Sr. No. of Question Paper : 1373   C

Unique Paper Code   : 32171301

Name of the Paper   : Inorganic Chemistry II : s- and p-Block Elements

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

Semester   : III

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 **five** questions in all. Question number **1** is compulsory.

3. **All** questions carry equal marks.

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

P.T.O.

(a) In spite of the ring strain in P_4 molecule, white phosphorus is stable relative to P_2.

(b) No reductant is required for the extraction of metals from HgO and Ag_2O.

(c) Helium and Neon do not form clathrate compounds.

(d) Carbon shows much greater tendency for catenation in comparison to silicon and nitrogen.

(e) The colour of halogens deepens down the group.

(f) Lithium forms predominantly the monoxide, sodium forms peroxide whereas potassium, rubidium and cesium form superoxides.

(g) Ionisation enthalpies of group 13 elements show irregular trends.

(3×5)

2. (a) Name the hydrides of group 15 elements and discuss the variation in their properties with reference to :

   (i) Basic. character

   (ii) Thermal stability

   (iii) Reducing character

(b) Carbon is capable of reducing all metal oxides provided the temperature of reduction is sufficiently high, however the use of carbon as reducing agent becomes impractical for metal oxides towards the bottom of Ellingham diagram. Comment and also explain why most of the lines slope upwards in the Ellingham diagrams.

(c) Draw the structure of diborane and discuss the bonding involved using molecular orbital theory. Also, give experimental evidences in support of the structure. (4;5,6)

3.   (a) What is diagonal relationship? Giving at least three examples explain how boron resembles silicon.

    (b) Give the oxidation sates of sulphur in Caro's acid and Marshall's acid. Draw their structures and write one reaction by which both can be differentiated.

    (c) Arrange the following in the increasing order of their acidic strength and Justify your answer.

       (i) H_3PO_4, H_3PO_3, H_3PO_2

       (ii) HBr, HI. HCl, HF

       (iii) $HClO$, $HClO_3$, $HClO_2$, $HClO_4$ (4,5,6)
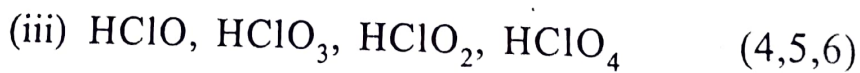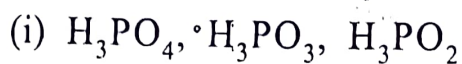
4.   (a) Draw and discuss the structure of P_4O_{10} and write the mechanism for its hydrolysis.

(b) Discuss the structure of 3-dimensional silicates with reference to zeolites and their application as ion exchanger.

(c) Comment on any **three** :

(i) XOX bond angle in Cl_2O is greater than that in F_2O.

(ii) Cesium iodide is much less soluble in water than Cesium fluoride, but Lithium flouride is less soluble than Lithium iodide.

(iii) Solubility of sulphates of alkaline earth metals decreases whereas it increases for their hydroxides on descending the group.
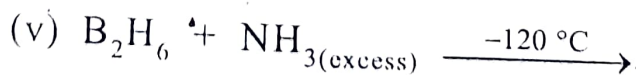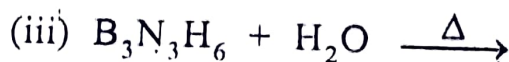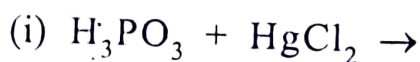
(iv) Chlorine has greater electron gain enthalpy than fluorine, yet fluorine is a stronger oxidizing agent.

(v) Thallium doesn't exist in (III) oxidation state, yet TII_3 exists. (4,5,6)

5. (a) Explain the dissimilarities between the two allotropic forms of carbon, namely graphite and diamond.

(b) Complete and balance the following equation : **(any four)**

(i) $H_3PO_3 + HgCl_2 \rightarrow$

(ii) $nPCl_5 + nNH_4Cl \xrightarrow{120-150\ °C}$

(iii) $B_3N_3H_6 + H_2O \xrightarrow{\Delta}$

(iv) $BCl_3 + LiAlH_4 \xrightarrow{ether}$

(v) $B_2H_6 + NH_{3(excess)} \xrightarrow{-120\ °C}$

(vi) $SiH_4 + AgNO_3 + H_2O \rightarrow$

(c) Draw the structure of **any three** :

    (i) Basic beryllium nitrate

    (ii) Mg-EDTA complex

    (iii) iodine heptafluoride

    (iv) 2,2,2-cryptand   (5,4,6)

6. (a) Discuss at least three points of similarities between halogens and pseudohalogens.

(b) Alkaline earth metals are harder, denser and have high melting points as compared to alkali metals. Explain.

(c) Write short notes on : **(any three)**

    (i) Cyanide Process

    (ii) Zone refining

    (iii) Interhalogen compounds

(iv) Solutions of alkali metal in liquid amm

(3,

Sr. No. of Question Paper : 1419   **C**

Unique Paper Code   : 32171303

Name of the Paper   : Chemistry C-VII Physical Chemistry III: Phase Equilibria and Electrochemical Cells

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

Semester   : III

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 **six** questions in all, selecting at least **two** questions from each section.

3. Question number **1** is compulsory.

4. Use of scientific calculator, log tables and graph paper is permitted.

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ and } 1 \text{ F} = 96500 \text{ C mol}^{-1}$$

$$E^0_{Cd^{2+}|Cd} = -0.403 \, V \; ; \; E^0_{I^-|AgI|Ag} = -0.1522 \, V; \; E^{\ominus}_{Fe^{2+}|Fe} = -0.44 \, V;$$

$$E^{\ominus}_{Fe^{3+}|Fe} = -0.036 \, V; \; E^{\ominus}_{Fe^{3+},Fe^{2+}|Pt} = 0.771 \, V; \; E^{\ominus}_{Cr^{3+}|Cr} = -0.74 \, V$$

$$E^{\ominus}_{Cd^{2+}|Cd} = -0.40 \, V; \; E^{\ominus}_{Cl_2|Cl^-} = 1.3595 \, V; \; E^{\ominus}_{Cu^{2+}|Cu} = 0.337 \, V; \; E^{\ominus}_{Ag^+|Ag} = 0.799 \, V$$

P.T.O.

1. Answer any **five** questions given below :

(i) How does the addition of naphthalene affect the CST of the phenol-water system at constant pressure. Explain giving reason.   (3)

(ii) Azeotropic mixtures have definite composition and definite boiling points yet they are not compounds. Explain.   (3)

(iii) Show that it is not possible to have more than three phases in equilibrium with each other in a one component system. What is the number of degrees of freedom when two phases are present?   (3)

(iv) Enthalpy of chemical adsorption of H_2 on the surface of Nickel is slightly positive yet the adsorption is spontaneous. Explain.   (3)

(v) Given the $E°$ values for the electrodes $Fe^{2+}(aq)|Fe(s)$ and $Pt(s)|Fe^{3+}(aq), Fe^{2+}(aq)$ as -0.44 V and $+0.77$ V respectively, calculate the $E°$ value for the electrode $Fe^{3+}(aq)|Fe(s)$.   (3)

(vi) How can liquid junction potential in a concentration cell be eliminated? Explain giving examples. (3)

(vii) Why can't we use a Voltmeter for determining the emf of a galvanic cell? (3)

SECTION A

2. (i) Find the number of components in the following cases :

   (a) $HCl(g)$ and $NH_3(g)$ in equilibrium with $NH_4Cl(s)$ when the equilibrium is approached by starting with HCl and NH_3 only.

   (b) KCl-KBr-H_2O system. (4)

   (ii) Derive the Duhem-Margules equation from Gibbs-Duhem equation for a binary system. (4)

(iii) On the basis of the critical temperatures, T_c of the gases given below, predict and explain which of the following gases will exhibit maximum adsorption on 1 g of charcoal at room temperature.   (4)

Gas	CO_2	NH_3	H_2
T_c/ K	304	405	33

3. (i) Derive the relation between the number of phases (P), components(C) and degrees of freedom (F) for a non-reactive system in which one component is present in all but one phases, and another one is present in only two phases. Rest of the components are present in all the phases.   (4)

(ii) Metals X and Y exhibit a simple eutectic diagram. Following table gives the break and halt points for various mixtures of X and Y.

Mass % of Y	0	20	40	50	70	85	100
Break temp./°C	800	600	400	-	415	500	600
Halt temp. /°C	350	350	350	350	350	350	350

Draw the phase diagram and label all the regions.

What is the maximum percentage of Y that can be recovered by crystallization of a mixture containing 85% of Y? (4)

(iii) What is the basic principle underlying steam distillation? A substance X, immiscible with water is distilled using this method. Derive an expression to calculate the relative mass of substances in the vapour phase in terms of their molar mass and vapour pressure. (4)

4. (i) With a suitable derivation, show that a multistage solvent extraction is more efficient than a single stage extraction using the same amount of solvent. (4)

(ii) To 100 mL of an aqueous solution of aspirin with concentration 3g / L, 50 mL of ether were added. The mixture was shaken and allowed to

equilibrate at 293 K. The distribution coefficient of aspirin between ether and water is 5.9.

(a) How much aspirin remains unextracted in the aqueous phase?

(b) If instead of 50 mL ether, the extraction is carried out with two successive 25 mL portions of ether, how much aspirin remains unextracted?   (4)

(iii) Discuss how the extent of adsorption varies on (i) increasing the surface area per unit mass of adsorbent (ii) increasing the temperature of the system and (iii) increasing the pressure of the gas?   (4)

5.   (i) Show that in a binary solution if one component behaves ideally then the other also does so.

                                                      (4)

(ii) At 353 K, the vapour pressures of pure ethylene bromide and propylene bromide are 22.93 and

16.93 kPa, respectively, and these compounds form a nearly ideal solution. A mixture of 3 mol of ethylene bromide and 2 mol of propylene bromide is contained in a cylinder with a piston. Slowly the pressure is decreased.

(a) Calculate the pressure at which the first bubble of vapour is formed.

(b) How many moles of each compound is present in this bubble?

(c) What is the composition of last droplet?

(4)

(iii) Define Critical solution temperature (CST). With the help of a suitable diagram, describe the sequence of steps that take place when the composition of a mixture of partially miscible liquids exhibiting lower C.S.T is varied at room temperature. Discuss with respect to the number of components, number of phases and degrees of freedom.   (4)

SECTION B

6.   (i) Construct a cell using the standard reduction potential values of the two half-cell reactions given.

$$Cr^{3+} + 3e^- \rightleftharpoons Cr$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$$
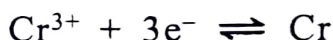
For the cell write (a) the cell reaction (b) Nernst equation.

