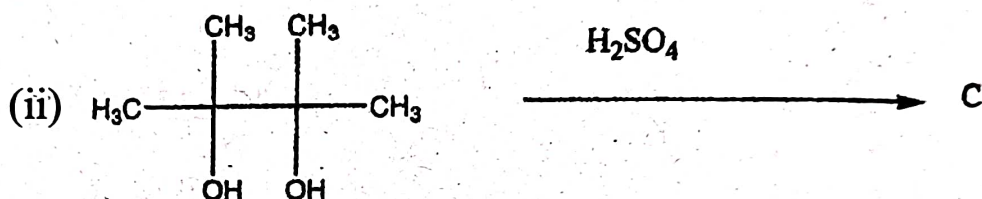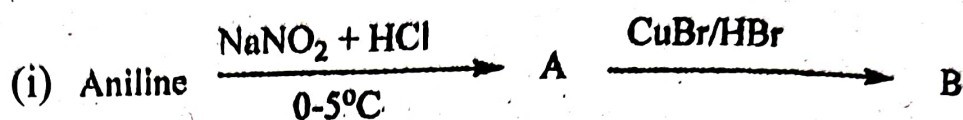[This question paper contains 8 printed pages.]

Instructions for Candidates

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

2. Attempt all parts of a question together.

3. Attempt any **four** questions in all.

4. Question no. **1** is compulsory.
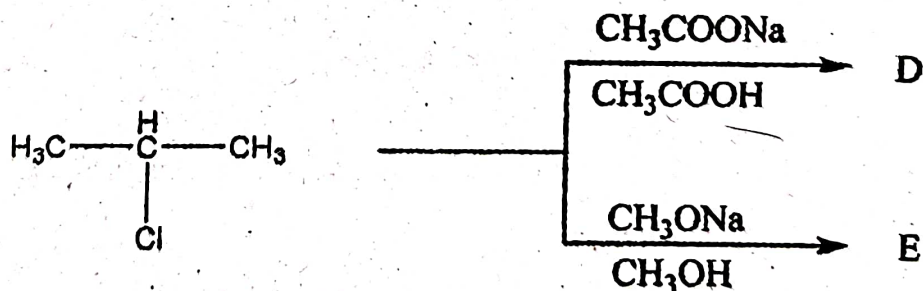
5. Each question carries **15** marks.

1. (a) Complete the following reaction as indicated, identify and write their names-

(i) Aniline $\xrightarrow[\text{0-5}^\circ\text{C}]{\text{NaNO}_2 + \text{HCl}}$ A $\xrightarrow{\text{CuBr/HBr}}$ B

(ii)

$$\underset{\overset{|}{\text{OH}}}{\overset{\overset{\text{CH}_3}{|}}{\text{H}_3\text{C}}}\!-\!\!\underset{\overset{|}{\text{OH}}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\!-\!\text{CH}_3 \qquad \xrightarrow{\text{H}_2\text{SO}_4} \qquad \text{C}$$

(b) Write products of the following reactions and identify the mechanism involved-

$$\text{H}_3\text{C}\!-\!\underset{\overset{|}{\text{Cl}}}{\overset{\overset{\text{H}}{|}}{\text{C}}}\!-\!\text{CH}_3$$

$\xrightarrow[\text{CH}_3\text{COOH}]{\text{CH}_3\text{COONa}}$ D

$\xrightarrow[\text{CH}_3\text{OH}]{\text{CH}_3\text{ONa}}$ E

(c) Write various steps in the reaction of given epoxide in the given conditions :
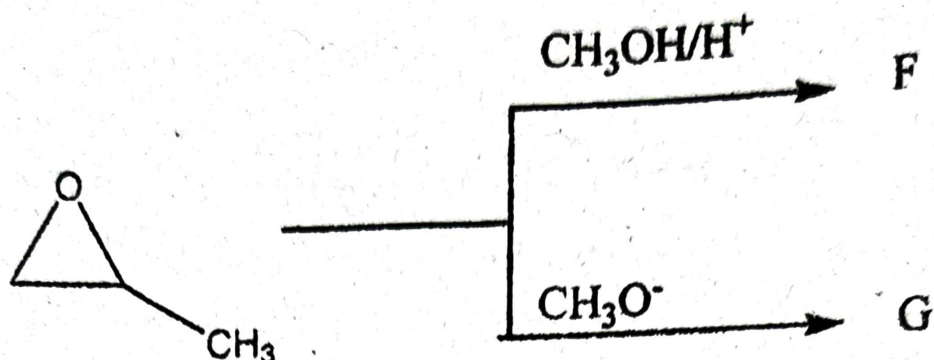
$$(5\times3=15)$$

2. Justify the given statements **(any three)**

(a) Ethyl bromide reacts differently with KNO_2 and $AgNO_2$.

(b) Aryl halides have very low reactivity towards Nucleophilic substitution reaction as compared to Alkyl halides and Benzyl halides.

(c) Di-tertiary Butyl ether cannot be prepared by Williamson's ether synthesis.

(d) Cleavage of phenyl alkyl ether with HI gives phenol and alkyl iodide. $(5\times3=15)$
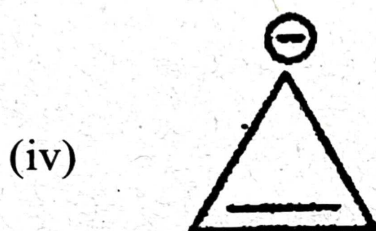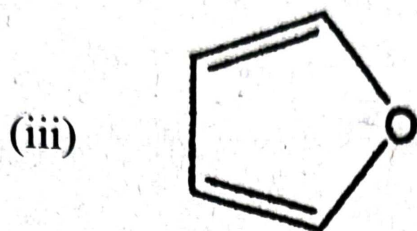
P.T.O.

