
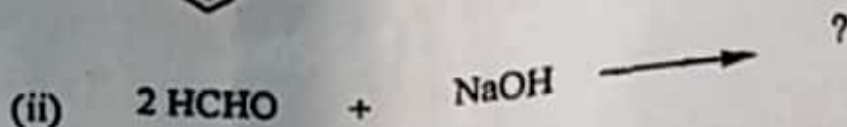
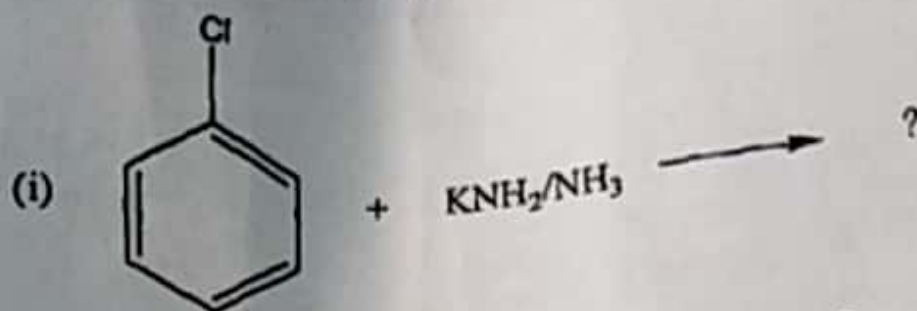
(c) How will you convert?

(i) Acetaldehyde to isopropyl alcohol

(ii) Acetyl chloride to acetaldehyde

(2×2,4½,2×2)

7. (a) Complete the following reaction



P.T.O.

(b) What is Lucas reagent? Describe Lucas test for distinguishing between primary, secondary and tertiary alcohol.

(c) Write the chemical reaction of acetone with phenyl hydrazine. (6,4,2½)

8. (a) Write short notes on any two of the following :

(i) Aldol condensation

(ii) Wittig reaction

(iii) Reimer-Teimann reaction

(b) What is oppenauer oxidation? Give its mechanism.

(4,4,4½)

[This question paper contains 6 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 6921

HC

Unique Paper Code : 42171205

Name of the Paper : Chemistry (Chemical Energetics,
Equilibria and Functional Group
Organic Chemistry - I)

Name of the Course : B.Sc. Programme

Semester : II

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Use of log tables and scientific calculators is allowed.
3. Use separate sheets for Section A and Section B.

Section A

(PHYSICAL CHEMISTRY)

Attempt three questions from this section.

Q. No. 1 is compulsory.

1. (a) Define :

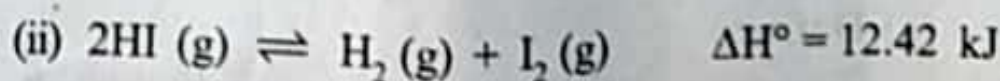
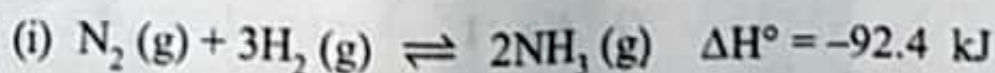
- (i) Integral heat of solution
- (ii) Solubility product

P.T.O.

- (b) State third law of thermodynamics. Why is it important in thermodynamics?
- (c) What is the difference between bond enthalpy and bond dissociation energy?
- (d) What is the significance of ΔG° ?
- (e) Calculate the pH of pure water at 40°C , given that K_w at 40°C is $3.8 \times 10^{-14} \text{ M}^2$.
- (f) Briefly explain the application of solubility product principle in purification of common salt.

(2,2,2,2,3,2)

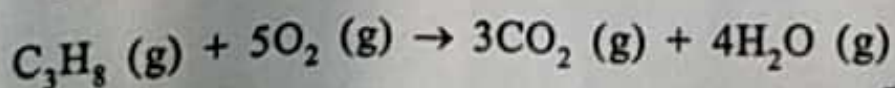
2. (a) Derive the expression for Kirchoff's equation for variation of enthalpy of reaction with temperature.
- (b) What will be the pH value of a solution obtained by mixing 5 g of acetic acid and 7.5 g of sodium acetate and making the volume to 500 cm^3 ? Given K_a of acetic acid = 1.8×10^{-5} at 25°C .
- (c) State Le Chatelier's Principle. Consider the reactions :



What is the effect of increase of temperature and pressure on the course of the above reactions?

(4,5,3)

3. (a) Define heat of formation and heat of combustion of a compound. Calculate the heat of formation of ethyl alcohol, given that heat of combustion of ethyl alcohol is $-1380.7 \text{ kJ mol}^{-1}$ and the heats of formation of $\text{H}_2\text{O (l)}$ and $\text{CO}_2 \text{ (g)}$ are $-286.6 \text{ kJ mol}^{-1}$ and $-394.5 \text{ kJ mol}^{-1}$ respectively.
- (b) Derive the law of chemical equilibrium thermodynamically.
- (c) What is the significance of Debye's T-cubed law?
- (d) Derive expressions for hydrolysis constant, degree of hydrolysis and pH for salt of weak acid and weak base. (4,3,1,4)
4. (a) A mixture of solid SrSO_4 and solid BaSO_4 is shaken up with water until saturation equilibrium is established. Given $K_{sp} (\text{SrSO}_4) = 7.6 \times 10^{-7} \text{ M}^2$ and $K_{sp} (\text{BaSO}_4) = 1.5 \times 10^{-9} \text{ M}^2$, calculate the concentrations of Sr^{2+} , Ba^{2+} and SO_4^{2-} .
- (b) Starting from the expression for K_p , derive relationships between K_p , K_c and K_x . The value of $K_p^\circ = 2.21 \times 10^{-5}$ at 25°C for the reaction, calculate the value of K_c° .
- (c) Propane has the structure $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_3$. Calculate the change in enthalpy for the following reaction :



P.T.O.

Given the average bond enthalpies (in kJ mol^{-1}) are :

C-C	C-H	C=O	O=O	O-H
347	414	741	498	464

(4,4,4)

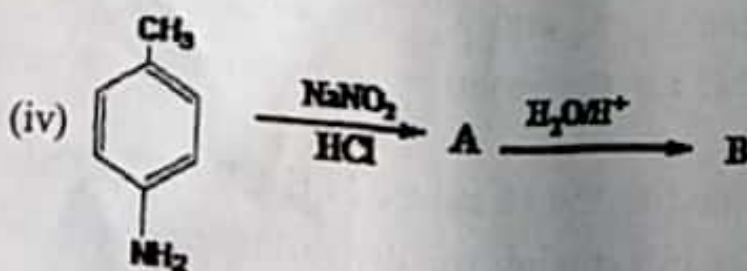
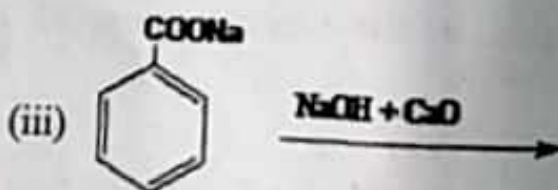
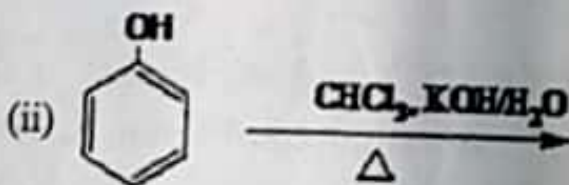
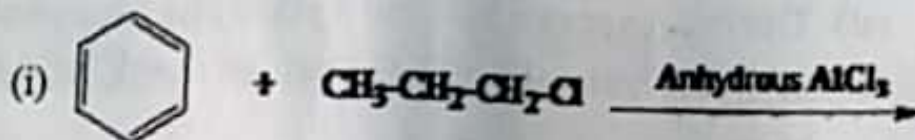
Section B

(Organic Chemistry)

Attempt three questions from this section.