Calculate the maximum work that can be obtained from the cell under the standard conditions.

(4)

  (ii) The potential of the cell $Cd|CdI_2(a_2)|AgI(s)|Ag(s)$ is 0.286 V at 25°C. Calculate the mean ionic activity of the ions in solution and the activity of the electrolyte.

(4)

  (iii) Derive Langmuir adsorption isotherm. Show that when a diatomic gas adsorbs as atom on the surface of a solid, the Langmuir adsorption isotherm becomes

$$\theta = \frac{(K.p)^{\frac{1}{2}}}{(1+K.p)^{\frac{1}{2}}}$$

where K is the equilibrium constant, p is the pressure and θ is the surface coverage. (4)

7.   (i) Differentiate between Galvanic and electrolytic cells using appropriate diagrams. (4)

(ii) Calculate the liquid junction potential (E_{ljp}) associated with the following cell if the transference number of H^+ is 0.83.

Ag(s), AgCl(s), HCl(m_1, γ_1): HCl(m_2, γ_2), AgCl(s), Ag(s)
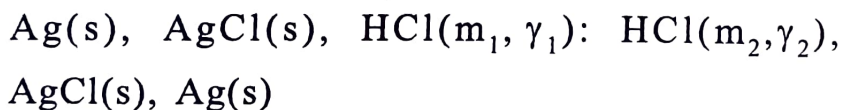
$m_1=1.0$ mol kg^{-1}; $\gamma_i = 0.809$; $m_2 = 0.05$ mol kg^{-1}; $\gamma_2 = 0.830$ (4)

(iii) How can the ionic product of water be determined using an electrochemical cell? Explain with the cell used, its reactions and the Nernst equation. (4)

8. (i) For the cell $Pt|H_2(g,1atm)|HBr(aq)|AgBr(s)|Ag(s)$

(4)

$$E^0 \text{ cell/V} = 0.07131 - 4.99 \times 10^{-4} \, (T/K - 298) - 3.45 \times 10^{-6} \, (T/K - 298)^2.$$

Evaluate change in standard reaction Gibbs energy, enthalpy and entropy at 298 K.

(ii) For the cell reaction,   (4)

$$2Fe^{3+} (aq) + Fe(s) \rightleftharpoons 3Fe^{2+}(aq)$$
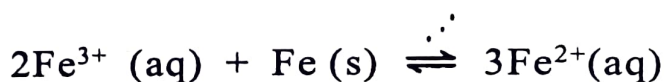
Construct two different galvanic cells using the following three half cells and calculate the standard cell potential for each of these cells. Compare the two cell potential values and comment on the result obtained.
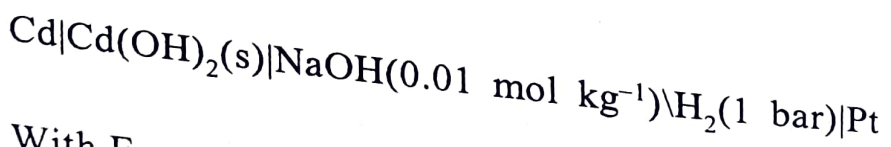
Given :

$Fe^{2+} + 2e^- \rightleftharpoons Fe$ $E^{\theta}_{Fe^{2+}\backslash Fe} = -0.44 \, V$

$Fe^{3+} + 3e^- \rightleftharpoons Fe$ $E^{\theta}_{Fe^{3+}\backslash Fe} = -0.036 \, V$

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^{\theta}_{Fe^{3+},Fe^{2+}|Pt} = 0.771 \, V$

(iii) Which of the following represents the variation of physical adsorption with 4 temperature? Explain your answer.

(4)

9.   (i) Given the cell,

$$Cd|Cd(OH)_2(s)|NaOH(0.01 \text{ mol kg}^{-1})\backslash H_2(1 \text{ bar})|Pt$$
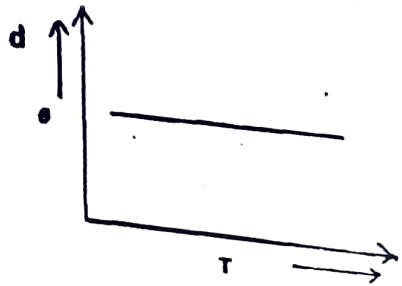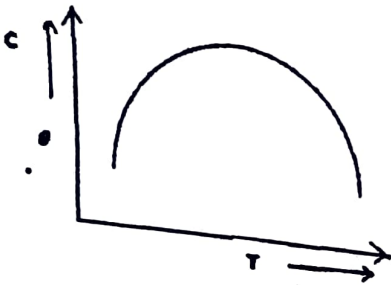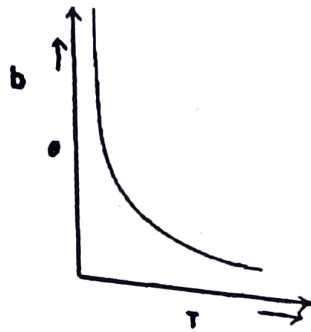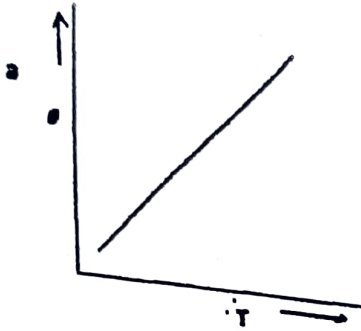
With $E_{cell} = 0$ V. at 298 K. Calculate the solubility product of $Cd(OH)_2$.

(4)

(ii) What are potentiometric titrations? Write the advantages of potentiometric titrations over conventional volumetric titrations.

(4)

(iii) Ascertain whether the following reaction will proceed in the (Vward or backward direction giving reasons.

$$2Fe^{2+} + Cl_2 \rightleftharpoons 2Fe^{3+} + 2Cl^-$$ (2)
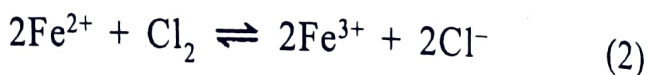
(iv) Can a copper spoon be used to stir a solution of silver nitrate? Give reason. (2)

[This question paper contains 8 printed pages.]

Your Roll No...............

Sr. No. of Question Paper : 1401   C

Unique Paper Code   : 32171302

Name of the Paper   : Organic Chemistry – II.
                           (Oxygen Containing Functional
                           Groups)

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

Semester   : III

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 **five** questions in all.

1. (a) An organic compound A $(C_5H_{10}O_2)$ on reduction with lithium aluminium hydride $(LiAlH_4)$ forms organic compounds B (C_3H_8O) and C (C_2H_6O). B on oxidation followed by heating with calcium oxide gives D $(C_5H_{10}O)$. C on reaction with NaOH/
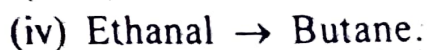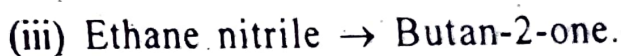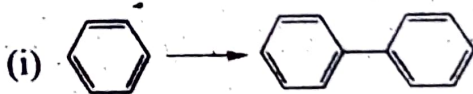
P.T.O.

b forms E and a yellow precipitate of CHI_3. Identify the organic compounds A, B, C, D and E. Give the name reaction involved during the conversion of C to E along with mechanism.

(b) Identify A having molecular formula $(C_{14}H_{12}O_2)$ in the following reaction. Give the name of the reaction and mechanism involved. Write down the role of cyanide ion in the following reaction :

(9,6)

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

(i)

(ii) Propanal → Propan-2-ol.

(iii) Ethane nitrile → Butan-2-one.

(iv) Ethanal → Butane.

(b) Identify A and B in the following reaction and justify your answer :

$$CH_3CH_2OH \longrightarrow \begin{cases} \xrightarrow[100^\circ C]{Conc.\ H_2SO_4} A \\[2ex] \xrightarrow[200^\circ C]{Conc.\ H_2SO_4} B \end{cases} \qquad (9,6)$$

(a) Carry out the synthesis of any three following compounds either from **EAA** (Ethyl acetoacetate) or DEM (Diethyl malonate) :

    (i) Methylsuccinic acid

    (ii) 4-Oxopentanoic acid

    (iii) Crotonic acid

    (iv) Antipyrine

(b) Differentiate between the following (give visible test only) and write down the reaction involved (any three) :

    (i) Acetaldehyde and acetophenone

    (ii) Ethanol and propan-2-ol

    (iii) Benzoic acid and p-cresol

    (iv) Ethylchloride and chlorobenzene   (9,6)

4. (a) Give reason for the following (any four) :

(i) The rate of hydrolysis of the carboxylic acid derivatives is:

$$CH_3COCl > (CH_3CO)_2O > CH_3CONH_2$$

(ii) S_N1 reactions are accompanied by racemization, while S_N2 reactions result in the inversion of the configuration.

(iii) 2,2-Dimethylpropanal gives Cannizzzaro's reaction, while 2-methylpropanal does not.

(iv) Carboxylic acid does not form oxime though they have carbonyl group ($>C=0$) in their structure.

(v) Malonic acid and β-keto carboxylic acid decarboxlate readily on heating 200°C.

(vi) Ketones cannot be prepared from acid chloride and RMgX although they can be prepared from acid chloride and R_2Cd/R_2CuLi.

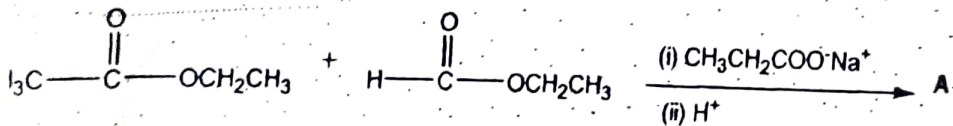(b) Prepare the following organic compound using Wittig reaction :
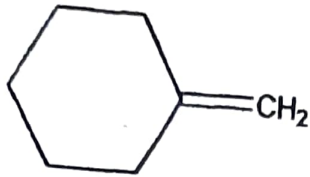
(12,3)

5.