3. (a) Giving reasons arrange the following compounds as mentioned in parentheses

      (i) t-butanol, n-butanol and isopropanol (towards lucas test)

      (ii) o-methyl phenol, p-methyl phenol and m-methyl phenol (increasing order of acidity)

(b) Define aromaticity. Classify the following as aromatic or antiaromatic giving suitable explanation –

(i)

(ii)

(iii)

(iv)
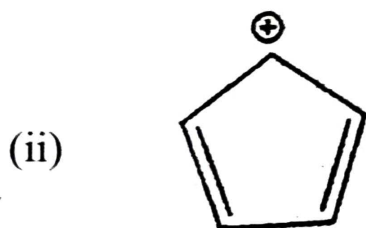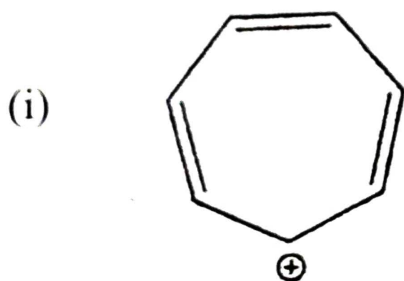
(c) Carry out the following conversions (Give complete chemical equations)

   (i) Benzene to m-Dinitrobenzene

   (ii) Methyl chloride to Ethanoic acid

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

4. Write reaction mechanism for the given reactions **(any three)**

(a) Cumene is oxidized in air and the resulting compound undergoes rearrangement in presence of an acid catalyst. Why is this method an industrial method of preparation?

(b) Esterification of ethyl alcohol with acetic acid in acidic medium.

(c) Reaction of ortho-bromotoluene with $NaNH_2$ in liq. NH_3.

(d) A compound 'A' reacts with CH_3MgBr to give Ethanol which upon oxidation with PCC gets converted to 'B'. Identify A and B. Write all the steps involved in the given reaction.

$(5 \times 3 = 15)$

5. (a) What happens when 2-Butanol is treated with Thionyl chloride in presence and in absence of Pyridine?

(b) Out of $C_6H_5CH_2Cl$ and $(C_6H_5)_2CHCl$ which is more easily hydrolyzed by aqueous sodium hydroxide under S_N1 and S_N2 conditions and why?

(c) What are the limitations of reaction of benzene with CH_3Cl? Why these limitations are not there in reaction of benzene and CH_3COCl?

$(5×3=15)$

6. (a) Explain why Halogens in haloarenes are (i) weakly deactivating (ii) ortho/para directing.

(b) Taking Nitrobenzene as an example explain how a Nitro group deactivates the benzene ring towards electrophilic substitution reaction but at the same time it activates the ring towards Nucleophilic substitution reaction

P.T.O.

(c) What happens when phenyl acetate is treated with $AlCl_3$ in presence of aq. HCl? Name the reaction and give mechanistic details.   (5×3=15)

[This question paper contains 4 printed pages.]

Sr. No. of Question Paper : 4665   **H**

Unique Paper Code   : 2176000008

Name of the Paper   : FORENSIC CHEMISTRY

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

Semester   : II/IV

Duration : 1 Hour   Maximum Marks : 30

Instructions for Candidates

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

2. Attempt any **two** questions in all.

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

P.T.O.

1. (a) State whether the following statements are True or False (**any five**) :—

    (i) Narcotic drugs do not affect central Nervous system.

    (ii) A fire man can also collect the evidences from fire crime scene.

    (iii) Heat, light and noise are generated at the time of explosion.

    (iv) Fingerprints of twins can be found identical.

    (v) Air -tight packages make the best containers for blood stained articles.

    (vi) On absorbing Iodine fumes, fingerprints become black in colour.

(b) Explain briefly about the Henry's classification system of fingerprints.

(c) Sketch a flowchart showing different steps of investigation at crime scene. (5,5,5)

2.   (a) Identify the fingerprint patterns of the following :
         (any five) :—

(b) Describe any one chemical method for developing the latent fingerprints from curved or rough surfaces?

(c) Write any three ethics related to forensic science.

(d) Write any three limitations to the quality of prints recovered from the crime scene.   (5,4,3,3)

                                                P.T.O.

3. (a) Match the following :–

   (i) Phenolphthalein.   (a) Fractional distillation

   (ii) Iodine method   (b) Rum

   (iii) Petroleum   (c) 1st fingerprint bureau

   (iv) Calcutta   (d) RDX

   (v) Explosive   (e) Chemical method

   (vi) Alcoholic beverage (f) Trap case

   (b) Define arson? Discuss the steps in the investigation of a fire scene.

   (c) Differentiate between edgeoscopy and poroscopy.

   (6,4,5)

4. (a) What is TLC? Discuss the applications of TLC in forensic science.

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

      (i) Drugs of abuse

      (ii) AFIS

      (iii) Fire tetrahedron

      (iv) Scope of forensic chemistry   (6,3×3)

(1000)

Sr. No. of Question Paper : 2997   **H**

Unique Paper Code   : 32171402

Name of the Paper   : Organic Chemistry III : Heterocyclic Chemistry

Name of the Course   : **B.Sc. (Hons.) 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 **six** questions in all.

3. Question No. **1** is compulsory and carries **15** marks.

4. All other questions are of **12** marks each.

1. (a) An organic compound A (C_3H_7NO) on treatment with bromine and aqueous NaOH forms a compound B (C_2H_7N). B on treatment with $NaNO_2$ and dil. HCl gives C (C_2H_6O) along with the

P.T.O.