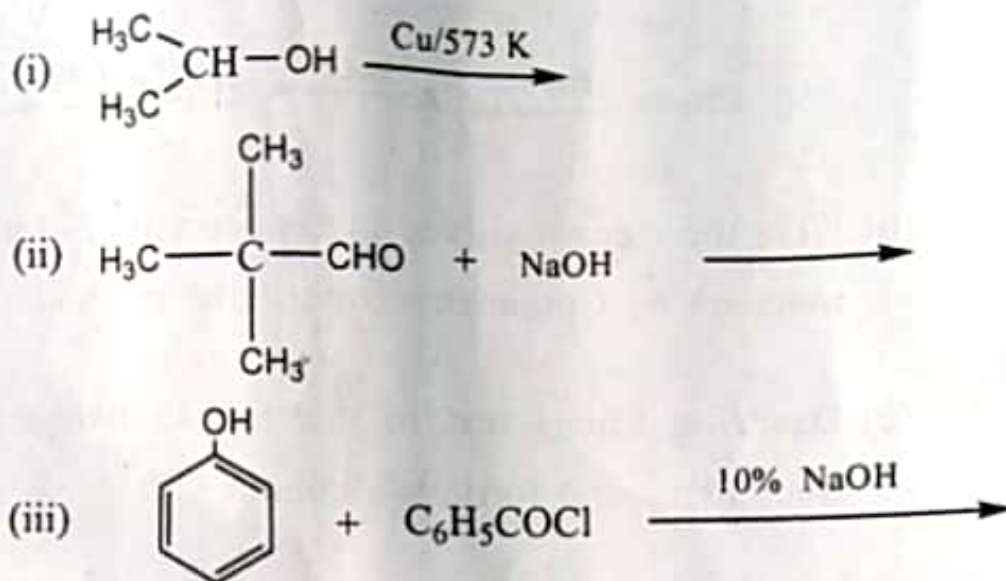
Q. No. 5 is compulsory.

5. (a) Complete the following reactions :





- (b) Give the steps involved in the formation of phenol from benzene by Cumenehydroperoxide method.
- (c) Describe Lucas test to distinguish between primary, Secondary and tertiary alcohols. (8,2,4)
6. (a) Write down key differences between the S_N^2 and S_N^1 mechanism followed by alkyl halides.
- (b) Explain why allyl chloride is more reactive than vinyl chloride towards nucleophilic substitution.
- (c) How will you synthesize Methyl propyl ether using Williamson ether synthesis and what are the products if this ether reacts with HI?
- (d) Describe the benzyne mechanism for nucleophilic substitution of aryl halide. (3,3,3,3)
7. (a) Reaction of carbonyl compounds with ammonia derivative occur under controlled pH condition. Why?
- (b) Complete the following reactions :



(c) What products are likely to be obtained when a benzyl alcohol and propyl alcohol is oxidized with PCC and alkaline KMnO_4 respectively? Explain with the help of an example.

(d) With the help of a suitable example write down $\text{S}_{\text{N}}^{\text{i}}$ mechanism. (3,3,3,3)

8. Write notes on any four of the following :

- (i) Iodoform reaction
 - (ii) Benzoin condensation
 - (iii) Pinacol- Pinacolone rearrangement
 - (iv) Houben - Hoesch condensation
 - (v) Wolf Kishner reduction
 - (vi) Aldol condensation
- (3,3,3,3)

[This question paper contains 6 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 2354

IC

Unique Paper Code : 42174404

Name of the Paper : Chemistry of S- & P- block
Elements, States of Matter
& Chemical Kinetics

Name of the Course : B.Sc. (Prog.)

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt 3 questions from Section A and 3 questions from Section B.
3. Please indicate the section you are attempting by putting a heading and do not intermix the sections.
4. The questions should be numbered in accordance to the number in the question paper.
5. Use of scientific calculator is permitted.
6. Graph paper may be provided.
7. Value of constant: $R = 8.314 \text{ JK}^{-1} \text{ Mol}^{-1}$

P.T.O.

Section A
(Inorganic Chemistry)
Attempt three questions in all.

1. Explain any five of the following :
- (i) The Hg – HgO line changes slope at 356°C in Ellingham diagram.
 - (ii) When heated, sulphur melts to a mobile liquid, but on further heating the viscosity increases sharply and then decreases again.
 - (iii) Despite having high ionization enthalpy, in aqueous solution Li is as good reducing agent as Cs.
 - (iv) The ionization enthalpies of group 13 elements are in the order of:
 $B > Al < Ga > In < Tl$.
 - (v) Aluminium carbide is called methanide whereas calcium carbide is called acetylide.
 - (vi) Aluminium shows certain similarities with beryllium.
 - (vii) Oxygen differs from the rest of the elements of group 16. (5×2.5=12.5)
2. (a) Carbon monoxide is a better reducing agent for metal oxides than carbon below a temperature of 710°C but above this temperature reverse is true. Explain.

(b) Arrange the following oxoacids of chlorine in order of increasing acidity :

HClO_4 , HClO_3 , HClO_2 , HClO . Justify your answer.

(c) Explain briefly the electronegativity in terms of Pauling's and Mullikan's scale.

(d) Give an example of :

(i) Oxoacid of phosphorous, where phosphorous exhibits: +1 oxidation state,

(ii) Hydride of nitrogen, where nitrogen exhibits: -1 oxidation state. (4,3.5,3,2)

3. (a) Discuss briefly the steps involved in Parke's process for recovering Ag and Au from Pb.

(b) Taking diborane as a representative example, explain what is meant by a three centre - two - electron bond.

(c) Identify the example, which best suits the property mentioned, giving reasons for your choice :

(i) Stronger base: NH_3 or N_2H_4 .

(ii) Stronger oxidizing agent: PbCl_2 or PbCl_4 .

(d) What happens when H_3PO_4 is heated?

(3,4,4,1.5)

4. (a) Draw the structure of the following :

(i) Peroxodisulphuric acid

P.T.O.

- (ii) Sulphuryl chloride
 - (iii) Perchloric acid.
- (b) Write a short note on – “Allotropes of carbon.”
- (c) What happens when PCl_3 and PCl_5 react with water.
- (d) Name the specific reduction method used to obtain the following metals from their ores :
- (i) Sodium
 - (ii) Manganese
 - (iii) Iron
 - (iv) Silver
- (3,3.5,4,2)

Section B

(Physical Chemistry)

Attempt three questions in all.

5. (a) Explain briefly the following :
- (i) A gas with van der Waals constant $a = 0$ cannot be liquefied.
 - (ii) The ideal gas equation of state is not valid for a real gas.
 - (iii) The compressibility factor, Z , for a real gas has a value different from unity.

(iv) As the pressure of the gas decreases the mean free path of the molecules of the gas increases but the collision frequency decreases.

(v) Viscosity of a gas increases with an increase in temperature but for a liquid usually the reverse is true.

(b) State the law of corresponding states and derive the mathematical expression for the same.

(2,2,2,2,2,2.5)

6. (a) Derive the expressions for the van der Waals constants a and b in terms of critical temperature, T_c and critical pressure P_c only.

(b) Determine the interplanar spacing between the (2 2 1) planes of a cubic lattice of length 450 pm.

(c) Benzene takes 46s to flow through an Ostwald's viscometer while water takes 68s at the same temperature. If the densities are 0.8 g mL^{-1} and 0.998 g mL^{-1} respectively and the coefficient of viscosity of water is $1.008 \times 10^{-3} \text{ Pa s}$, calculate the coefficient of viscosity of benzene.