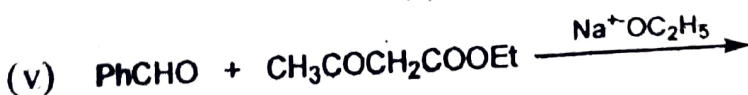(a) Identify the organic compounds (A, B) and explain their formation with the help of mechanism.
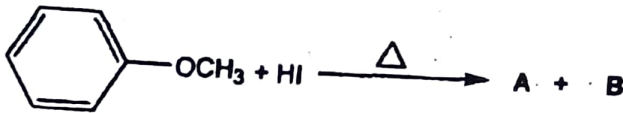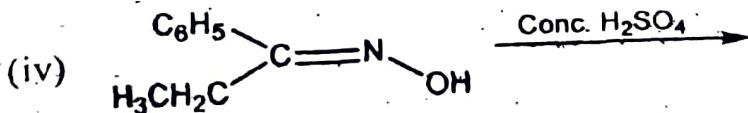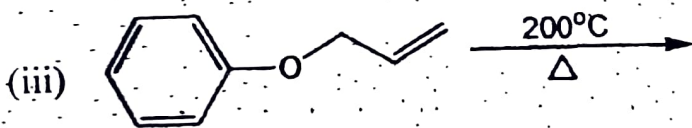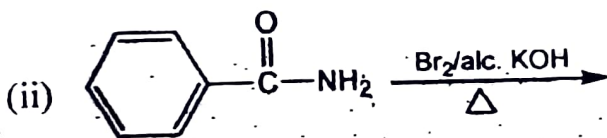

OR

Identify the organic compound (A) formed in the following reaction and explain its formation with the help of mechanism.

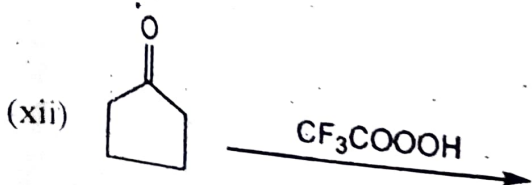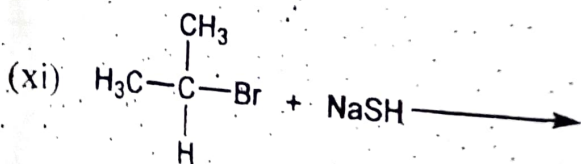(b) Benzene on reaction with propene in the presence of a Lewis acid forms A (C_9H_{12}). A on aerial oxidation forms B ($C_9H_{12}O_2$). B on acidic hydrolysis gives C (C_6H_6O) and D (C_3H_6O). Identify the organic compounds A, B, C and D.

P.T.O.

(c) (i) Write down the products obtained on heating α, β and γ-hydroxycarboxylic acid separately.

(ii) Tertiary alkyl halides are not good substrates for nucleophilic substitution reactions. Explain.

(iii) p-Chlorotoluene on reaction with NaNH₂ in liq. NH₃ forms m-toluidine along with p-toluidine. Explain.   (4,2,3,3,3)

6. Complete the following reactions :

(i) $CH_3CH_2COOH \xrightarrow{Cl_2/Red\ P}$

(ii) $\xrightarrow[\Delta]{Br_2/alc.\ KOH}$

(iii) $\xrightarrow[\Delta]{200°C}$

(iv) $\xrightarrow{Conc.\ H_2SO_4}$

(v) $PhCHO + CH_3COCH_2COOEt \xrightarrow{Na^+OC_2H_5}$

(vi) $H_3C-\overset{\overset{O}{\|}}{C}-CH_2CH_3 \xrightarrow{\text{Zn-Hg/HCl}}$

(vii)

$\xrightarrow{\text{CH}_3\text{OH/H}^+}$

(viii) $CH_2\overset{\text{COOC}_2\text{H}_5}{\underset{\text{COOC}_2\text{H}_5}{<}}$ + $\overset{\text{H}_2\text{N}}{\underset{\text{H}_2\text{N}}{>}}C=O \xrightarrow{\Delta}$

(ix) $CH_3CH_2CH_2CH_2OH \xrightarrow{\text{PCC}}$

(x) $CH_3CH_2CHO \xrightarrow[\text{(ii) } \Delta]{\text{(i) Dil. NaOH}}$

(xi) $H_3C-\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{H}{|}}{C}}-Br$ + NaSH $\longrightarrow$

(xii)

$\xrightarrow{\text{CF}_3\text{COOOH}}$

(xiii) $H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-Br$ + $CH_3O^-Na^+$ ⟶

(xiv) $\underset{\displaystyle CH_2COOH}{\overset{\displaystyle CH_2COOH}{|}}$ $\xrightarrow{\Delta}$

(xv) $\underset{\displaystyle CHO}{\overset{\displaystyle CHO}{|}}$ $\xrightarrow{\text{Conc. NaOH}}$
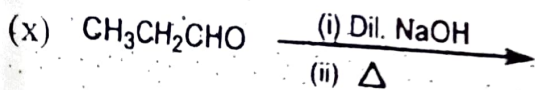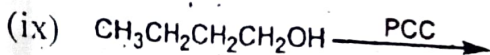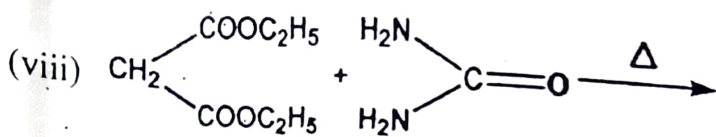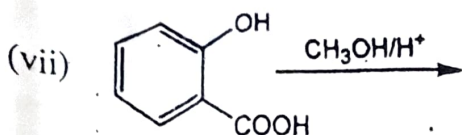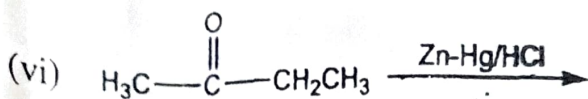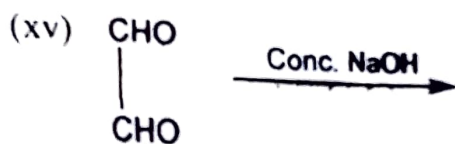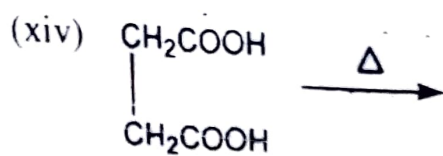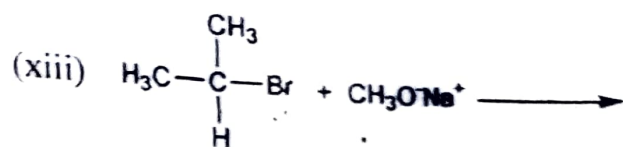
Sr. No. of Question Paper : 1005   C

Unique Paper Code   : 32171501

Name of the Paper   : Organic Chemistry IV: Biomolecules

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

Semester   : V

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 any **6** questions. **All** Questions carry equal marks.

1. (a) (i) β- D-Glucose and α-D-Glueose have different specific rotations. When either anomer is dissolved in water, their rotations change until a fixed value results. Name the term used to describe this change and discuss the mechanism. (3)

     (ii) Draw Fisher projection of β-D-glucose, convert it to Haworth structure and then to the chair conformation. (3)

(b) A pentapeptide X having an empirical composition, Lys, Phe, Thr, Leu, Asp, gave DNP-Thr on treatment with DNFB followed by hydrolysis. Treatment of X with Carboxypeptidase released Asp. Treatment of X with Trypsin gave a tripeptide, (Lys, Leu, Thr) and a dipeptide (Asp, Phe). Elucidate the sequence of amino acids in X. What products are obtained on treatment of X with Chymotrypsin?   (6.5)

2.   (a) Differentiate between nucleosides and nucleotides. Draw the structure of Cytidine.   (4)

(b) Define acid value and saponification value of an oil. Calculate the saponification value of glyceryl tripalmitate.   (4.5)

(c) When D-Glucose is treated with dilute aqueous alkali, a mixture of D-Mannose, D- Fructose and D-Glucose is obtained. Explain the mechanism of this reaction. What is the name of this reaction?   4

3.   (a) Outline significant differences between catabolism and anabolism.   (3)

(b) Which steps in glycolysis consume ATP and which ones produce ATP? How many molecules of ATP are obtained from each molecule of glucose that is metabolized to pyruvate?   (3.5)

(c) What is transcription. Explain.   (6)

4. (a) Give the structure of disaccharide maltose. How was the nature of linkage between its two monosaccharide units established? (3)

    (b) Give the reaction catalysed by the following enzymes. To which class of enzymes do they belong according to enzyme commission

        (i) Phosphofructokinase

        (iii) Fumarase (4)

    (c) Explain the principal of electrophoresis. How can it be used to separate a mixture of Alanine, Lysine and Glutamic acid? (3.5)

    (d) Give the structure of NAD+. (2)

5. (a) Explain oxidative rancidity in oils and fats giving an example. Suggest a method to prevent it. (4)

    (b) Explain the term hardening of oils by taking a suitable example. (4)

    (c) Explain the process of replication? (4.5)

6. (a) Discuss the effect of substrate concentration on the activity of an enzyme. (4.5)

    (b) Give the products from the reaction of methyl α-D-Glucopyranoside with HIO_4. (2)

(c) Discuss the various steps involved in the TCA cycle giving the names of enzymes and structures of intermediates. (6)

7. (a) (i) Explain the use of dicyclohexylcarbodiimide (DCC) in peptide synthesis. Use chemical reactions to illustrate. (3)

     (ii) Outline the synthesis of either Methionine or Proline using any method. (3.5)

(b) A carbohydrate **X** with molecular formula $C_{12}H_{22}O_{11}$ gives a positive test with Benedict reagent, it forms an osazone and undergoes mutarotation. Hydrolysis with aqueous acids or by emulsin produces only D-Glucose. Methylation of X gives an octamethyl derivative which on hydrolysis affords 2,3,4,6 tetra O-methyl D-Glucose and 2,3,4 tri-O-methyl D-Glucose. Workout the structure of X. (6)

8. (a) Give the reactions involved in Killiani -Fischer synthesis starting with D-arabinose.
What is the stereochemical relationship between the aldohexoses obtained? (4)

(b) What is allosteric inhibition? Explain using an example. (4.5)

(c) What are the different types of RNA? Explain the role of any one of them. (4)

Your Roll No...............

Sr. No. of Question Paper : 1041   **C**

Unique Paper Code   : 32171502

Name of the Paper   : Physical Chemistry V: Quantum Chemistry & Spectroscopy

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

Semester   : V

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 **six** questions in all, **three** questions each from Sections **A** and **B**.

3. Attempt all part of a question together.

4. **All** questions carry equal marks.

5. Use of a non-programmable scientific calculator is allowed.

P.T.O.