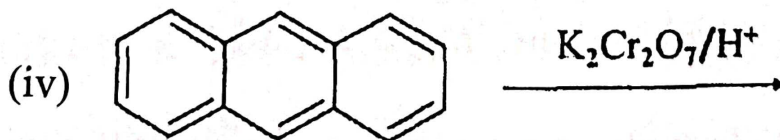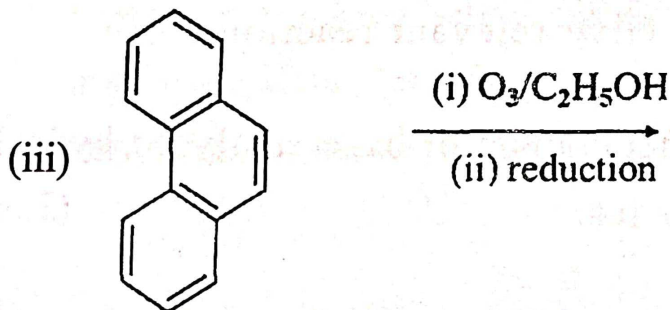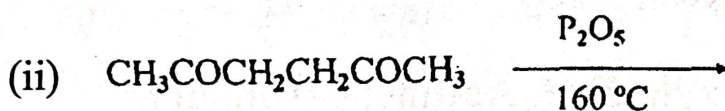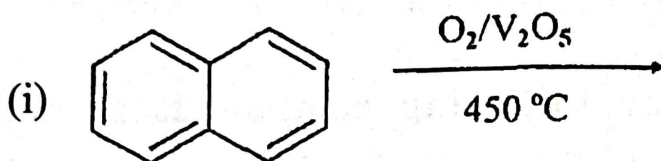evolution of N_2 gas. C forms iodoform with iodine and aqueous Na_2CO_3. Identify 'A', 'B' and 'C'. Give the sequence of the reactions involved. Name the reaction involved in the conversion of A to B with mechanism.

(b) Sulphonation of Naphthalene gives different products at low and high temperatures. Give reactions and explain.

(c) Explain the order of reactivity of furan, thiophene, and pyrrole towards electrophilic substitution reaction. Draw suitable structures to justify your answer.

(d) Citral forms two semicarbazones with different melting points. Justify your answer with structures and their names.   (6,3,3,3)

2. (a) Describe Haworth's method for the synthesis of Phenanthrene.

(b) Electrophilic substitution reaction in Anthracene occurs preferably at C-9. Explain by drawing the relevant resonating structures.

(c) C_1-C_2 bond in Naphthalene is shorter than C_2-C_3 bond. Explain.
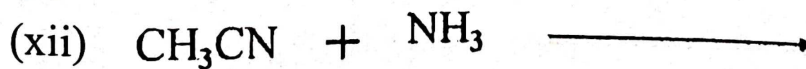
(d) Write the sequence of reactions which establish that naphthalene consists of two benzene rings fused together.   (3,3,3,3)

3. (a) How do primary, secondary, and tertiary nitroalkanes react with nitrous acid? Give the reactions involved.

(b) Arrange the following compounds in order of decreasing basic strength. Give reason to justify your answer :

Cyclohexylamine; Aniline; p-Toluidine

(c) How will you distinguish between nitriles and isonitriles? Give relevant reactions.

(d) Write the mechanism of base catalysed hydrolysis of alkyl nitriles.   (3,3,3,3)

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

     (i) Naphthalene into β-naphthol

     (ii) Thiophene into thiophene-2-carboxylic acid

     (iii) Aniline into p-bromoaniline

     (iv) Nitrobenzene into m-bromophenol

P.T.O.

(b) Coupling reactions of diazonium salts take place in either mild acidic or mild alkaline conditions. Explain using suitable reactions. (3,3,3,3)

5. Write the products formed : **(any 12)**

(i) $\xrightarrow[450\,°C]{O_2/V_2O_5}$

(ii) $CH_3COCH_2CH_2COCH_3$ $\xrightarrow[160\,°C]{P_2O_5}$

(iii) $\xrightarrow[\text{(ii) reduction}]{\text{(i) } O_3/C_2H_5OH}$

(iv) $\xrightarrow{K_2Cr_2O_7/H^+}$

(v) $\xrightarrow{KMnO_4}$

(vi)

$$\text{[pyridine]} \xrightarrow[\text{100 °C}]{\text{n-C}_4\text{H}_9\text{Li}}$$

(vii)

$$\text{[indole]} \xrightarrow[\text{120 °C}]{\text{SO}_3/\text{pyridine}}$$

(viii)

$$\text{[furfural]—CHO} \xrightarrow[\text{NaOC}_2\text{H}_5]{\text{CH}_3\text{CH}_2\text{COOC}_2\text{H}_5}$$

(ix)

$$\text{[thiophene]} \xrightarrow[\text{180 °C}]{\text{H}_2/\text{Raney Ni}}$$

(x) $CH_3NC \xrightarrow{250 \text{ °C}}$

(xi)

$$\text{[p-nitrotoluene]} \xrightarrow{\text{Zn}/\text{NH}_4\text{Cl}}$$

(xii) $CH_3CN + NH_3 \longrightarrow$

P.T.O.

(xiii)