(4.5,4,4)

7. (a) Calculate the critical temperature of a van der Waals gas for which P_c is 100 atm and b is $50 \text{ cm}^3 \text{ mol}^{-1}$.

- (b) A reaction has the experimental rate equation $\text{Rate} = k[A][B]$. If the concentration of A is doubled, and the concentration of B is halved, what happens to the reaction rate?
- (c) Derive the Integrated Arrhenius equation for showing effect of temperature on reaction rate.
- (d) Addition of sodium nitrate increases the surface tension of water while the addition of detergent decreases it. Explain. (4,3,3,2.5)
8. (a) The decomposition of N_2O_5 is an important process in tropospheric chemistry. The half-life for the first-order decomposition of this compound is 2.05×10^4 s. How long will it take for a sample of N_2O_5 to decay to 60% of its initial value?
- (b) The distance between two consecutive (110) planes of a crystal is 1.678×10^{-10} m. What will be the glancing angle for an X-ray of wavelength 0.65×10^{-10} m incident on the plane for first order reflection?
- (c) Write a short note on Law of constancy of interfacial angle.
- (d) Derive the expression for the collision frequency, Z_{11} , for a gas. (4,4,2,2.5)

(3500)

[This question paper contains 3 printed pages]

Your Roll No.

:

Sl. No. of Q. Paper

: **2387** **IC**

Unique Paper Code

: 32173909

Name of the Course

: **B.Sc.(Hons.) Chemistry /
B.Sc. (Programme) : SEC**

Name of the Paper

: Pharmaceutical
Chemistry

Semester

: II

Time : 2 Hours

Maximum Marks : 38

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
 - (b) Attempt any **three** questions.
 - (c) Question **NO.1** is compulsory.
1. (a) Define antilaprosy drugs. Give **one** example. 2
- (b) Differentiate between medicine and drugs. 2

P.T.O.

- (c) Give full form of AZT and where is it used. 2
- (d) Differentiate between Aerobic and Anaerobic Fermentation. 2
- (e) Give structure of penicillin and paracetamol. 2
2. (a) Define antifungal drugs. Give **one** example of any sulpha drugs. 3
- (b) Discuss the production of citric acid in fermentation process. 5
- (c) What do you understand by Retrosynthesis? Explain retro synthesis with a suitable example. 6
3. (a) Write a short note on Non-steroidal anti-inflammatory drugs with suitable example. 4
- (b) What are Phenobarbitals? Discuss any one drugs synthesis of Phenobarbitals. 5

- (c) Discuss the industrial preparation of Penicillin. 5

OR

Discuss the synthesis of Vitamin C.

4. (a) Differentiate between sulpha drugs and sulphur drugs with suitable example. 2
- (b) What do you understand by cardiovascular drugs? Give **one** example. 2
- (c) Discuss the synthesis of Vitamin B-12 and give its any **two** uses. 5

OR

Discuss the synthesis of Lysine by fermentation process.

- (d) What is Structure Activity Relationship (SAR)? Discuss it with a suitable example. 5

9

[This question paper contains 3 printed pages]

Your Roll No. :

Sl. No. of Q. Paper : **2388** **IC**

Unique Paper Code : 32173910

Name of the Course : **B.Sc.(Hons.) Chemistry /**
B.Sc. (Prog.) : SEC

Name of the Paper : Chemistry of Cosmetics
and Perfumes

Semester : IV

Time : 2 Hours

Maximum Marks : 38

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
- (b) Attempt **four** questions in all.
- (c) Question **NO.1** is compulsory.
- (d) Attempt any **three** other questions.

1. (a) "A product can be a cosmetic or drug or both."
Explain with examples. 3
- (b) What is the role of sequestering agents in shampoo? Give an example. 3

P.T.O.

- (c) List the ingredients in the preparation of talcum powder. 2
- (d) What are essential oils? Give **two** examples. 2
- (e) List the ideal characteristics of a good lipstick. 2
- (f) Mention the role of plasticizer in preparation of hair spray. Give an example of a plasticizer. 2
2. (a) Explain cleansing action of shampoo and give an example of an antidandruff agent. 4
- (b) What are the various categories of hair dye? Explain them briefly. 4
3. (a) What are antiperspirants and deodorants? Give the preparation of liquid antiperspirants. 4
- (b) What are sunscreen lotions? Explain the term SPF and give its formula. 4

4. (a) Describe the method for preparation of cold cream and mention the function of various ingredients. 4

(b) What are various methods developed in the extraction of essential oils from natural sources? Explain them briefly. 4

5. Write short notes (any **two**): $2 \times 4 = 8$

(a) Nail polish and nail remover

(b) Chemical hair removers

(c) Artificial flavours

(12) [This question paper contains 4 printed pages]

Your Roll No.

:

Sl. No. of Q. Paper

: **2434** **IC**

Unique Paper Code

: 32173908

Name of the Course

: **B.Sc.(Prog.) : SEC**

Name of the Paper

: Green Methods in
Chemistry

Semester

: VI

Time : 2 Hours

Maximum Marks : 38

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
- (b) Attempt **four** questions in **all**.

1. (a) Differentiate between :

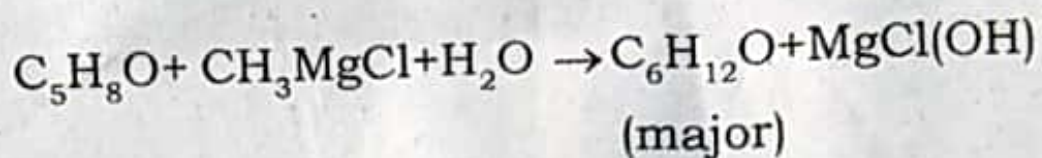
4

(i) Turnover number and Turnover frequency

(ii) Heterogeneous Catalysis and Phase Transfer Catalysis

P.T.O.

- (b) Calculate the % atom economy of the major product in the given reaction :



Does atom economy affect the % yield of a reaction product ? 3

- (c) Discuss trans-esterification with reference to synthesis of Biodiesel. 2.5

2. (a) 'What you don't have can't harm you'. Explain this statement in context of Green Chemistry. 2.5

- (b) What is supercritical carbon dioxide ? What are its advantages over organic solvents ?

3

- (c) Explain *ultrasonic cavitation*. How does it lead to high temperature generation in a liquid ?

4

3. (a) Discuss Flixborough accident. Outline the Asahi's process for cyclohexanol synthesis comparing it with conventional route. 5
- (b) How can zeolites be classified as green catalysts over synthetic catalysts ? 2.5
- (c) Define antifoulants and give an example of a green antifoulant. 2
4. (a) Write short notes on (any **two**) : 4×2=8
- (i) Ionic Liquids
 - (ii) Rightfit[®] pigments
 - (iii) Atom uneconomic reactions
- (b) Reduced derivatisation makes a reaction greener. Explain. 1.5

2434

5. (a) Outline the synthesis of PLA from corn starch. 3

(b) Give **one** example each for : 1.5×2=3

(i) microwave assisted reaction in water.

(ii) photochemical reaction.

(c) Explain goals of green chemistry.

3.5

This question paper contains 7 printed pages]

Roll No.

--	--	--	--	--	--	--	--	--	--	--

S. No. of Question Paper : 8834

Unique Paper Code : 42177926 HC

Name of the Paper : Organometallics, Bioinorganic
Chemistry, Polynuclear Hydrocarbons
and UV, IR Spectroscopy

Name of the Course : B.Sc. (Prog.) Chemistry-DSE 2B

Semester : VI

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt *three* questions each from Section A and Section B.

Sections A and B are to be attempted in separate answer sheets.

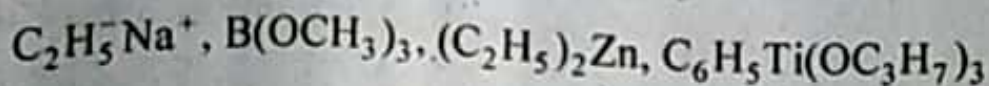
All questions carry equal marks.