Physical constants

Atomic mass unit	$=1.66 \times 10^{-27}$ kg
Planck's constant	$= 6.626 \times 10^{-34}$ J s
Velocity of Light	$= 3 \times 10^{8}$ m s^{-1}
Boltzmann constant	$= 1.381 \times 10^{-23}$ J K^{-1}
Mass of Electron	$= 9.1 \times 10^{-31}$ kg
Avogadro's number	$= 6.023 \times 10^{23}$ mol^{-1}
Nuclear magneton	$= 5.05 \times 10^{-27}$ J T^{-1}
Bohr magneton	$= 9.274 \times 10^{-24}$ J T^{-1}

SECTION A

(Quantum Chemistry)

1. (a) Discuss the postulates of quantum mechanics.

   (b) Write the complete Hamiltonian operator for Li atom explaining all the terms. Write the modified Hamiltonian operator after applying Born Oppenheimer approximation.

   (c) Show that the eigenvalues of a Hermitian operator are always real. (4.5,4,4)

2. (a) A particle of mass m, in a one-dimensional box of length a can be represented by the function,

$$\psi_n = \sin\frac{n\pi x}{a} \quad (n = 1,2,3...)$$ Normalize the given function ψ_n and find whether it is an eigen function of (i) $\widehat{P_x}$ (ii) $\widehat{p_x^2}$.

(b) A particle of mass, m, in a one-dimensional box of length a can be represented by the following normalized trial wave function where N is the normalization constant.

$$\psi_{trial} = N\{x(a-x)\}$$

(i) Calculate the expectation value of energy, (E), of this particle in the ground state using the trial wave function.

(ii) Compare this energy with the actual energy. Calculate the percentage error.

(iii) Is the trial wave function acceptable? Explain on the basis of variation theorem.

(4.5,(4,2,2))

3. (a) Plot the radial functions and radial probability distribution functions for an electron in hydrogen atom for all wave functions having n = 2. Write the number of nodes in each case.

(b) Evaluate the expectation value of the radius, $\langle r \rangle$, at which the electron in the ground state of Hydrogen atom (Z=1) is found. Given the wave function for this state is

$$\Psi_{1,0,0} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_o} \right)^{\frac{3}{2}} e^{\frac{-Zr}{a_o}} \quad \text{where } a_o \text{ is the Bohr radius}$$

and $\int_0^\infty r^n e^{-ar} \, dr = \frac{n!}{a^{(n+1)}}$.

(c) Giving reason, state which of the following are acceptable wave functions in the indicated interval.

(i) sin x $(0, 2\pi)$

(ii) e^{-x} $(-\infty, \infty)$

(iii) $\frac{1}{x}$ $(0, \infty)$

(iv) $\sin^{-1} x$ $(-1, 1)$ $(4.5,4,4)$

4. (a) By applying the procedure of separation of variables on the following Schrodinger equation for an electron in a hydrogen atom, derive three equations, one dependent on variable, r, second dependent on variable, θ and third dependent on variable, ϕ. In this equation $\psi(r, \theta, \phi)$ is the function of three independent variables r, θ and ϕ. Considering $\psi(r, \theta, \phi) = R(r) * \Theta(\theta) * \Phi(\phi)$,

$$\left[-\frac{h^2}{8\pi^2 \mu r^2}\left\{\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) + \frac{1}{\sin^2\theta}\frac{d^2}{d\varphi^2}\right\} - \frac{z\,e^2}{r}\right]\psi = E\psi$$

(b) Set up the Hamiltonian operator for a particle oscillating about a mean position (a simple harmonic oscillator). Explain the significance of zero-point energy of a simple harmonic oscillator.

(c) Starting from the expression for total energy of a rigid rotator, setup the Schrodinger equation for the system in Cartesian coordinates.

(4.5,4,4)

SECTION B

(Spectroscopy)

5. (a) Chlorine gas is microwave and infra-red inactive but Raman active. Explain.

    (b) How will the microwave spectrum of HCl^{35} change if Cl^{35} is replaced by Cl^{37}?

    (c) The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines 0.71433 cm^{-1} apart. Calculate the rotational constant, B, the moment of inertia and bond length of the molecule.   (4.5,4,4)

6. (a) How do the P, Q and R branches arise in the Vibrational-Rotational spectrum. Why is Q branch not observed for most of the heteronuclear diatomic molecules?

    (b) What is the ratio of the number of protons in each spin state at temperature 300 K, given that the ^1H NMR spectrometer is operating at 60MHz and $g_n = 5.585$ for the ^1H nucleus.

(c) The fundamental and first overtone transitions of $^{14}N^{16}O$ are centered at 1876.06 cm^{-1} and 3724.20 cm^{-1}, respectively. Calculate the equilibrium vibration frequency and anharmonicity constant.

(4.5,4,4)

7. (a) A molecule AB_2 has the following Infrared and Raman spectra :

v (cm^{-1})	Infrared	Raman
519	Active (PQR)	Active (Polarized)
1151	Active(PQR)	Active (Polarized)
1367	Active(PQR)	Active (Depolarized)

Predict the geometry of the molecule with justification and assign the observed wavenumbers to the specific vibration mode.

(b) What is Raman effect? Explain the origin of Stokes and Anti-Stokes line.

(c) Arrange the following groups in increasing order of their absorption frequencies: Give Justification

(i) CF, CCl, CBr, CH

(ii) C-C, C=C, C≡C   (4.5,4,4)

8.   (a) A ^{1}H NMR spectra of an organic compound with the molecular formula $C_3H_6Br_2$ gives three signals (p1, p2 and p3) with their respective intensity ratios as follows: 1(sixtet): 2 (doublet): 3(doublet) (δ values are in the order p1>p2> p3). Write the probable structure and justify your answer.

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

     (i) Difference between internal conversion and intersystem crossing.

     (ii) Factors affecting the intensity of transition.

     (iii) Larmor precession.   (4.5,4,4)

[This question paper contains 6 printed pages.]

Your Roll No...............

Sr. No. of Question Paper : 1038   **D**

Unique Paper Code   : 2172011102

Name of the Paper   : DSC 2-Basic Concepts and Aliphatic Hydrocarbons (Organic Chemistry-1)

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

Semester   : I

Duration : 3 Hours   Maximum Marks : 90

Instructions for Candidates

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

2. Attempt any **SIX** questions.

3. All questions carry **15** marks.

4. This paper contains 8 questions.

1. (i) Acid catalysed dehydration of Neopentyl alcohol gives two alkenes A and B as major and minor product(s). Identify the two alkenes A and B and explain the mechanism involved.

P.T.O.

(ii) Out of following, which is more stable and why?

(a) O_2N—⬡—$\overset{\ominus}{C}H_2$ H_3CO—⬡—$\overset{\ominus}{C}H_2$

(a)   (b)

(b) $C_6H_5CH_2^+$, $C_6H_5CH_2CH_2^+$
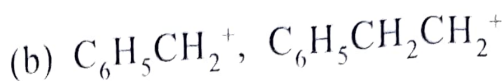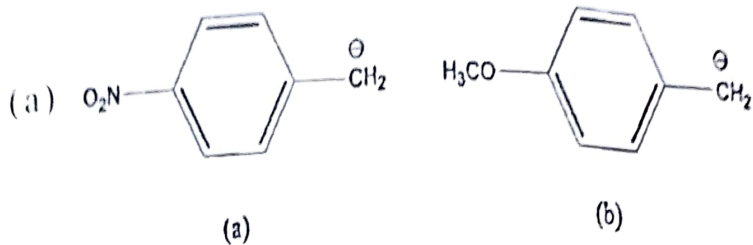
(iii) Define the terms racemic mixture and resolution of racemic mixture. Illustrate the chemical method for the resolution of a racemic mixture with an example.   (5,5,5)

2. (i) Write down the Fischer Projection of all the possible stereoisomers of 2,3-Dibromo pentane. Designate erythro and threo nomenclature to all the stereoisomers and assign absolute configuration (R/S) at each chiral centre.

(ii) (a) Give name and structure of one mcso compound. Meso compounds are optically active or inactive? Give reason in support of your answer.

(b) Indicate whether each of the following compound is E or Z
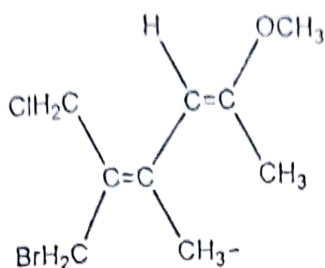
(iii) Give the Structure and hybridisation of Carbocation and Carbenes. (5,5,5)

3. (i) Draw all the conformations of cyclohexane and arrange them in order of increasing stability. Give reasons for stability order.
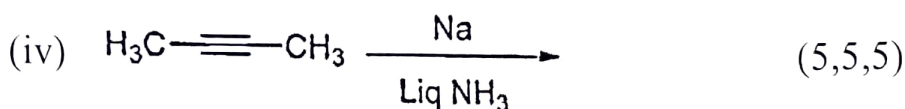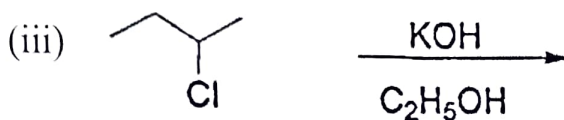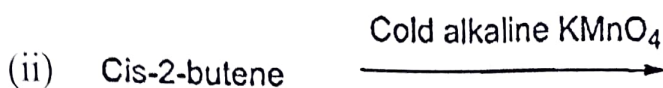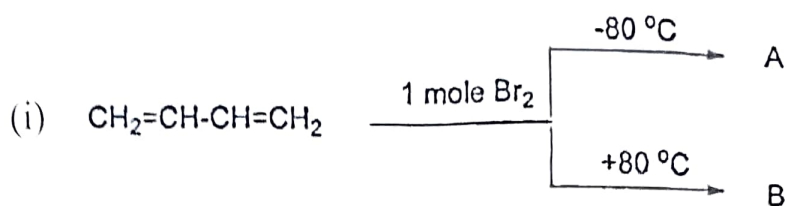
(ii) (a) "Staggered conformation of n-butane is more stable than Eclipsed". Explain with suitable example.

(b) Define plane polarised light and specific rotation.

(iii) Differentiate between enantiomers and diastereomers with example. Among these two, which can be easily separated and why?