(xiv)   (12×1=12)
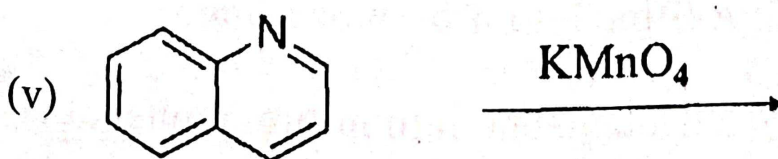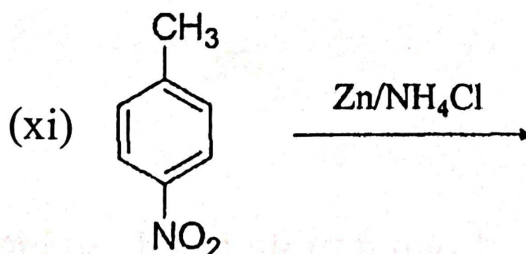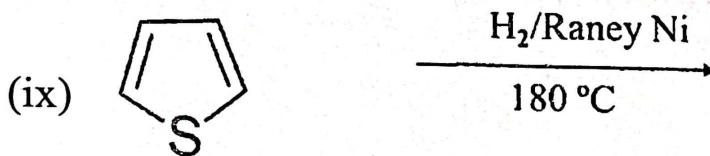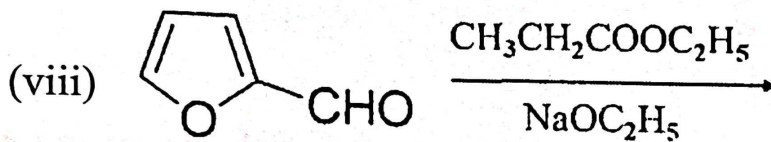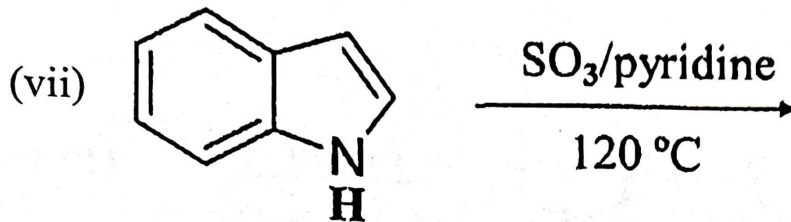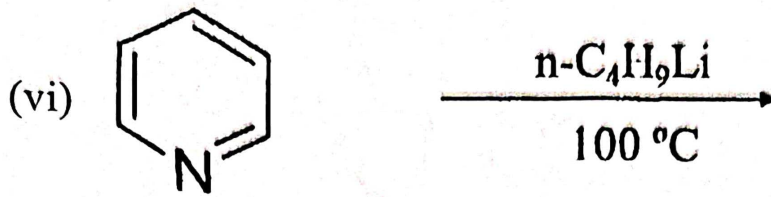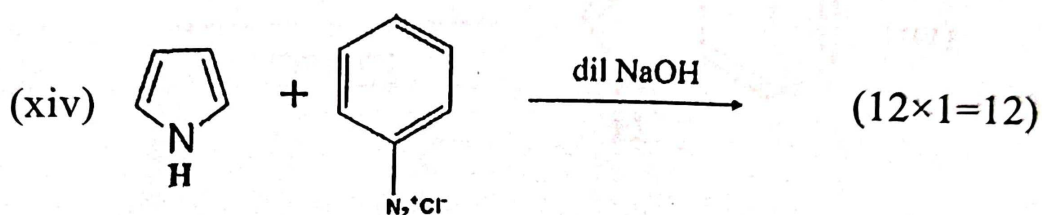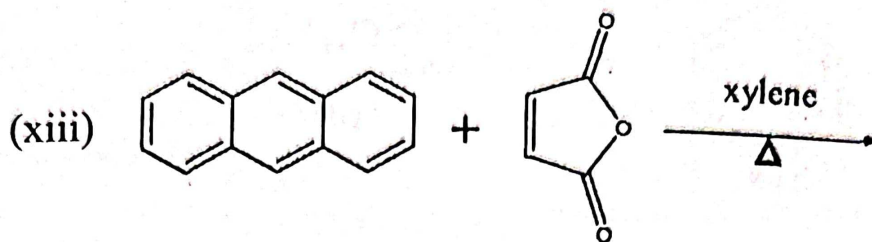
6. (a) Define 'Isoprene rule'. Mark out the isoprene units in the following compounds with dotted lines.

(i)   (ii)
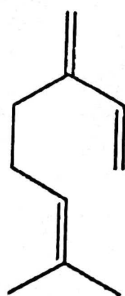
(b) How the positions of two double bonds in citral is established? Give the relevant reactions.

(c) Give synthesis of nicotine from nicotinonitrile.

(d) Explain the reaction which indicates the position of linkage between pyridine and N-methyl pyrrolidine in nicotine. (3,3,3,3)

7. (a) Explain the fact that pyridine reacts with electrophiles as well as nucleophiles with the help of resonating structures.

(b) Electrophilic substitution reaction in Indole occurs at C-3. Explain by drawing suitable resonating structures.
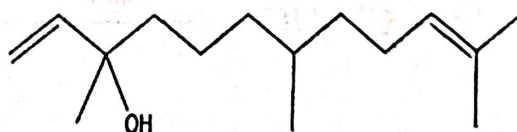
(c) Pyrrole undergoes ring expansion with $CHCl_3$ and NaOH. Give the reaction and its mechanism.

(d) The reactions of furan cannot be done in the acidic medium. Give reason and the reaction involved. (3,3,3,3)

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

(i) Skraup synthesis of quinoline

(ii) Hantzsch-pyridine synthesis

(iii) Hinsberg method

P.T.O.

(b) Outline the reaction sequence involved in the Hoffmann exhaustive methylation procedure of hydrogenated pyridine. (4,4,4)

(500)

[This question paper contains 12 printed pages.]

Sr. No. of Question Paper : 3108   **H**

Unique Paper Code   : 32171403

Name of the Paper   : Physical Chemistry – IV

Name of the Course   : **B.Sc. (Hons.) 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 **six** questions in all.

3. Question No. **1** is compulsory.

4. Attempt at least **one** question from each Section.

5. Use of scientific calculators is permitted.

NOTE:

$R = 8.314 \ JK^{-1}mol^{-1}$, $h = 6.626 \times 10^{-34} \ Js$, $k_B = 1.381 \times 10^{-23} \ JK^{-1}$, $F = 96485 \ C \ mol^{-1}$

P.T.O.

1. Explain any **five** of the following :

   (a) Quantum efficiency of Fluorescence decreases with the increase in concentration of the solution.