The questions should be numbered in accordance
to the number in the question paper.

SECTION A (Inorganic Chemistry)

(Attempt any *three* questions)

1. (a) Which of the following is not considered an organometallic compound and why ?



P.T.O.

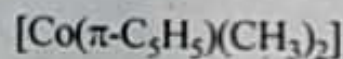
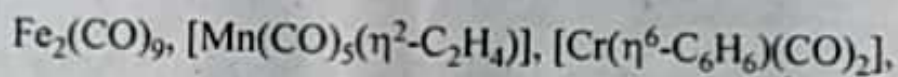
(b) On the basis of VBT predict the shape of $\text{Cr}(\text{CO})_6$ which is found to be diamagnetic.

(c) Why is $\text{Na}^+\text{C}_5\text{H}_5^-$ more stable than $\text{Na}^+\text{C}_5\text{H}_{11}^-$?

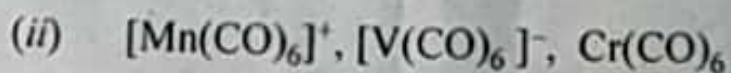
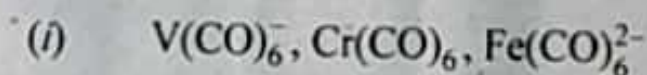
(d) The C-C distance in Zeise's salt is 137.5 pm in comparison with 133.7 pm in free ethylene. Explain the statement in detail.

4,2,2,4,5

2. (a) Calculate the effective atomic number or 18 e^- count in the following compounds :



(b) Arrange the following species in their decreasing CO stretching vibrational frequencies and explain the reason :



(c) Write down any *one* the method for the preparation of $\text{Fe}(\text{CO})_5$. Using VBT explain the structure of $\text{Fe}(\text{CO})_5$. Are all the Fe-C bond lengths identical at room temperature ? Explain.

4,4,4,5

3. (a) Inability to synthesize transferrin may result in anaemia as well as overload of iron. Explain.

(b) How will you explain the binding of oxygen by hemoglobin by considering the change in magnetic behaviour of iron (II) in haemoglobin and oxyhemoglobin.

(c) What do understand by essential and non-essential elements ? In which category—essential, non-essential or toxic elements, will you place the following :

Ca, Sr, Cd, Hg, Cu.

4,4,4,5

4. (a) When alkali is added to an orange coloured solution of compound A, it is converted into yellow coloured solution of compound B which gives yellow precipitate on adding lead acetate. To alkaline solution of compound B, 30% H_2O_2 is added, a red-brown coloured paramagnetic compound C is formed whereas neutral or slightly acidic solution of compound A, on reaction with H_2O_2 gives blue-violet coloured diamagnetic compound D is formed. Identify compounds A to D and write their oxidation states.

(b) Equivalent mass of $KMnO_4$ in acidic medium is one-fifth of its molecular weight. Explain by giving reaction.

(c) Draw the structure of chlorophyll 'a'. Explain the role of Mg^{2+} in chlorophyll.

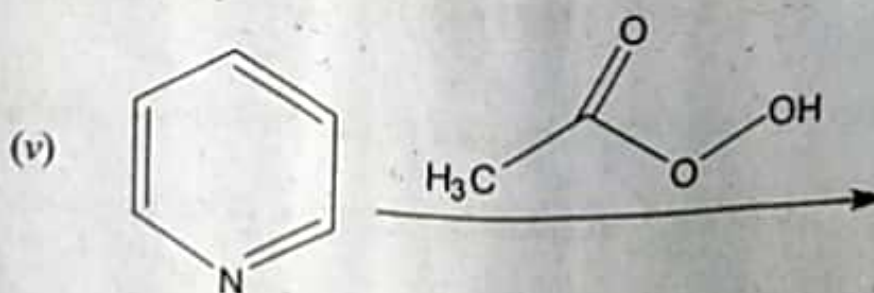
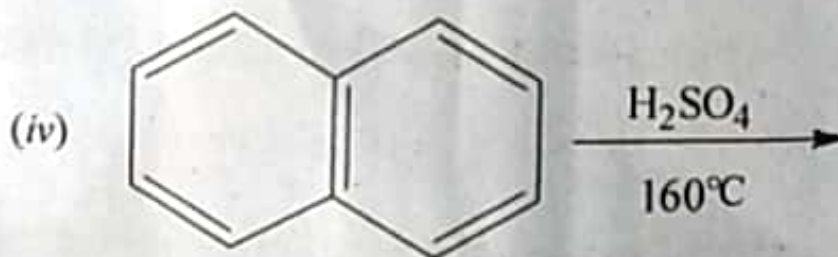
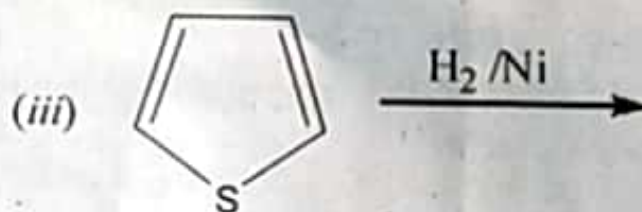
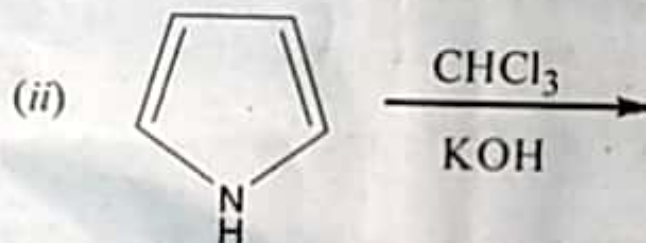
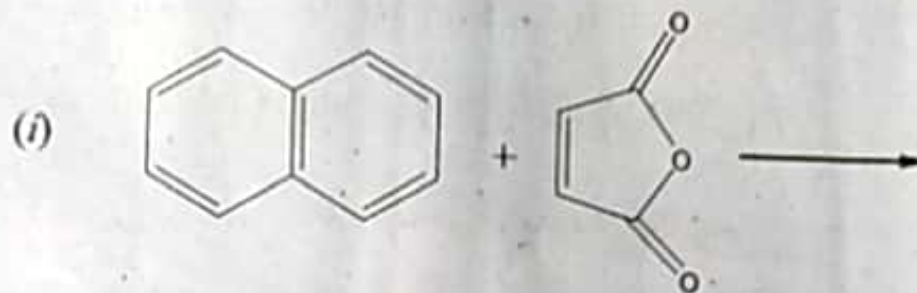
6,2,4,5

P.T.O.