(5,5,5)

4

4. Write the products with mechanism and appropriate stereochemistry wherever applicable : (Attempt any three)

(i) $CH_2=CH-CH=CH_2$ $\xrightarrow{\text{1 mole Br}_2}$

$\xrightarrow{-80\,°C}$ A

$\xrightarrow{+80\,°C}$ B

(ii) Cis-2-butene $\xrightarrow{\text{Cold alkaline KMnO}_4}$

(iii) [structure: 2-chlorobutane with CI] $\xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{KOH}}$

(iv) $H_3C-\!\!\!\equiv\!\!\!-CH_3$ $\xrightarrow[\text{Liq NH}_3]{\text{Na}}$ (5,5,5)

5. (i) Chlorine is more reactive while bromine is more selective in its reaction with Propane. Explain.

(ii) Calculate the percentage of isomers formed during the monobromination of 2,3-dimethylbutane. The relative reactivity for 1°, 2°, 3° hydrogens are 1, 82 and 1600, respectively.

(iii) Compare the reactivity of alkene and alkynes towards electrophilic addition reactions.

(5,5,5)

6.   Give reasons :

   (i) Propene reacts with HBr in presence of peroxide to give 1-bromopropane whereas in absence of peroxide it gives 2-bromopropane.

   (ii) Electromeric effect is temporary effect while Inductive effect is permanent effect.

   (iii) Bromination of trans-2-butene gives meso dibromo product while bromination of cis-2-butene gives racemic mixture?   (5,5,5)

7.   (i) Arrange the following in increasing order of acidity with giving suitable reasons-

      (a) Acetic acid, 1-chloro acetic acid and Propanoic acid.

      (b) Phenol, Ethanol. Acetic acid

   (ii) Define hyperconjugation. Explain on the basis of hyperconjugation, why 2,3-dimethyl but-2-ene is more stable than 2-methyl but-l-ene.

(iii) Vinyl chloride is less reactive than Allyl chloride towards nucleophilic substitution reactions.

(5,5,5)

8. Write short on the followings **(any three)**

(i) Wurtz reaction (with mechanism and limitations)

(ii) Saytzeff Vs Hofmann elimination

(iii) Baeyer's Strain Theory

(iv) Diels-Alder reaction $(5\times3=15)$

[This question paper contains 8 printed pages.]

Sr. No. of Question Paper : 1057   **D**

Unique Paper Code   : 2172011103

Name of the Paper   : DSC 3: Gaseous and Liquid
State (Physical Chemistry-I)

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

Semester   : I

Duration : 2 Hours   Maximum Marks : 60

Instructions for Candidates

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

2. Attempt **FOUR** questions in all. Question No. 1 is compulsory.

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

P.T.O.

4. Use of Scientific Calculator is permitted.

(R = 8.314 JK^{-1} mol^{-1} k = 1.38 × 10^{-23} JK^{-1}

N_A = 6.023 × 10^{23}mol^{-1})

1. Answer **any 5** of the following:

(a) The viscosity of liquids decreases while that of

gases increases with rise in temperature. Explain.

(3)

(b) Explain the effect of temperature and pressure on

collision number of a gas.   (3)

(c) Roughly sketch the Maxwell distribution curve for

the gas molecules in terms of molecular velocities.

Label both axes and explain the effect of

temperature on the distribution curve.   (3)

(d) The composition of gases in the earth's atmosphere varies with height. Explain. (3)

(e) Discuss the effect of detergent concentration on the surface tension of water giving graphical representation. Why surface tension becomes nearly constant at higher concentrations of detergent? (3)

(f) Explain the dependence of surface tension on temperature and why the surface 3 tension of a liquid becomes zero at its critical temperature.

(3)

2. (a) Describe the reasons for deviation of gases from ideal behaviour. Derive van der Waals equation of state for a real gas. (5)

(b) The coefficient of viscosity of CO_2 gas is 148 μP

at 20 °C. Calculate its collision diameter and mean

free path.   (5)

(c) Draw labelled diagram of P-V isotherms of CO_2.

Explain these isotherms and continuity of states.

                                                 (5)

3.   (a) Using the van der Waals equation of state, derive

the following universal relation:

$$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r}$$ (5)

(b) Calculate the fraction of methane gas molecules

at 27 °C and 1 atm possessing velocities between

450±10 m/s.   (5)

(c) Derive an expression for the coefficient of viscosity of a gas, η in terms of the mean free path, λ and show that η of a gas is dependent on temperature, but is independent of pressure.   (5)

4.   (a) Derive the expression: $P = P_0 \exp(-Mgh/RT)$. Explain the effect of temperature of the gas on the variation of pressure with height in the light of this equation.   (5)

(b) Determine the molar mass of a gas if its pressure falls to one-third of its value in a vertical distance of 4 meters at 27 °C.   (5)

(c) The values of critical constants of a gas are: $P_c = 45.6$ atm, $V_c = 0.0987$ dm^3 mol^{-1} and $T_c = 190.6$ K. Calculate the van der Waals constants and critical compressibility factor.   (5)

5. (a) What do you mean by vapour pressure of a liquid? Explain the effect of temperature on vapour pressure of liquid giving expressions. (5)

(b) The enthalpy of vaporization of cyclohexane at its boiling point 127 °C is 400 J/g. If it is to be distilled at 26 °C to what value must the pressure be reduced? (5)

(c) Calculate the surface tension of liquid benzene and the radius of the capillary tube, if the level of water and benzene rose in the capillary is 9.9 cm and 4.5 cm, respectively. Given surface tension of water at 20 °C = 72.75 dyne cm^{-1}, density of water = 998.2 kg m^{-3} and density of benzene = 900 kg m^{-3}. (5)

6. (a) Describing the origin of viscosity in liquids, define coefficient of viscosity. Write units of viscosity. Derive the expression for determination of viscosity of a liquid by using Ostwald's viscometer method.

    (5)

    (b) The viscosity of a liquid is 6×10^{-4} N s m^{-2} at 27 °C and 3×10^{-4} N s m^{-2} at 327 °C. Calculate the energy of activation of viscous flow assuming it to be constant over this temperature range.

    (5)

    (c) (i) The viscosity of glycerol is very high as compared to that of water. Explain. (2)

    (ii) Comment on the effect of addition of sucrose on the viscosity of water? (2)

(iii) Is it possible to liquefy an ideal gas? Explain.

(1)

Sr. No. of Question Paper : 1092

Unique Paper Code : 32177901

Name of the Paper : DSE: Novel Inorganic Solids

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

Semester : V

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 **FIVE** QUESTIONS in all.

3. **All** Questions carry equal marks.

1. (a) How zeolites are prepared using the sol-gel method? What are the advantages and disadvantages associated with this method?

    (b) What are Silver nanoparticles? Discuss one method of synthesis of Silver Nanoparticles in detail.

(c) Write a short note on liquid crystals and their applications.   (5×3=15)

2. (a) What are ceramics? Give their classification and applications in daily life.

(b) What are graphite intercalation compounds? How are they prepared? Explain with a suitable example.

(c) Discuss the conduction mechanism of conducting polymer polyparaphenylene. Also, give its applications.   (5×3=15)

3. (a) Illustrate the general characteristics of solid electrolytes. How are they classified? Give examples of each.

(b) Describe the working of a solid oxide fuel cell. What are its advantages and disadvantages? List the main applications of fuel cells.

(c) Describe the slow relaxation process of molecular magnets. Why are molecular magnets useful and specify in which areas are they potentially used?   (5×3=15)

4. (a) What are one-dimensional solids? Give examples and illustrate its electronic properties.

   (b) What are the properties of an ideal inorganic pigment? How will you distinguish dyes and pigments? Why do inorganic solids show color?

   (c) What is the fundamental principle of surface plasmon resonance? Comment upon the optical properties of nanoparticles and their applications.

$$(5 \times 3 = 15)$$

5. (a) What are quantum dots? Compare the band energies for a quantum dot nanocrystal and a bulk semiconductor.

   (b) Give the equation that relates the size of the crystallite in a solid to the broadening of a peak in a diffraction pattern. Mention the factors on which the ultimate resolution of SEM depends?

   (c) Explain the difference between the top-down and bottom-up approach for the fabrication of nanomaterials giving one example each.

$$(5 \times 3 = 15)$$

4

6. (a) Distinguish between static and dynamic self-assembly. What role does self-assembly play in the synthesis of nanomaterials?

   (b) What are the limitations of the Bake and Shake method? Suggest three different ways of overcoming these limitations.

   (c) Discuss the Dynamic Light Scattering (DLS) technique of characterization of nanomaterials.

   $(5\times3=15)$

7. (a) What is the conventional way of preparing solid $MgAl_2O_4$? Explain with the help of the mechanism. On the basis of it describe the Kirkendall effect.

   (b) How does the structure of Zirconia. ZrO_2 supports it to function as a solid electrolyte? Discuss in detail.

   (c) What are ion-exchange resins? How do they function? Give their classification. $(5\times3=15)$

[This question paper contains 8 printed pages.]

Sr. No. of Question Paper : 1189   C

Unique Paper Code   : 32177903

Name of the Paper   : DSE-2 Applications of
                             Computers in Chemistry

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

Semester   : V

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 **six** questions in all.

3. Question **1** is compulsory. Attempt any **five** questions out of remaining **six** questions.

4. Attempt all parts of the question together.

5. Use of calculator is allowed.

1. (a) Write the BASIC expression for the given algebraic expression **(any three)**

(i) $\nu = \dfrac{1}{2\pi c}\left(\dfrac{k}{\mu}\right)^{1/2}$

(ii) $r = \dfrac{k_1 k_2 I_a [A]}{k_2 [A] + k_3}$

(iii) $n = 2d \sin \theta / \lambda$

(iv) $K = Ae^{-E_a / RT}$

(b) Identify the valid and invalid numeric and string variables giving reason.

    (i) A12

    (ii) CLS

    (iii) IB$

    (iv) NUM 1

    (v) NAME$12

    (vi) BA_C1

(c) Write the full form of the following **(any three)**

    (i) VLSI

    (ii) VDU

    (iii) BIT

    (iv) CAD

(d) What is the purpose of the following Library functions? Explain each with example **(any three)**

(i) FIX

(ii) SQR

(iii) ABS

(iv) RND

(e) Identify the valid and invalid numeric and string constants giving reason.