   (b) Role of Uranyl ion in photochemical decomposition of oxalic acid.

   (c) The first order reaction never achieves completion.

   (d) The activation energy of a reaction cannot be zero or negative.

   (e) The molar conductivity of Li^+ ion is less than that of Cs^+ ion in aqueous medium.

   (f) The transport number of Cd^{2+} in concentrated solution of CdI_2 is negative.   (5×3)
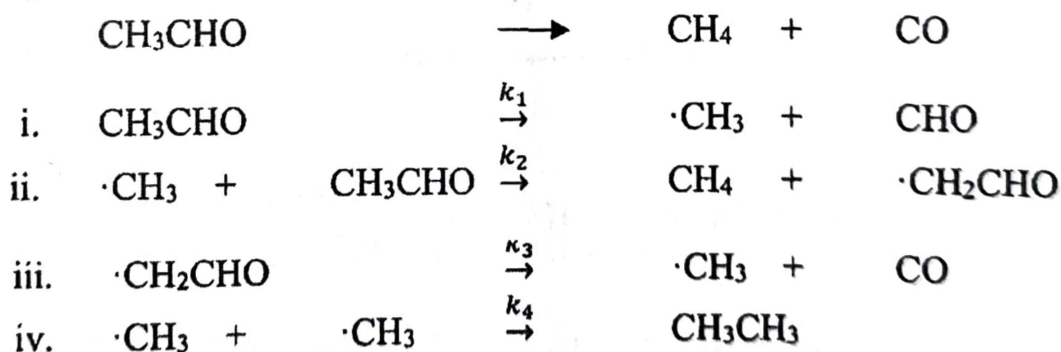
SECTION A

2. (a) Compare the rate constants as given by Collision Theory and the Activated Complex Theory. Hence, the steric factor p of collision theory may be interpreted in terms of entropy of activation.

                                            (5)

(b) The reaction $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

is first order and has a rate constant 2.24×10^{-5} s^{-1} at 320°C. What fraction of a sample of $SO_2Cl_2(g)$ remains after being heated for 5 Hrs. at 320°C? How long will a sample of SO_2Cl_2 (g) take to decompose 92.0% of the initial amount present at 320°C?   (4)

(c) Derive an expression for half-life time of a nth order reaction.   (3)

3. (a) Considering the following mechanism for the thermal decomposition of acetaldehyde :

	CH_3CHO		$\longrightarrow$	CH_4 +	CO
i.	CH_3CHO		$\xrightarrow{k_1}$	$\cdot CH_3$ +	CHO
ii.	$\cdot CH_3$ +	CH_3CHO	$\xrightarrow{k_2}$	CH_4 +	$\cdot CH_2CHO$
iii.	$\cdot CH_2CHO$		$\xrightarrow{k_3}$	$\cdot CH_3$ +	CO
iv.	$\cdot CH_3$ +	$\cdot CH_3$	$\xrightarrow{k_4}$	CH_3CH_3	

  P.T.O.

Derive the differential rate law for the formation of CH_4 using steady state approximation and also determine the chain length for the same reaction. (4)

(b) For a reversible first-order reaction

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$
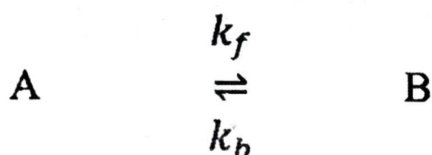
$k_f = 10^{-2}$ s^{-1} and $\dfrac{[B]eq}{[A]eq} = 4$. If $[A]_0 = 0.01$ mol L^{-1} and $[B]_0 = 0$, what will be concentration of B after 30 s? (4)

(c) The rate constant for the dissociation of ethane

$$C_2H_6 \longrightarrow 2\, CH_3$$
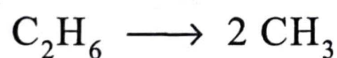
is given by $k = 5 \times 10^6 \exp\left(\dfrac{-368\ kJ}{RT}\right)$.

Calculate the entropy of activation for this reaction at 850 K. (4)

4. (a) The initial rate of oxidation of sodium succinate to form sodium fumerate in presence of the enzyme succinate dehydrogenase at different sodium succinate concentrations is given below

Sodium succinate conc $\times 10^3$ /mol dm^{-3}	10.0	2.0	1.0	0.5	0.33
Initial rate $\times 10^6$ mol s^{-1}	1.17	0.99	0.79	0.62	0.50

Determine the Michaelis constant and the limiting rate of equation. (5)

(b) Given below is the mechanism of acid-base catalysis

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^+ + H_2O \overset{k_2}{\rightarrow} P + H_3O^+$$

P.T.O.
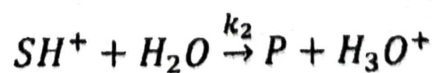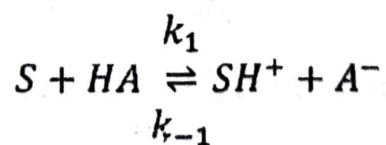
Derive the expression for the rate of formation of product.

$$\frac{dP}{dT} = \frac{k_2 k_1 [S][HA]}{k_{-1}[A^-] + k_2}$$

Show under what conditions a given catalytic reaction may be classified into general acid catalysis and a specific hydrogen ion catalysis.

(4)

(c) Define Turnover number of enzymes.   (3)

SECTION B

5. (a) (i) The amide ion in liquid ammonia has an abnormally high transference number. Explain.