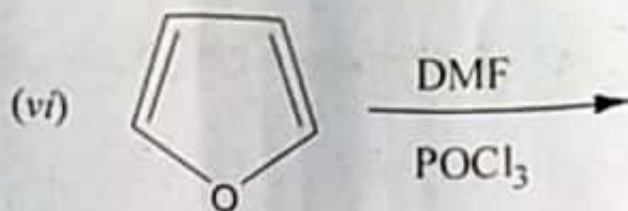
SECTION B (Organic Chemistry)

(Attempt any three questions)

5. (a) Complete the following reactions :



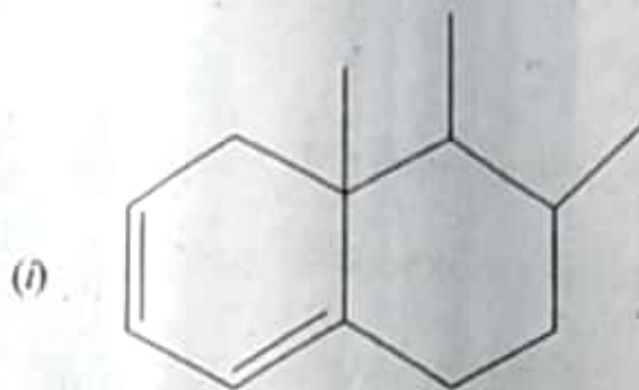
(5)



- (b) Pyridine is more basic than pyrrole. Justify.
- (c) Electrophilic substitution in naphthalene takes place at 1 position. Explain.
- (d) Give the steps of preparation of Haworth synthesis of Naphthalene. 6,2,2,2,5
6. (a) Write reactions for the preparation of any *three* of the following from ethylacetoacetate :
- (i) Succinic acid
- (ii) 4-oxopentanoic acid
- (iii) Crotonic acid
- (iv) Adipic acid
- (b) Arrange pyrrole, thiophene and furan in increasing order of their aromaticity with suitable explanation.
- (c) Anthracene undergoes electrophilic substitution reactions at C9, C10 positions. Explain.
- (d) Write the mechanism for the preparation of Ethylacetoacetate by Claisen Condensation. 6,2,2,2,5

P.T.O.

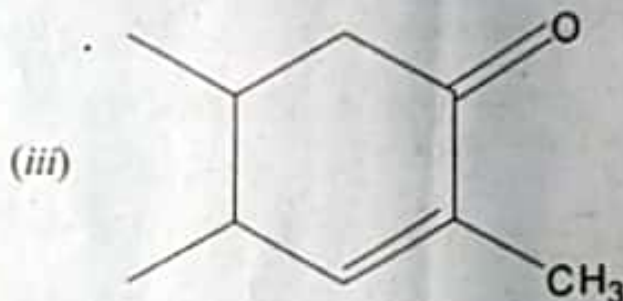
7. (a) Calculate λ_{\max} of any *three* of following structures :



Base value = 253 nm



Base value = 217 nm



Base value = 215 nm

- (b) A conjugated diene absorbs at higher wavelength as compared to diene in which the double bonds are isolated. Explain.
- (c) Hydrogen bonding changes the position of absorption (O-H stretching) in IR spectroscopy. Justify.

(d) Explain auxochrome and chromophore with suitable examples.

(e) How will you distinguish between the following pairs of compounds by IR spectroscopy :

(i) CH_3COOH and $\text{CH}_3\text{COOCH}_2\text{CH}_3$

(ii) CH_3COCH_3 and $\text{CH}_3\text{CH}_2\text{OCH}_3$ 4.5,2,2,2,2

8. (a) Explain :

(i) $\nu_{\text{C-O}}$ stretching in amides occur at lower frequency than corresponding acids.

(ii) Explain the fingerprint region in IR spectroscopy.

(iii) Define bathochromic and hypsochromic shift.

(iv) Furan is the only five membered heteroaromatic compound which undergoes Diels Alder Reaction.

(v) Draw the resonating structures of anthracene.

(b) Calculate the number of fundamental vibrational modes in the following molecules : 10,2,5

H_2O and CO_2 .

This question paper contains 7 printed pages]

Roll No.

--	--	--	--	--	--	--	--	--	--	--

S. No. of Question Paper : 2924

Unique Paper Code : 32175913 IC

Name of the Paper : Chemistry of s- and p-Block
Elements, States of Matter &
Chemical Kinetics

Name of the Course : Generic Elective Chemistry for
Honours

Semester : IV/II

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt six questions in all, three questions from each Section.

Use separate answer-sheets for Section A and Section B

and do not intermix the sections.

Section A

(Inorganic Chemistry)

Attempt any three questions.

Question No. 1 is compulsory.

P.T.O.

1. Explain :

(a) CCl_4 is not hydrolysed with water while SiCl_4 is readily hydrolysed. 2

(b) Oxygen exists as O_2 molecules while sulphur exists as S_8 molecules. 2

(c) The properties of Li and Mg are similar. 2

(d) Which is more stable PbCl_2 or PbCl_4 ? 2

(e) What is the difference between mineral and ore ? 2

(f) Arrange in the increasing order of acidic character HF, HI, HBr, HCl. 2

(g) Which is more reactive white P or red P ? 1.5

2. (a) Give the structure of the following : 3

(i) P_4O_{10}

(ii) Caro's Acid

(iii) ClF_3

- (b) Is it possible to reduce TiO_2 with C ? Explain. 3
- (c) Explain the method for refining of Ti and Zn. 3
- (d) Name the allotropes of carbon. Give their structure and properties. 3
3. (a) Define electronegativity. What are different scales of electronegativity ? Explain briefly. 4
- (b) Give the names and structure of the oxyacids of sulphur. 4
- (c) N-N bond is weaker than P-P single bond. Explain. 2
- (d) Which is stronger reducing agent NH_3 or PH_3 ? 2
4. Explain any *three* : $3 \times 4 = 12$
- (i) Hydrometallurgy
 - (ii) Carbides
 - (iii) Electrolytic refining
 - (iv) Ionization energy.

P.T.O.

Section B

(Physical Chemistry)

Question No. 5 is compulsory

Use of scientific calculators or logarithmic table is allowed

but they cannot be shared.

Avogadro's number, $N_A = 6.023 \times 10^{23}$.

Boltzmann Constant, $K = 1.38 \times 10^{-23} \text{ JK}^{-1}$

Universal Gas Constant, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

Pressure, $1 \text{ atm} = 1.01325 \times 10^5 \text{ Nm}^{-2}$.

5. Attempt any five :

$5 \times 2\frac{1}{2}$

(a) Viscosity of glycerol is much more than that of ether.

Explain.

(b) It is not possible to liquefy an ideal gas. Explain.

(c) If the hard sphere of O_2 gas has molecular diameter 290 pm, what will be the mean free path of O_2 at 500 K and 100 kPa ?

(d) If the activation energy of a reaction is zero, will the rate of reaction still depend on temperature ?

(e) Calculate the Miller indices of the faces having the following intercepts with the three axes perpendicular to each other :

(i) $\frac{a}{2}, 2b, \infty c$

(ii) $2a, 3b, 4c.$

(f) Explain why small drops of liquid are spherical.

6. (a) Derive the expression for the critical temperature, pressure and volume of a gas in terms of van der Waals' constants a and b .

(b) Critical temperature and critical pressure of a gas are 473 K and 30 atm respectively. Calculate its van der Waals constants and the critical volume.

(c) What is the effect of temperature on viscosity of liquid ? 6, 3, 3½

7. (a) Derive the expression for the half-life for the second order reaction having same reactant concentrations.

(b) At a certain temperature the half-life periods for the decomposition of ammonia in contact with tungsten were as follows :

Pressure (mm of Hg)	50	100	200
Half-Life period (min)	3.52	1.82	0.93

Find the order of the reaction.

7, 5½

8. (a) Derive the Bragg's equation for the reflection of X-rays from faces of a crystal.

- (b) Calculate the angles at which first and second order are obtained from the planes 500 pm apart, using X-rays of wavelength of 100 pm.
- (c) Molybdenum forms body-centred cubic crystal whose density is 10.3 g cm^{-3} . Calculate :
- edge length of unit cube
 - distance between (111) planes. Mass of Molybdenum = 95.94 g mol^{-1} . 5½. 3, 4

[This question paper contains 6 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 3049

IC

Unique Paper Code : 32175916

Name of the Paper : Chemistry of d-block Elements,
Quantum Chemistry and
Spectroscopy

Name of the Course : **Generic Elective for
Honours : Chemistry**

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **SECTION A** and **SECTION B** on **SEPARATE** answer sheets.
3. Use of scientific calculator is permitted.

SECTION A

INORGANIC CHEMISTRY

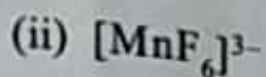
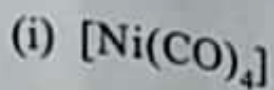
Attempt ANY THREE questions.