(i) 16,000

(ii) "1A2378"

(iii) Rs. 1000

(iv) 12E-40

(v) "CHEMISTRY"

(vi) 148.62 (5×3)

2. (a) Convert the following numbers :

(i) $(10.625)_{10}$ to octal number

(ii) $(A12.21)_{16}$ to binary

(b) Write the correct BASIC command for the following statements

(i) Draw a box whose diagonal coordinates are (x_1, y_1) and (x_2, y_2)

(ii) Draw a semicircle of radius r and the center (x,y)

(iii) Locate the top right of screen and print "CHEMISTRY"

(iv) To create a window of (0,0) to (50,100) in SCREEN 2

(c) Write a program in BASIC to arrange given numbers in increasing order

3, 67, 8, 10, 85, 33, 17, 19, 99, 0   (4,4,4)

3.   (a) Find the errors in following programs and write correct form

(i) REM TO PRINT A MATRIX
FOR J=1 to 3
FOR I=1 to 3 STEP -1
READ A(I, J)
B(I, J)=A(I, J)+ 21 – J
PRINT B(J,I)
NEXT J
PRINT
NEXT I
DATA 1,2,3,4,5

(ii) REM To FIND ROOTS OF QUADRATIC EQUATION
INPUT A,B,C$
D=B^2-4AC

```
        IF D<0 THEN ELSE 10
10  E=SQR(D)
     R=-B+E/2*A
     S=-B-E/(2*A)
     PRINT "ROOTS ARE=";R,S
     PRINT "NO REAL ROOTS"
     END
```

(b) Explain the binary bisection method to solve the polynomial.

(c) Write a program in BASIC to find the root for the following equation using binary bisection method

$$x^4 - 2x^3 + 4x^2 - 6 = 0$$ (6,2,4)

4. (a) Write a program in BASIC to calculate multiplication of any two given matrices. Print all the three matrices.

(b) What is the output of following programs :

   (i) A$="DELHI UNIVERSITY"
        B$=LEFT$(A$,5)
        C$=RIGHT(A$,7)
        D$=MID$(A$,7,3)
        L=LEN(A$)
        PRINT B$, C$;
        PRINT L, D$

(ii)   READ A,B
      RESTORE
      READ C,D
      READ E,F,G,H
      PRINT A;B;C;D
      PRINT E,F,G,H
      DATA 3,5,7,8,9,12,15,18

(iii) PRINT STRING$(5,"*")
      For I= 2 to 4
      PRINT TAB(I);"*"
      NEXT I
      PRINT STRING$(5,"*")
      END   (6,6)

5.   (a) Write a program in BASIC to calculate sine of an angle by using series summation.

$$Sin\ x = \sum_{m=0}^{\infty} (-1)^m x^{2m+1}/(2m + 1)!$$

Value should be accurate till 4th decimal place.

(b) What is the difference between interpreted and compiled program? Explain each term giving suitable examples.

(c) Write a program in BASIC to fit λ_m and $\sqrt{c}$ to a straight line using least square fit and equation:

$\lambda_m = \lambda_m'' - k\sqrt{c}$ and calculate λ_m'' and k.

Concentration/M	17.2	10.8	2.6	1.3	0.8	0.2
	42.5	45.9	51.8	54.1	55.8	57.4
Molar conductance(Sm2/mol)						

Given that

$$slope = \frac{N\sum x_i y_i - \sum x_i \sum y_i}{N\sum x_i^2 - \sum x_i^2}, constant = \frac{\sum x_i^2 \sum y_i - \sum x_i \sum x_i y_i}{N\sum x_i^2 - \sum x_i^2}$$

(5,2,5)

6. (a) Write a program to print the following output from given string "CHEMISTRY"

C
CH
CHE
CHEM
CHEMI
CHEMIS
CHEMIST
CHEMISTR
CHEMISTRY

(b) What is the difference between screen 0, 1 and 2? Explain.

P.T.O.

(c) Write a program to Calculate the binomial coefficient using subroutine. Given

$$^nC_r = \frac{n!}{(n-r)!\,r!} \qquad (4,4,4)$$

7. (a) Write a program in BASIC to draw 10 concentric circles at the center of the SCREEN 1.

(b) Explain trapezoidal rule for numerical integration. Write a program in BASIC using trapezoidal rule to find the enthalpy change by using

$$\Delta H = \int_{T1}^{T2} (A + BT + CT^2)dT$$

(c) Distinguish between :

   (i) Bug and Virus

   (ii) Operating System and Application software

   (iii) RAM and ROM

   (iv) CPU and ALU $\qquad (4,4,4)$

Your Roll No................

Sr. No. of Question Paper : 1550   **C**

Unique Paper Code   : 42171103

Name of the Paper   : Atomic Structure, Chemical Bonding, General Organic Chemistry & Aliphatic Hydrocarbons

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

Semester   : I

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 separate answer booklet for each section.

3. Attempt all parts of a question together.

4. Use of calculator is allowed.

SECTION A

(*Attempt any* **THREE** *questions from Section A*)

1. (a) Write the time independent Schrodinger wave equation for hydrogen atom and define the terms involved in it.

(b) Melting points of NaCl and CuCl are 442°C and 800°C respectively. Justify.

(c) Predict the hybridization of NH_3, SO_4^{2-}, XeF_2.

(d) Draw the molecular orbital diagram for O_2 molecule. Predict its magnetic character.

(3,3,3,3.5)

2. (a) Write the Born-Lande expression for Lattice energy and define the terms involved in it.

(b) Bond angle in CH^4 is 109.5° whereas in NH3 the bond angle is 107.5°. Explain.

(c) Draw the radial probability distribution plots for 2s, 2p and 3p orbitals.

(d) Arrange the following in terms of increasing order of their lattice energy and Explain the order. LiF, CaF_2, MgS.   (3,3,3,3.5)

3. (a) Arrange O_2, O_2^+, O_2^-, O_2^{2-} in the increasing order of their bond length.

(b) Arrange the following in the increasing order of their melting point and explain the order.

CaF_2, $CaCl_2$, $CaBr_2$ and CaI_2

(c) Calculate the wavelength of a line in the Balmer series of the hydrogen spectra that corresponds to an electronic transition from 4th orbit. $R =$ 109679 cm^{-1}.

(d) Calculate the lattice energy of KCl using Bom-Haber Cycle

Sublimation energy of K(s) = 89 $KJmol^{-1}$, Ionization energy of K (g) = 425 $KJmol^{-1}$, Dissociation energy of Cl_2(g) = 244 $KJmol^{-1}$, Electron gain enthalpy for Cl(g) = −355 $KJmol^{-1}$ and heat of formation of KCl (s) = −438 $KJmol^{-1}$.

(3,3,3,3.5)

4. (a) Calculate the % ionic character in the HX molecule, if the dipole moment is 1.92D, bond length is 1.2A^0 and charge on H is 4.8×10^{-10} esu.

(b) Draw the resonating structures of CO_3^{2-} and N_3^-.

(c) Write the complete electronic configuration of two transition metals exhibiting anomalous pattern.

(d) Write a short note on Fajan's rule.   (3,3,3,3.5)

SECTION B

ORGANIC CHEMISTRY

(*Attempt any* **TWO** *questions from Section B*)

1. (a) Give reasons for the following :

(i) Cyclopentadienyl anion is aromatic while cyclopentadiene is not.

(ii) pka of nitroacetic acid is 1.68 while pk$_a$ of acetic acid is 4.76.

(iii) Benzyl carbocation is more stable than Isopropyl carbocation.

(iv) Trans alkenes have lower boiling point than cis alkenes.

(v) Racemic Mixture is optically inactive.

$(1\frac{1}{2}\times5=7\frac{1}{2})$

(b) Assign R/S or E/Z to the following compounds
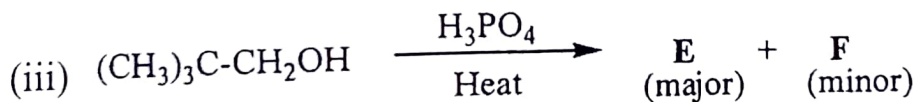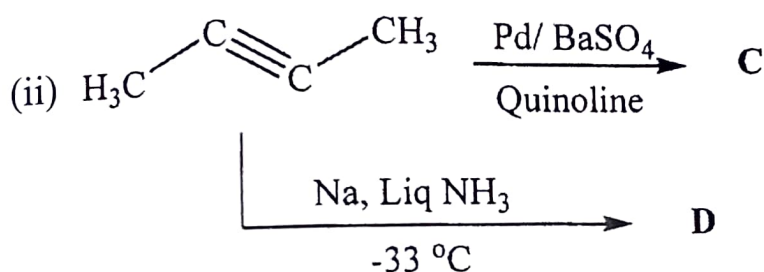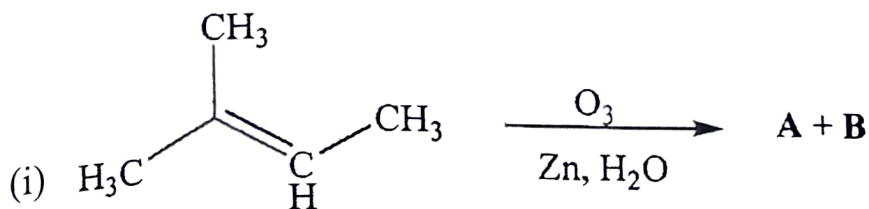

(I)   (II)   (III)   (IV)
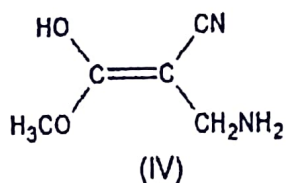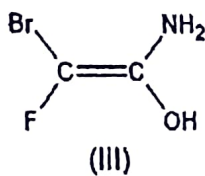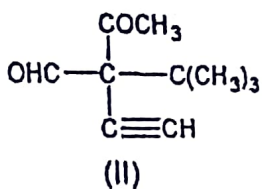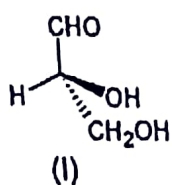
$(2\times4=8)$

(c) Carry out the following conversions :

(i) Propane to 2,3-Dimethyl butane

(ii) Propyne to Pent-2-yne

(3)

2. (a) Write the products of the following reactions :

(i) $\xrightarrow[\text{Zn, } H_2O]{O_3}$ A + B

(ii) $\xrightarrow[\text{Quinoline}]{\text{Pd/ BaSO}_4}$ C

$\xrightarrow[\text{-33 °C}]{\text{Na, Liq NH}_3}$ D

(iii) $(CH_3)_3C\text{-}CH_2OH$ $\xrightarrow[\text{Heat}]{H_3PO_4}$ E + F
(major) (minor)

(6)

(b) How many optical isomers are possible for 2,3-Dicholoropentane? Drawtheir Fischer projections and give the relationship between them. (6)

(c) What happens when propane is subjected to chlorine gas in presence of light? Predict the product(s) and give the mechanism involved.