(ii) In the conductometric titration, the solution to be added from the burette is much stronger than the solution taken in the conductometric cell. Why? (2+2)

(b) Discuss Hittorf's method to determine the transference number of ions. (4)

(c) The specific conductance of a saturated solution of BaSO, is 3.48×10^{-4} S/m. The conductivity of pure water is 0.50×10^{-4} S/m. Calculate the solubility and solubility product of $BaSO_4$ (Limiting ionic conductance of Ba^{2+} and SO_4^{2-} are 127.26×10^{-4} and 160.04×10^{-4} $Sm^2 mol^{-1}$ respectively). (4)

6. (a) At 25°C, the specific conductance of distilled water is 58.0×10^{-7} Sm^{-1} and the λ°_m values of H^+ and OH^- ions are 349.8×10^{-4} and 198.5×10^{-4} $Sn^2 mol^{-1}$, respectively. Assuming that λ_m differs very little from λ°_m, calculate the ionic product of water at 25°C. (4)

(b) What is Transference number? How the

P.T.O.

transference number is related to the absolute velocity of the ion. Derive the related expression.

(4)

(c) A solution of 0.10 M in LiCl with conductivity 1.06×10^{-2} S/cm is placed in a moving boundary cell of cross-sectional area 1.17 cm². It was electrolyzed for 131 minutes with a constant current of 9.42 milliamperes. The Li^+ was observed to move a distance of 2.08 cm. What is the transport number of Li^+ in the solution? (4)

7. (a) (i) State Faraday's Laws of Electrolysis.

(ii) How does ionic mobility differ from ionic speed? What is the unit of ionic mobility?

(2+2)

(b) State Kohlrausch Law of independent migration of Ions. How will you calculate the molar

conductance and equivalent conductance at infinite dilution of Potash alum [$K_2SO_4.Al_2(SO_4)_3.24H_2O$]? How are they related to each other? (4)

(c) At 25°C a solution of KCl having a conductivity of 0.14088 S/m exhibits a resistance of 654 ohm in a particular conductivity cell. In this same cell, a 0.10 mol/L solution of NH_4OH has a resistance of 2524 ohm. Calculate

    (i) the cell constant

    (ii) the molar conductivity of NH_4OH solution

    (iii) the degree of dissociation of the 0.10 mol/L NH_4OH

    (iv) the dissociation constant of NH_4OH.

(Limiting molar ionic conductivities of NH_4^+ and OH^- are 73.55×10^{-4} and 198.3×10^{-4} Sm^2 mol^{-1} respectively) (4)

SECTION C

8. (a) Given the following mechanism

$$(i) \quad HI + h\nu \xrightarrow{I_{abs}} H + I$$

$$(ii) \quad H + HI \xrightarrow{k_2} H_2 + I$$

$$(iii) \quad I + I \xrightarrow{k_3} I_2$$

$$(iv) \quad H + I_2 \xrightarrow{k_4} HI + I$$
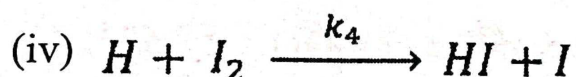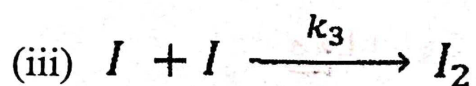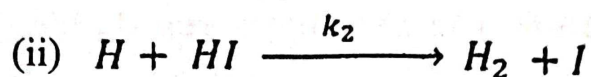
Show that the quantum efficiency of the decomposition of HI is

$$\varphi_y = \frac{2}{1 + \dfrac{k_4}{k_2}\dfrac{[I_2]}{[HI]}} \qquad (5)$$

(b) A mixture of hydrogen and chlorine was irradiated with radiation of wavelength 400 nm. In a given

interval of time, 7×10^{-5} J were absorbed by the reactant chlorine. If φ_{HCl} is 2.6×10^6 J, how many moles of HCl are formed per joule of energy absorbed. (4)

(c) The quantum yield for the photochemical reaction

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

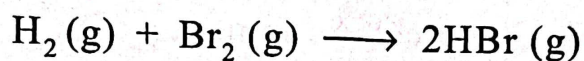Is ~ 0.01 while that for the reaction.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$
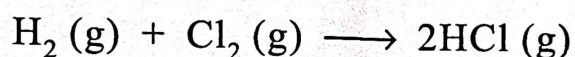
is $\sim 10^4 - 10^6$. Explain. (3)

9. (a) A monochromatic light of certain wavelength was passed through a solution of certain concentration using a cell of 0.5 m and 25% of the incident light was absorbed. What is its absorbance? If the concentration of the solution is doubled, what will be the length of the cell which absorbs 60% of the incident light. (4)

(b) Discuss the asymmetric effect and electrophoretic

effect. How these effects can be minimized?

(4)

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

(i) Pseudo-unimolecular reactions

(ii) Chemical Actinometer (4)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 4132   **H**

Unique Paper Code   : 2172012403

Name of the Paper   : Electrochemical Cells and Chemical Kinetics

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

Semester   : IV

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 **(SIX)** Questions in all. **First** question is Compulsory.

3. Use of a Scientific calculator is permitted.

4. Graph paper will be provided.

P.T.O.

1. (Attempt any **Five** Parts)

(a) First-order reaction never goes to completion. Explain.

(b) It is rare for a reaction to have a molecularity of more than three.

(c) A first order reaction, A → products, has a rate of reaction of 0.00250 M s^{-1} when [A] = 0.484 M.

   (i) What is the rate constant, k, for this reaction?

   (ii) Does $t_{3/4}$ depend on the initial concentration?

(d) Polarities of cathode and anode in a galvanic cell are opposite to those in an electrolytic cell. Explain.

(e) Why can we not use a voltmeter for determining the e.m.f. of a galvanic cell?