1. (a) Giving reasons for any **four** of the following :

P.T.O.

- (i) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is square planar while $[\text{ZnBr}_4]^{2-}$ is tetrahedral.
- (ii) Cobalt (II) is easily oxidized to cobalt (III) in the presence of strong field ligands.
- (iii) Potassium dichromate is highly coloured.
- (iv) Radii of elements of third transition series are similar to those of second transition series.
- (v) Transition metals form large number of complexes.
- (b) How many stereoisomers are there for the octahedral complex $[\text{CoBr}_2\text{Cl}_2(\text{en})]^-$? How many of these stereoisomers are optically active?
(10,2.5)
2. (a) Write the IUPAC names for any **three** complexes
- (i) $\text{K}_2[\text{O}_5\text{Cl}_5\text{N}]?$
- (ii) $\text{Na}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$
- (iii) $[\text{Cu}(\text{NH}_3)_4]$ $[\text{PtBr}_4]$
- (iv) $[(\text{NH}_3)_4\text{Co}-\text{NH}_2-\text{O}_2-\text{Co}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}_2$

(b) Using VBT predict the geometry and magnetic moment for the following complexes.



(c) Draw the crystal field splitting diagram for d^6 metal ion placed in tetrahedral environment. Calculate CFSE in terms of Δ_t . (4.5,5,3)

3. (a) Write the formulae for the following complexes :

(i) Tetramethylammoniumheptaiodidozirconate(IV)

(ii) Barium tetrafluoridobromate(III)

(iii) Hexaminechromium(II) hexanitrochromate (III)

(iv) μ -imido- μ -superoxidotetrakis(ethylenediamine)dicobalt(III)nitrate

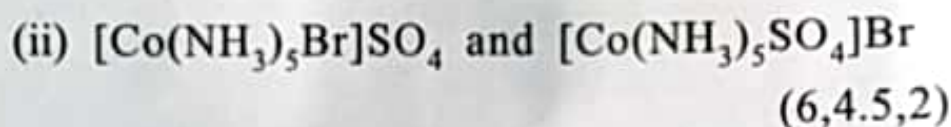
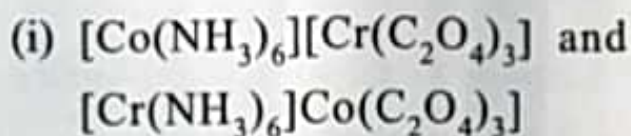
(b) Crystal field splitting are listed in the following table for three complexes of chromium. Explain the differences in values

Complex	(cm^{-1})
$[\text{CrF}_6]^{3-}$	15,000

P.T.O.



(c) Name the type of isomerism in the following :



4. (a) Compare and contrast the magnetic and spectral properties of elements of d- and f- block elements.

(b) Write short notes on any **two** :

(i) Separation of lanthanides by ion exchange process

(ii) Inner and outer orbital octahedral complexes.

(iii) Catalytic activity of transition metals

(c) For Fe^{3+} ion, the electron pairing energy $P = 28,000 \text{ cm}^{-1}$, Δ_0 values, for complexes $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ are 21,000 and 38,500 cm^{-1} respectively. Calculate CFSE for both the complexes.

(4,5,3.5)

SECTION B
PHYSICAL CHEMISTRY

Attempt any THREE questions.

1. (a) Arrange the following in order of descending energy :
 10cm^{-1} , $1 \times 10^{-23}\text{ J}$, 0.01m , 1 MHz .
- (b) State the two laws of photochemistry.
- (c) Is the wavefunction $\exp(ax)$, where a is a constant, an eigenfunction of the operator $\{d^2/dx^2 + 2(d/dx) + 3\}$? If so, give the eigenvalue. (4.5,4,4)
2. (a) Consider a particle of mass m existing in a one-dimensional box of length L . Set up the relevant Schrodinger equation and derive the expression for the energy E_n .
- (b) Explain the terms degeneracy and node using the particle in a one - dimensional box as an example.
- (c) Explain briefly the phenomenon of fluorescence. (5.5,4,3)
3. (a) A strong absorption band is observed for $^{12}\text{C}^{16}\text{O}$ in the IR region at 2170 cm^{-1} . Assuming harmonic potential, calculate the force constant and zero point energy for the C-O bond.

- (b) A certain substance in a cell of length l absorbs 10% of the incident light. What fraction of the incident light will be absorbed if the length of the cell is $4l$?
- (c) The rotational spectrum of $^1\text{H}^{19}\text{F}$ shows the $J=0 \rightarrow J=1$ absorption at 41.11 cm^{-1} . Calculate the bond length of the molecule. (4,4,4.5)
4. Write short notes on the following :
- (a) Free Electron Molecular Orbital (FEMO) model to explain electronic transitions.
- (b) Bathochromic and hypsochromic shift.
- (c) Effect of isotopic substitution on rotational spectra of a diatomic molecule. (4.5,4,4)

PHYSICAL CONSTANTS

Planck's constant $6.626 \times 10^{-34} \text{ Js}$

Velocity of light $3 \times 10^8 \text{ ms}^{-1}$

Avogadro's number $6.023 \times 10^{23} \text{ m}$

1 a.m.u $1.66 \times 10^{-27} \text{ kg}$

This question paper contains 4+2 printed pages]

Roll No.

--	--	--	--	--	--	--	--	--	--

S. No. of Question Paper : 7670

Unique Paper Code : 32175913 HC

Name of the Paper : Chemistry of s and p block elements,
states of matter and chemical kinetics

Name of the Course : Generic Elective : Chemistry

Semester : III/IV

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt six questions in all, three questions from each section.

Use separate sheets for Section A and Section B.

Use of scientific calculator is allowed.

Section A

(Inorganic Chemistry)

1. (a) Carbon can be used to reduce any metal oxide if a sufficiently high temperature is used. Justify this statement using the Ellingham Diagram. 3.5
- (b) Discuss briefly the Van Arkel-de Boer process for refining of metals. 3
- (c) Explain the role of flux (Acidic and basic) in the extraction of metals. 3

P.T.O.

Or

Explain electrolytic purification of metals.

(d) Differentiate between any *two* of the following : 2×1.5

- (i) Mineral and ore
- (ii) Calcination and roasting
- (iii) Gangue and slag.

2. (a) Discuss allotropy in carbon. 3.5

(b) Explain any *two* of the following : 2 \times 1.5

- (i) Tl(I) is more stable than Tl(III). Why ?
- (ii) Ionization enthalpy of Oxygen is less than that of Nitrogen although general trend suggests an increase in ionization enthalpy along a period. Give reasons.
- (iii) Why is Gallium smaller in size as compared to Aluminium ?

(c) Make pairs of the following on the basis of similarity in properties. Why do these elements show similar behaviour ? 3

Li, C, B, Be, Mg, Al, Si, P

- (d) Explain briefly the electronegativity in terms of Pauling's scale and Mulliken's scale. 3
3. (a) Describe multicentre bonding using diborane as an example. 3.5
- (b) Write name, formula and structure of any two oxoacids of Phosphorous. 3
- (c) Answer any two of the following reactions : 3
- (i) $\text{Ag}^+ + 2\text{NH}_3 \rightarrow$
- (ii) $\text{PCl}_5 + 4\text{H}_2\text{O} \rightarrow$
- (iii) $\text{H}_2\text{SO}_4 + \text{SO}_3 \rightarrow$
- (d) What happens when hydrazine reacts with chlorine ? 3
4. (a) Write Industrial applications of ammonia. 3.5
- (b) Arrange oxoacids of chlorine in increasing order of acidic strength. Give reasons. 3
- (c) Write short notes on any two of the following : 2×3
- (i) Oxohalides
- (ii) Mond's process
- (iii) Hydroxylamine.