(4)

(d) Explain why addition of HBr to propene in presence and absence of peroxide give different products.   (3)

3. (a) Arrange the following in the order mentioned in parentheses with suitable reasons :

(i) CH_3^-, $(CH_3)_2CH^-$, $(CH_3)_3C^-$ (decreasing order of stability)

(ii) $HCOOH$, CH_3COOH, CH_3CH_2COOH (decreasing order of acid strength)   (4)

(b) Why terminal alkynes are acidic in nature in comparison to alkanes and alkenes? How will you chemically distinguish a terminal and non-terminal alkyne?   (3)

(c) What happens when 3-Methylbutene is subjected to hydroboration oxidation? Give the steps involved and name of the product formed?   (2½)

(d) Write short notes on any **three** of the following :

(i) Mesomeric Effect and its Applications

P.T.O.

(ii) Conformations of n-Butane

(iii) Oxymercuration Demercuration Reaction

(iv) E1 and E2 Reactions   (3×3=9)

Your Roll No...............

Sr. No. of Question Paper : **1705**   **C**

Unique Paper Code   :   42174304

Name of the Paper   :   Solutions, Phase Equilibria, Conductance, Electrochemistry & Functional Group Organic Chemistry-II

Name of the Course   :   **B.Sc. Prog.**

Semester   :   III

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. **Section A** and **Section B** carry equal marks

3. Use separate answer sheets for **Section A** and **Section B**.

4. Use of simple calculator is allowed.

P.T.O.

SECTION A

(Attempt any **three** *questions in all.)*

1.   Explain Why?

(a) (i) Metallic conductance decreases while electrolytic conductance increases with rise of temperature.

(ii) A DC current cannot be used for conductance measurements.

(iii) H^+ and OH^- ions have exceptionally high ionic conductivities.

(b) State and explain Kohlrausch's law of independent migration of ions. How this law is useful to obtain, $\Lambda°$, molar Conductance of weak electrolyte at infinite dilution?

(c) The conductance of a cell containing an aqueous 0.0560 M KCl solution is 0.0239 Ω^{-1}. when the same cell is filled with an aqueous 0.0836 M NaCl solution, its conductance is 0.0285 Ω^{-1}. Given that

the equivalent conductance of KCl is 134.5 Ω^{-1} equiv^{-1} cm^2, calculate the equivalent conductance of NaCl solution.   (3+1.5,4,4)

2.   (a) Find :

      (i) F(degree of freedom) for a system consisting of solid sucrose in equilibrium with aqueous sucrose solution.

      (ii) F(degree of freedom) for an aqueous solution of weak acid HCN.

  (b) State Nernst Distribution law. Also discuss the preconditions of its validity.

  (c) Draw and label Phase diagram of Sulphur.

  (d) Define CST (taking example of Phenol – Water system). How is it different from MST. Draw temperature – composition curve for Phenol-Water system and label appropriately.

                                            (2+1.5,3,3,3.5)

3. (a) Write the Anodic, Cathodic and overall cell reaction for the following electrochemical cell

$$Zn(s) + ZnSO_4(0.1M) \rightarrow ZnSO_4(1.0 \text{ M}) + Zn(s)$$
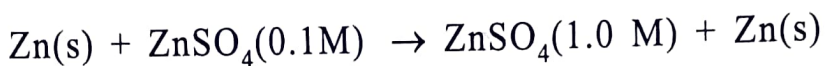
What is the term used for this type of cells.

(b) Consider the following cell:

$$Ag(s)|AgCl(s)|NaCl(aq)|Hg_2Cl_2(s)|Hg(l)|Pt$$
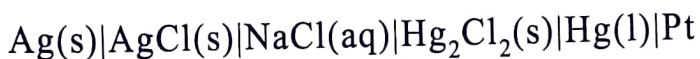
The standard emfs of the cell at several temperatures are as follows :

T/K	291	298	303	311
E^0/mV	43.0	45.4	47.1	50.1

Calculate the values of $\Delta G°$, $\Delta S°$ and $\Delta H°$ for the reaction at 298 K.

(c) Discuss briefly the principle underlying the potentiometric titrations, explaining schematic curve for the potentiometric titrations of strong acid vs strong base. Name one reference and an indicator electrode which can be used in laboratory for acid-base titration. (4,4,4.5)

4. Write short notes on any five of the following. Draw labeled diagram where ever required

(a) Steam Distillation

(b) Azeotropes

(c) Gibb's phase rule

(d) Conductometric titrations (acid – base)

(e) Simple Eutectic system (Pb – Ag)

(f) Calomel electrode $(5 \times 2.5 = 12.5)$

SECTION B

(*Attempt any* **three** *questions in all.*)

5. (a) Synthesize Ala-Gly by using Merrifield Solid phase peptide synthesis.

(b) What is Perkin Condensation? Explain its mechanism.

(c) Explain the methods to determine N-terminal and   7

C-terminal ends in proteins.   (4.5,4,4)

6. (a) Give the products and the name of the reaction

when :

(i) Aniline reacts with Benzoyl Chloride in

basic medium

(ii) Fructose reacts with excess of phenyl

hydrazine.

(iii) Benzene diazonium chloride reacts with

Aniline at low temperature $(0°C\text{-}5°C)$.

(b) Draw the Haworth projections formula for (i) α-

D-Glucopyranose (ii) β-D- Fructofuranose.

(c) Giving suitable explanation arrange the acid

derivatives (ester, acid chloride, acid anhydride

and amide) in increasing order of reactivity towards

nucleophilic acyl substitution reaction.

$(3×1.5,2×2,4)$

7. (a) How can D-aldopentose be converted into D-aldohexose? Give name of the reaction involved.

(b) Convert :

    (i) Aniline to p-Nitro aniline

    (ii) o-Toluidine to o-Cresol

(c) An aliphatic amine with molecular formula C_2H_7N exists in two isomeric forms 'A' and 'B'. When warmed with chloroform and KOH only 'A' reacts resulting into foul smell. What are the structures and names of 'A' and 'B'? Give name of the reaction and chemical equation involved in it. Compare the basicity of 'A' and 'B'.

$$(4.5, 2 \times 2, 4)$$

8. (a) Discuss the Hinsberg test used for identification of 1°, 2°, 3° amines. Outline the chemistry involved.

(b) Arrange the following in the order of increasing acidic strength and justify your answer:

(i) C_6H_5COOH, CH_3COOH, $p-NO_2C_6H_4COOH$

(ii) CH_3COOH, $ClCH_2COOH$, $BrCH_2COOH$

(c) How will you prepare the following :

(i) Alanine using Strecker synthesis

(ii) Ethyl amine using Gabriel-Phthalimide synthesis $(4.5,2\times2,2\times2)$

Your Roll No................

Sr. No. of Question Paper : 1001   **D**

Unique Paper Code   : 2172511101

Name of the Paper   : DSC- Basic Concepts of Organic Chemistry

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

Semester   : I

Duration : 2 Hours   Maximum Marks : 60

Instructions for Candidates

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

2. Attempt any **four** questions.

3. **All** questions carry equal marks.

1. Answer the following : **(any five)**

   (a) Arrange the following in decreasing order of their stability and give reasons

   $(CH_3)_3C^+$, CH_3^+, $CH_3CH_2^+$, $(CH_3)_2CH^+$

P.T.O.

(b) Why is the reaction of carbonyl compound with 2,4-dinitrophenylhydrazine carried out in weakly acidic medium?

(c) What is an ambidient ion? How can you prepare Nitrite and Nitro from a given alkyl halide?

(d) Why benzylamine is more basic than aniline?

(e) Differentiate between D/L and d/l notations.

(f) Explain, formic acid is stronger acid than acetic acid.

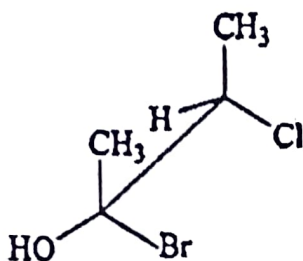(g) Giving reasons, arrange the following in increasing order of reactivity towards ring bromination:

OH   CH₃   NO₂
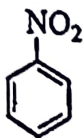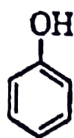
(3,3,3,3,3)

2. (a) Draw the different conformers of cyclohexane and arrange them in increasing order of stability.

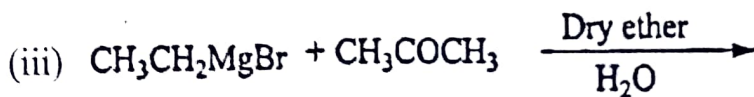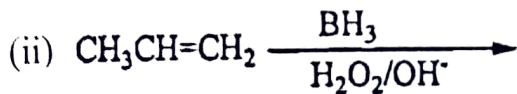(b) Assigning the priority and designate E/Z or R/S to the following :

(i)

    COOH
H──┬──CH=CH₂
HO─┼──OCH₃
    CH₂OH

(ii)

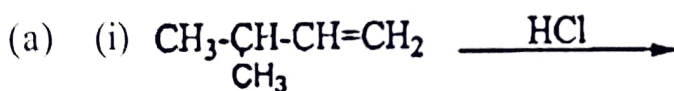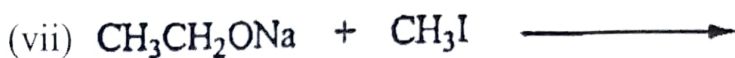
HOH₂C and OCOCH₃ on top, H₃COCO and COCH₃ on bottom of C=C
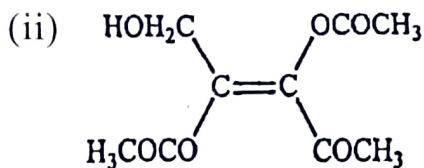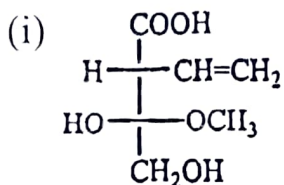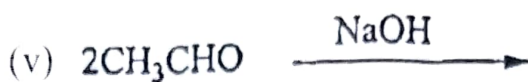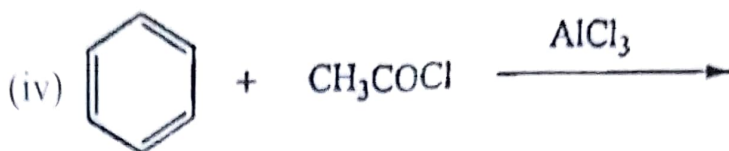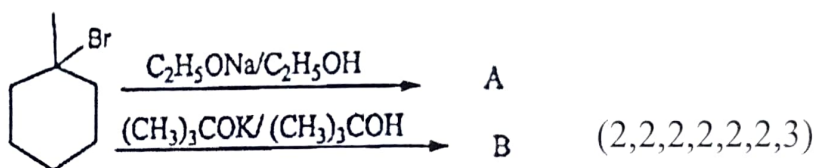
(c) Convert the following into fischer projection :

(d) Define enantiomers and diastereomers with at least one example each.   (4,6,2,3)

3. Complete the following reactions (any Six)

(a) (i) CH₃-CH-CH=CH₂ ───HCl──→
              |
              CH₃

    (ii) CH₃CH=CH₂ ──BH₃/H₂O₂/OH⁻──→

    (iii) CH₃CH₂MgBr + CH₃COCH₃ ──Dry ether/H₂O──→

P.T.O.