(f) Set up the galvanic cell for the following reactions:

$$Fe_{(s)} + Cl_{2(g)} \rightleftharpoons \rightleftharpoons FeCl_{2\ (aq)}$$

$$2Cr_{(s)} + 3Hg_2Cl_{2(s)} \rightleftharpoons 2Cr^{3+}_{(aq)} + 6Cl^{-1}_{(aq)} + 6Hg_{(l)}$$
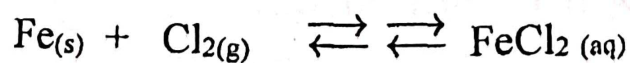
(g) What is the difference between the Turnover Number (k_{cat}) and the Michaelis constant (K_M)? (5×3)

2. (a) Describe briefly the potentiometric method for the determination of emf of a cell.

(b) Determine the cell reaction and EMF for the cell at 25°C

$$Mg(s) \mid MgI_2(0.1 \ M) \mid I_2(s) \mid Pt(s)$$

Given that : $E°_{I^-|I_2} = 0.535 \ V$ and $E°_{Mg^{2+}|Mg} = -2.363 \ V$

(c) Describe the calomel half cell and derive its Nemst equation. (3×5)

3. (a) Determine the cell reaction and E_{cell} for the given cell at 25°C. Assume activity and fugacity equal to molar concentration and pressure (atm), respectively

$$Ag \mid AgBr(s) \mid HBr \ (0.02 \ mol \ dm^{-3}) \mid H_2(0.5 \ bar) \mid Pt$$
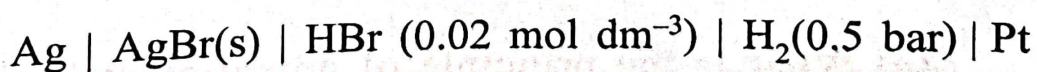
$$E°_{Br^-|AgBr|Ag} = 0.0713 \ V$$

(b) The emf of the cell

$$Ag \,|\, AgCl(s) \,|\, KCl \,(aq) \,|\, Hg_2Cl_2(s) \,|\, Hg$$

is 0.0455V at 298 K and the temperature coefficient is 3.38×10^{-4} VK^{-1}. What is the reaction taking place in the cell and what are the free energy, enthalpy and entropy changes at 298 K?

(c) Describe the glass electrode. Explain, how the pH of a solution is determined using the glass electrode. Also mention its limitations.   (3×5)
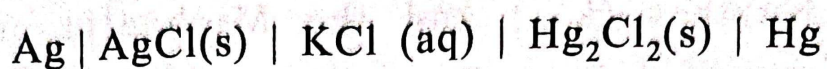
4. (a) Derive the expression for calculating liquid junction potential for a cell in which electrode are reversible with respect to anion. How can it be eliminated?

(b) Determine the standard equilibrium constant for the following reaction at 298 K.

$$2Fe^{3+} + Sn^{2+} \leftrightarrow 2Fe^{2+} + Sn^{4+}$$
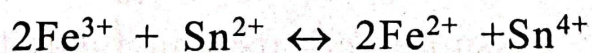
Given, $E^{\circ}_{Fe3+, \, Fe^{2+}} |_{Pt} = 0.771$ V and $E^{\circ}_{Sn^{4+}, \, Sn^{2+}} |_{Pt} = 0.150$V

(c) What is the principle of potentiometric titration? Briefly discuss the potentiometric titration curve for acid-base titration.   (3×5)

5. (a) What is the difference between order and molecularity of the reaction?

(b) Derive the integrated rate equation for the zero-order reaction. How the value of rate constant can be determined using the graphical method?

(c) In the reduction of nitric oxide 50% of the reaction was completed in 140 seconds when the initial pressure was 258 mmHg and in 224 seconds when the initial pressure was 202 mmHg. Find the order of the reaction. (3×5)

6. (a) Describe the collision theory of bimolecular gaseous reactions Show that it leads to the rate expression

$$r = p\{\pi\, \sigma^2_{AB}(\{\frac{8KT}{\pi\mu}\}^{1/2}\, N_A{}^*\, N_B{}^*\,)\, exp^{(-E_o}RT)$$

(b) Discuss the effect of temperature on reaction rates. How is the activation energy of a reaction calculated?

(c) Lindemann mechanism for the first order reaction is as follows :

P.T.O.

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A \qquad \text{(in rapid equilibrium)}$$

$$A^* \xrightarrow{k_2} product \qquad \text{(slow)}$$

Show that it leads to

$$\frac{d(product)}{dt} = \frac{k_2 k_1 [A]^2}{k_{-1}[A] + k_2}$$

Under what conditions will the order of the reaction be equal to one? (3×5)

7. (a) For the reaction

$$C_2H_5I + OH^- \rightarrow C_2H_5OH + I^-$$
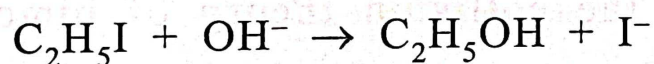
The rate constant was found to have a value of 5.03×10^{-2} mol^{-1} dm^3 s^{-1} at 289 K and 6,71 mol^{-1} dm^3 s^{-1} at 333K. What is the activation energy of reaction. What is the rate constant at 305K.

(b) For the reaction :

$$2\,NO + O_2 \rightleftharpoons 2\,NO_2$$
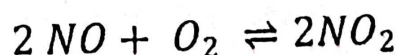
Two mechanisms have been proposed:

(i) $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ (rapid equilibrium)

$N_2O_2 + O_2 \overset{k_2}{\rightarrow} 2NO_2$ (slow)

(ii) $NO + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3$ (rapid equilibrium)

$NO + NO_3 \overset{k_2}{\rightarrow} 2NO_2$ (slow)
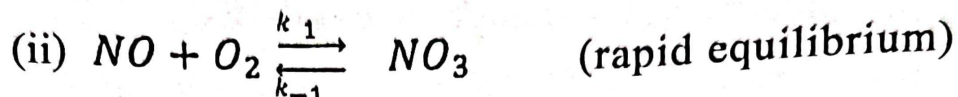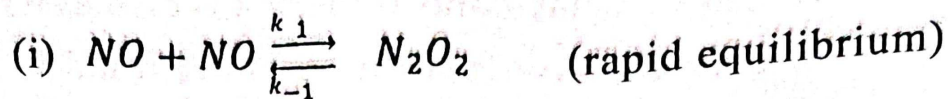
Show that both the mechanisms lead to the same rate law.