Section B

(Physical Chemistry)

5. (a) Write the mathematical expression for the Maxwell distribution of molecular speeds of a gas. Explain briefly the terms involved. How does the change in temperature influence the distribution of molecular speeds ? 4
- (b) Calculate the most probable velocity, average velocity and root mean square velocity of CO at 298K. 4
- (c) Derive the relations :
- $$P_c = a/27b^2 \text{ and } T_c = 8a/27Rb \quad 4.5$$
6. (a) Define the surface tension of liquid. Describe the drop number method for the determination of the surface tension of a liquid. 4.5
- (b) With the given viscometer, the times of flow at 20°C for water and an unknown liquid ($d = 1.22 \text{ g cm}^{-3}$) were found to be 155 sec and 80 sec respectively. Calculate the absolute viscosity of the unknown liquid at 20°C if viscosity and density of water are 1.005 centipoise and 1 g cm^{-3} respectively. 4

(c) Explain why the viscosity of gas increases with temperature but that of liquid decreases with temperature. 4

(a) What are the differences between crystalline and amorphous solids ? 4

(b) When a certain crystal was studied by the Bragg's method using X-rays of wavelength 229 pm, first order X-ray reflection was observed at an angle of $23^{\circ}20'$:

(i) What is corresponding inter-planar spacing ?

(ii) When another X-ray source was used, a reflection was observed at $15^{\circ}26'$. What was the wavelength of these X-rays ? 4.5

(c) Write short notes on any *two* of the following :

(i) Law of rational indices

(ii) Law of constancy of interfacial angle

(iii) Schottky defect and Frenkel defect. $2 \times 2 = 4$

8. (a) Derive the integrated rate law equation for a second order reaction when the initial concentrations of both reactants are same. 4.5

- (b) The rate constant at a certain temperature of the first order decomposition of hydrogen peroxide in a suitable medium is $5 \times 10^{-4} \text{ sec}^{-1}$. Calculate the time required to complete one-third of the reaction. 4
- (c) Starting from the integrated rate law equation, show that the half-life period of a first order reaction is independent of the initial concentration. 4

[This question paper contains 8 printed pages]

Your Roll No.

:

Sl. No. of Q. Paper

: **7668** **HC**

Unique Paper Code

: 32175902

Name of the Course

: **Generic Elective:
Chemistry**

Name of the Paper

: Chemical Energetics,
Equilibria & Functional
Organic

Semester

: IV

Time : 3 Hours

Maximum Marks : 75

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
- (b) Attempt **3** questions from section **A** and section **B**.
- (c) Please indicate the section you are attempting and do not intermix the sections.
- (d) The questions should be numbered in accordance to the number in question paper.
- (e) Calculator and log table may be used.

P.T.O.

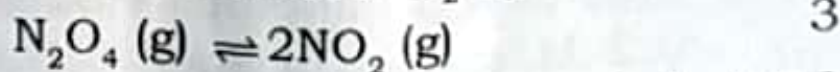
Section-A

(Attempt any **three** Questions in all)

1. (a) Calculate the entropy change when one mole of ethanol is evaporated at 351K. The molar heat of vaporization of ethanol is $39.84 \text{ kJ mol}^{-1}$ 2
 - (b) Derive Kirchoff's equation showing the variation of ΔH with temperature. 2
 - (c) State and explain the Le Chatelier principle by predicting the effect of temperature and pressure on the following equilibrium reactions 4.5
 - (i) $\text{PCl}_5 (\text{s}) \rightleftharpoons \text{PCl}_3 (\text{g}) + \text{Cl}_2 (\text{g}) \quad \Delta H = \text{+ive}$
 - (ii) $3 \text{H}_2 (\text{g}) + \text{N}_2 (\text{g}) \rightleftharpoons 2 \text{NH}_3 \quad \Delta H = \text{-ive}$
 - (d) Calculate pH of 0.2 M $\text{Ba}(\text{OH})_2$ solution at 25°C . Assume complete dissociation. 2
 - (e) At certain temperature degree of dissociation of pure water is 1.81×10^{-9} . Calculate ionic product of water. 2
2. (a) Define standard state of a substance and standard heat of formation ΔH_f° of compound. Calculate ΔH for the reaction

$$\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$$
 Given ΔH_f° for $\text{CO}_2(\text{g})$; $\text{CO}(\text{g})$, $\text{H}_2\text{O}(\text{g})$ are -395.0 , -111.31 and $-248.8 \text{ kJ mol}^{-1}$ respectively. 4
- 2

- (b) The degree of ionization of N_2O_4 is 16.7% at 298 K and 1 atm. Calculate the equilibrium constant K_p and K_c . The dissociation reaction of N_2O_4 is



- (c) The solubility product of $Pb_3(PO_4)_2$ is 1.5×10^{-32} . Determine its solubility in $g L^{-1}$.

2

- (d) Give the application of solubility product in cation analysis

2

- (e) Differentiate between bond enthalpy and bond dissociation enthalpy

OR

Differentiate between Differential and integral heat of solution.

1.5

3. (a) Why is standard enthalpy of neutralization (ΔH°) of one mole of strong acid with one mole of strong base is constant i.e. $-57.3 \text{ kJ mol}^{-1}$. What will happen to heat of neutralization in the following cases ?

(i) 200 mL of 1M strong acid and 100 mL of 1M strong base are mixed

(ii) 100 mL of 1M weak acid and 100 mL of 1M strong base are mixed.

4

- (b) What are buffer solutions ? Discuss acidic and basic buffers with one example each. Derive Henderson- Hasselbalch equation to calculate pH of the buffer solution. Calculate pH of buffer solution containing 0.2 M sodium acetate (CH_3COONa) and 0.15M acetic acid (CH_3COOH). Given K_a (acetic acid) = 1.8×10^{-5} 6
- (c) Find out the relationship between K_p , K_x and K_c . Under what conditions all the three equilibrium constants are identical, that is $K_p = K_x = K_c$ 2.5
4. (a) State and explain third law of thermodynamics. What is its importance in chemistry ? 3
- (b) State and explain Hess law of constant heat of summation. Is it applicable for other thermodynamic variables ? 3
- (c) What do you understand by the hydrolysis of salt, degree of hydrolysis and hydrolysis constant of the salt ? Why a salt of strong acid and strong base do not get hydrolyzed/ change the pH of aqueous solution on hydrolysis ? Derive an expression for pH of the solution made upon hydrolysis of a salt

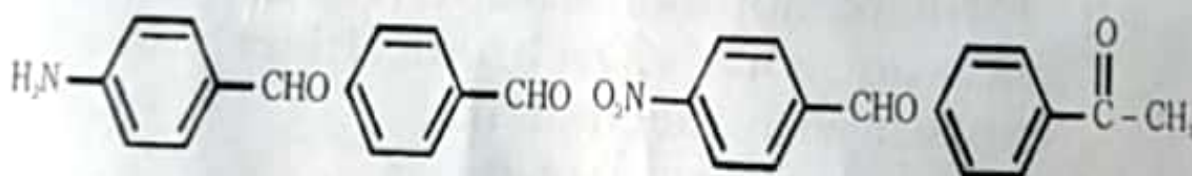
of weak acid and strong base. Given that K_a is dissociation constant of the acid and K_h is the hydrolysis constant of the salt, h is degree of hydrolysis and c is the concentration of the salt.