(iv) + CH_3COCl $\xrightarrow{AlCl_3}$

(v) $2CH_3CHO$ $\xrightarrow{NaOH}$

(vi) CH_3CH_2CHO + NH_2NH_2 $\xrightarrow{H^+}$

(vii) CH_3CH_2ONa + CH_3I $\xrightarrow{\hspace{2cm}}$

(b) Write the product.

$\xrightarrow[\text{(CH}_3)_3\text{COK/ (CH}_3)_3\text{COH}]{C_2H_5ONa/C_2H_5OH}$ A
B   (2,2,2,2,2,2,3)

4. Explain the following : **(Any three)**

(a) Hydrolysis of 2-Bromo-3-methyl butane gives only 2-methyl-2-butanol.

(b) Differentiate between E1 and E2 reactions.

(c) Methyl group in toluene is o, p-directing and activating.

(d) Arrange the following carbonyl compounds in decreasing order of reactivity towards nucleophilic addition reaction and justify

C_6H_5CHO, CH_3CHO, CH_3COCH_3, HCHO
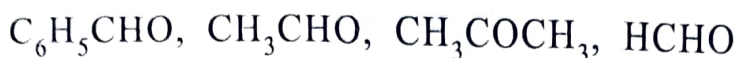
(5,5,5)

5. Attempt (Any three)

(a) Chloro benzene reacts with $NaNH_2$ in liquid NH_3 at room temperature to form aniline. Explain.

(b) Discuss the mechanism of addition of HBr to propene in the presence of peroxide. Explain, Why the peroxide effect is shown by HBr only and not by HCl and HI?

(c) Why SN2 reaction of alkyl halides are accompanied by inversion of configuration. Explain the mechanism.

(d) Compare the reactivities of Bromobenzene, Allyl bromide and Bromo ethane in nucleophilic substitution reactions. (5,5,5)

6. Write short note on any three of the following with emphasis to (i) the functional group that undergo these reactions (ii) product formed (iii) reaction conditions (iv) mechanism.

(a) Friedel craft acylation reaction

(b) Birch reduction

(c) Pinacol-pinacolone rearrangement

(d) Perkin reaction

(e) Reimer-Tiemann   (5,5,5)

Your Roll No...............

Sr. No. of Question Paper : 1573   C

Unique Paper Code   : 42177925

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

Name of the Course   : **B.Sc. Program**

Semester   : V

Duration : 3 Hours   Maximum Marks : 75
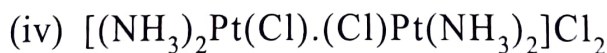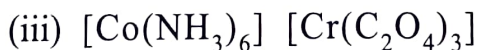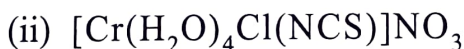
Instructions for Candidates

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

2. Attempt **six** questions in total with **three** from **SECTION A** and **three** from **SECTION B**.

3. Attempt **SECTION A** and **SECTION B** on separate answer sheets.

4. Use of scientific calculator and Log table is allowed.

P.T.O.

SECTION A

INORGANIC CHEMISTRY

Attempt **ANY THREE** questions. Attempt **any three** questions in this section. **All** questions carry equal marks.

1. (a) Name **any three** of the following complexes according to the IUPAC system of nomenclature:

(i) $Na[Co(CO)_4]$

(ii) $[Cr(H_2O)_4Cl(NCS)]NO_3$

(iii) $[Co(NH_3)_6]$ $[Cr(C_2O_4)_3]$

(iv) $[(NH_3)_2Pt(Cl).(Cl)Pt(NH_3)_2]Cl_2$

(b) Indicate the isomerism exhibited in the following pairs of compounds and give one method to distinguish between them :

(i) $[Co(NH_3)_5Br]SO_4$ and $[Rh(NH_3)_5 SO_4]$ Br

(ii) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ and $[Cr(H_2O)_6]Cl_3$
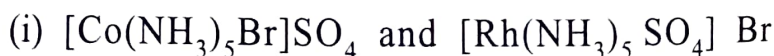
(c) Give brief reasons for **any two** of the following :

(i) Transition metals and their complexes have catalytic properties.

(ii) Ca & Sc$^+$ are isoelectronic but have different electronic configuration.

(iii) $CuSO_4.5H_2O$ is coloured and anhydrous $CuSO_4$ is colourless.   (4.5,4,4)

2.   (a) Write the formulae of **any three** of the following according to IUPAC convention :

   (i) Potassium tetrahydroxidozincate(II)

   (ii) μ-hydroxido-μ-superoxidobis{pentaammine-chromium(III)} chloride

   (iii) Pentaamminesulphatorhodium(III) tetrahydroxidoferrate(II)

   (iv) Potassium amminepentachloridoplatinate(IV)

   (b) $[Co(NH_3)_5Cl]^{2+}$ undergoes ligand substitution reaction when treated with $NaNO_2$ to give two products A & B, depending on the experimental conditions. A & B are isometric pentaamine ions. Draw their structures and indicate the isomerism.

(c) Predict the appropriate choice and give brief reasons :

　　(i) Greater Value of Δ_0 $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$

　　(ii) Chelating ligand ethylenediamine, Pyridine

　　　　　　　　　　　　　　　　　　(4.5,4,4)

3.　(a) The complex $[Cr(NH_3)_2 (C_2O_4)_2]$ exists in two isomeric forms A & B. A is optically active but B is not. Explain the reason briefly and draw the structures of A & B.

　　(b) Chromium(II) fluoride and Manganese(II) fluoride, both have a central metal ion surrounded by six Fluoride ligands. All the Mn-F bond lengths are equal, but two of the Cr-F bond lengths are shorter than the remaining four. Explain.

　　(c) Calculate CFSE in terms of Δ_0 of a d^3 metal ion placed in a tetrahedral field. Draw the splitting diagram.　　　　　　　　　　(4.5,4,4)

4.　(a) For the complex ion $[Mn(H_2O)_6]^{3+}$, given mean pairing energy, $P = 28,000$ cm^{-1}, and magnitude of Δ_0 is $21,000$ cm^{-1}, calculate CFSE corresponding to high spin and low spin states. In which of the states the complex is more stable?

(b) The Latimer diagram for Fe in acidic medium is given below:

$$FeO_4^{2-} \xrightarrow{2.20} Fe^{3+} \xrightarrow{+0.77} Fe^{2+} \xrightarrow{-0.47} Fe$$
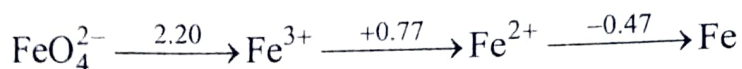
Answer the following questions :

(i) Is there any state which undergoes disproportionation? Explain.

(ii) Calculate skip step potential for Fe^{3+} ---- Fe change.

(iii) Is there any tendency of Fe^{2+} to reduce to Fe? Give reason for your answer.

OR

(b) Briefly discuss **any two** of the following :

(i) Limitations of Valence Bond Theory

(ii) Spectrochemical Series

(iii) Separation of lanthaniods by ion exchange method

(c) Using VBT predict the geometry and magnetic behaviour of :

(i) $[Mn(CN)_6]^{4-}$

(ii) $[Mn(Cl_4)]^{2-}$ (4.5,4,4)
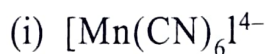
SECTION B

Planck's constant, $h = 6.626 \times 10^{-34}$ Js;

Velocity of light, $c = 3 \times 10^8 ms^{-1}$

Mass of an electron, $m_e = 9.1 \times 10^{-31}$ kg

Attempt **any three** questions.

1.   (a) Normalize the function $f(x) = \dfrac{x^2}{2}$ in the range $0 \le x \le a$.

   (b) What is Lambert's law? How is it modified by Beer?

   (c) The spacing of lines in the microwave spectrum of $^1H^{35}Cl$ is 11.2 cm^{-1}. Calculate the moment of inertia and bond length of the molecule.
                                             (4,4,4.5)

2. (a) Find if the function $f(x) = ae^{x^2}$ is an Eigen function

    of the operator $\dfrac{d}{dx}$?

    (b) What is the significance of normalization condition?

    (c) What is phosphorescence? Draw jablonski diagram and explain the process of phosphorescence.

    (d) The absorption band in IR spectrum of $^{12}C^{16}O$ is at $2045\ cm^{-1}$. Calculate its zero point energy and force constant of the bond.   (2,2,4,4.5)

3. (a) A particle of mass m is confined in a one dimensional box of length L. Calculate the probability of finding the particle between L/4 and L/2 if it is present in the ground state and is

    represented by the wave function $\psi = \sqrt{\dfrac{2}{L}}\sin\dfrac{n\pi x}{L}$.

    (b) As the number of conjugated atoms in a molecule increase the $\pi^* \rightarrow \pi$ transition shifts to higher wavelength. Explain.

    (c) Calculate the transmittance, absorbance and molar extinction coefficient of a solution which absorbs

80% of light of wavelength 520nm passed through a 0.25M solution contained in a cell of path length 1 cm. (4,4,4.5)

4.   (a) Find the commutator of the operators $\dfrac{d}{dx}$ and $3x^2$.

(b) Arrange the bonds C – Cl, C – F and C – Br in order of increasing frequency of IR signal for stretching of the bond. Give reason for your answer.

(c) The quantum efficiency of a reaction is 0.55. A sample absorbs light of wavelength 260nm at the rate of 0.75 J min^{-1}. Calculate the moles of product formed in 30 minutes. (4,4,4.5)