6.5

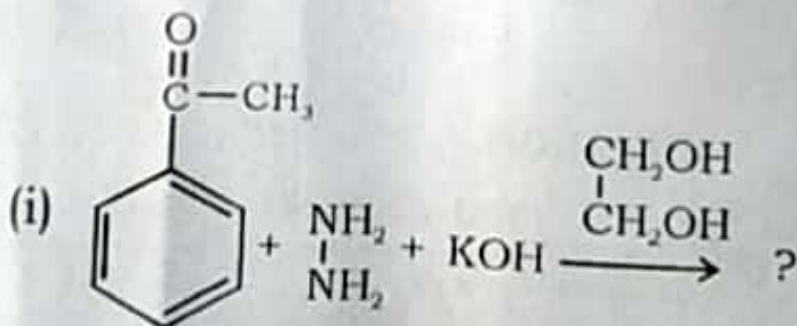
Section-B

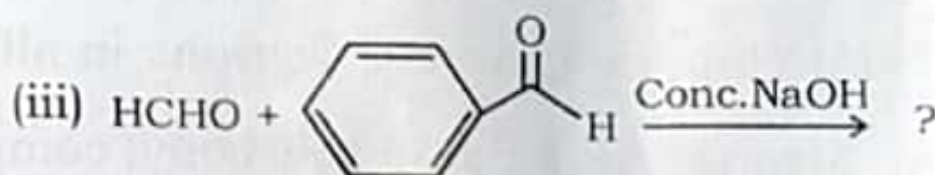
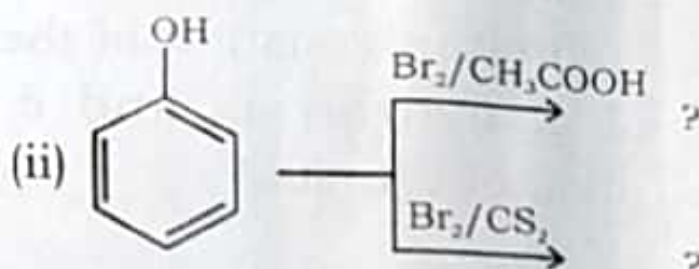
(Attempt any **three** Questions in all)

5. (a) Arrange the following carbonyl compounds in increasing order of their reactivity towards nucleophilic addition reaction and offer explanation ?



- (b) Complete the following reactions and mention 'Name reaction' if any ?

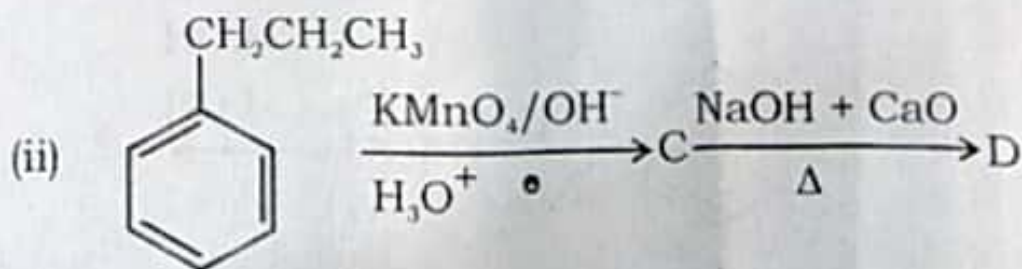
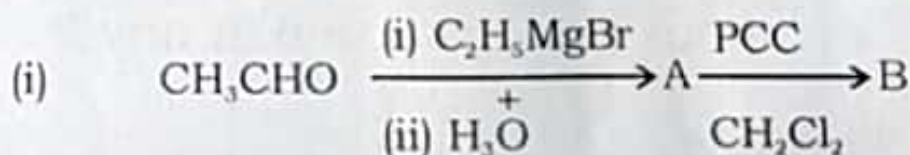




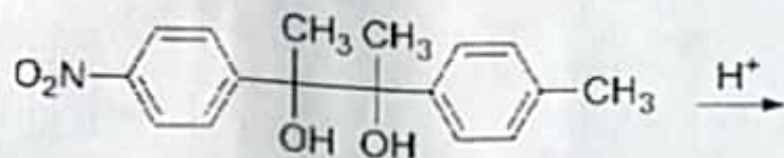
(c) During nitration of benzene with mixture of concentrated nitric acid and concentrated sulphuric acid, nitric acid acts as a base. Explain.

(d) P-Nitrochlorobenzene reacts more easily with aqueous KOH than chlorobenzene, explain with mechanism. 4,4,2,2.5

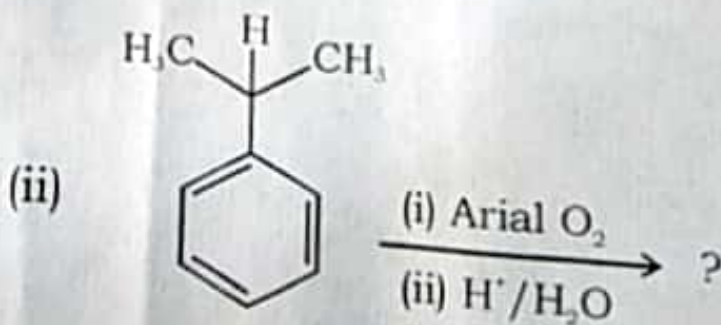
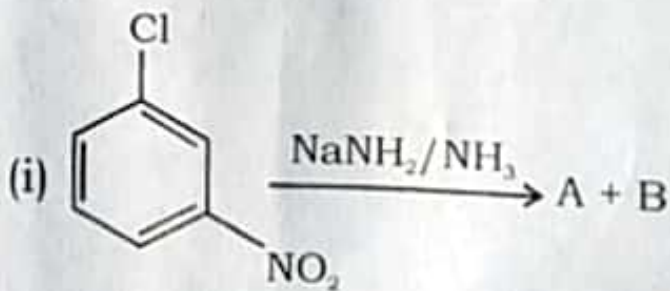
6. (a) Complete the following reactions :

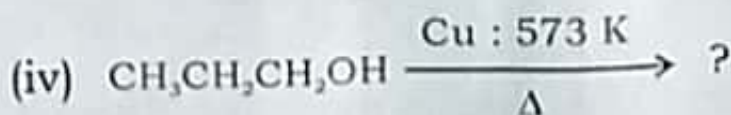
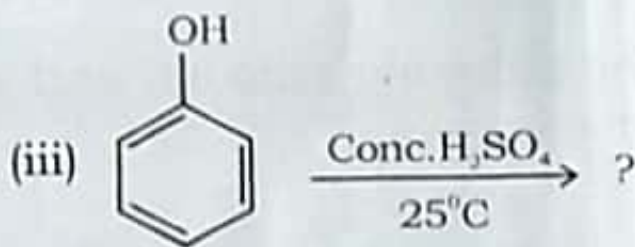


- (b) Explain base catalysed hydrolysis of ethyl acetate.
- (c) Name the following reaction and give its mechanism.

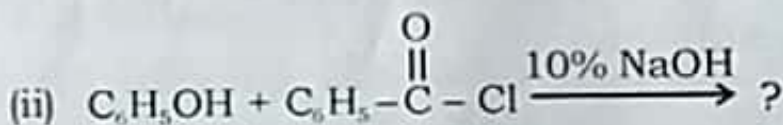
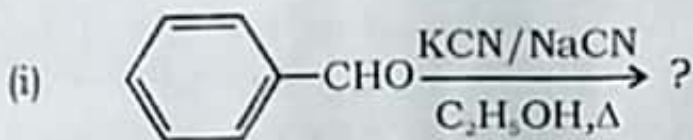


- (d) Benzyl chloride is more reactive than aryl chloride towards nucleophilic aromatic substitution. Why?
7. (a) Give S_N2 mechanism for alkyl halide by taking suitable examples and discuss the stereochemistry of the product so formed.
- (b) Predict the product of the following reactions.





(c) Complete the following reactions with mechanism.



4.5,4,4

8. Short notes (any **three**):

4.5,4,4

(a) Cannizzaro reaction

(b) Wittig reaction

(c) Gattermann Koch reaction

(d) Reimer Teiman reaction