(c) Write short note :

    (i) Chain Reactions

    (ii) Steady State Approximation   (3×5)

8.   (a) The mechanism of an acid-base-catalyzed reaction is given below. Derive the corresponding rate law
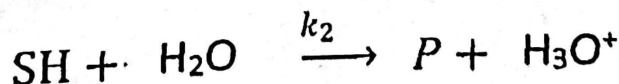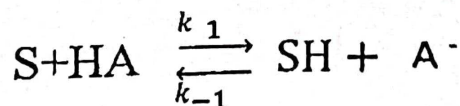
$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH + A^-$$

$$SH + H_2O \overset{k_2}{\longrightarrow} P + H_3O^+$$

$$\frac{d(P)}{dt} = \frac{k_2 k_1 [S][HA]}{k_{-1}[A-] + k_2}$$

P.T.O.

Under what conditions a given catalytic reaction may be classified into a general acid catalysis and specific hydrogen ion catalysis?

(b) (i) Differentiate between Homogeneous and heterogeneous catalysis.

(ii) The use of a catalyst provides an alternate path. Comment.

(c) Discuss briefly the kinetics of Heterogeneous catalysis for unimolecular surface reactions.

(3×5)

(1500)

[This question paper contains 4 printed pages.]

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

Sr. No. of Question Paper : 2925   H

Unique Paper Code   : 32171601

Name of the Paper   : Core: Inorganic Chemistry IV: Organometallic Chemistry

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

Semester   : VI

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 **six** questions.

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

1.   (i) What are the general methods of preparation of simple carbonyls ? Give one reaction for each.

     (ii) Describe the Perutz mechanism of oxygenation of haemoglobin and indicate the trigger for this mechanism?

     (iii) What are trace elements? What is their role in functioning of human body?   (5,5,2.5)

P.T.O.

2. (i) An aqueous solution contains Fe^{3+} and Cr^{3+} ions. Suggest suitable reagents to separate the cations. Give a confirmatory test each for the two cations.

(ii) Give the complete cycle describing each step in the working of the Wilkinson's catalyst for hydrogenation of alkenes.

(iii) Why does *cis*-platin act as anti-cancer agent and not its *trans* isomer, explain.   (5,5,2.5)

3. (i) Is Wilkinson's catalyst sensitive to the nature of the phosphine ligand attached to Rh and the alkene substrate? Explain.

(ii) Discuss giving examples, the changes observed in the IR stretching frequency of the C–O bond in (i) terminal and bridging carbonyl group (ii) in carbonyl compounds of the same metal when some CO molecules are replaced by poor π acceptor groups ?

(iii) Explain why arsenic and lead are toxic for human health.   (5,5,2.5)

4. (i) Why is phosphate ion an interfering ion? Explain giving reactions. Give a scheme for the removal of phosphate ions. Why is the Group II centrifugate boiled with a few drops of concentrated nitric acid before proceeding to Group III?

(ii) What do you mean by reductive carbonylation? Give a suitable example for this. The symmetric CO stretching frequencies in isoelectronic series of $[V(CO)_6]^-$, $Cr(CO)_6$ and $[Mn(CO)_6]^+$ are 1860 cm^{-1} 2000 cm^{-1} and 2090 cm^{-1} respectively. Explain these observations.

(iii) Discuss the aromatic character of Ferrocene.

(5,5,2.5)

5.   (i) Give the use of following reagents in the identification of ions with relevant equations :

   (a) Sodium hexanitrocobaltate(III)

   (b) Sodium nitroprusside

   (c) Zirconyl nitrate

   (d) Ammonium polysulphide

   (e) Ammonium thiocyanate

   (ii) Name the active metal in carboxypeptidase-A? What is the coordination number and how is it satisfied?

   (iii) Draw the structure of dimerictrialkyl aluminium and explain why all Al – C bond lengths are not identical.   (5,5,2.5)

6.   (i) Discuss the working of the sodium-potassium pump. How is it important for a cell?

P.T.O.

(ii) Explain synergism in Zeise's salt. How will the carbon – carbon bond length be affected if the hydrogen atoms of ethene in Zeise's salt are replaced by fluorine?

(iii) Name the two gases involved in the formation of synthetic gasoline by Fischer-Tropsch process. What is the name given to the mixture of these gases?   (5,5,2.5)

7.   (i) What is meant by π acidity? Is CO a stronger π acid ligand than NO^+? Justify your answer.

(ii) A mixture of salts, when heated with ethanol and conc. H_2SO_4 gave a gas which burnt with a green-edged flame when ignited. The mixture also gave a red gas B when heated with potassium dichromate and conc. H_2SO_4. The pungent gas evolved on heating the mixture with sodium hydroxide solution gave a brown precipitate C with potassium tetraiodomercurate (II). The residue left on boiling the mixture with dilute HCl is soluble in hot water and the hot solution gives a white precipitate D with dilute sulphuric acid and a yellow precipitate E with potassium chromate solution. Identify (with formula) A, B, C, D and E and give reactions.

(iii) Differentiate between the significant roles played by myoglobin and haemoglobin in human body.   (5,5,2.5)

[This question paper contains 8 printed pages.]

Sr. No. of Question Paper : 2979   **H**

Unique Paper Code   : 32171602

Name of the Paper   : Organic Chemistry V : Spectroscopy

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

Semester   : VI

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 **Six** questions in all.

1. Attempt any **five** questions :

   (a) How many different types of protons are present in vinyl acetate molecule? Show and give splitting pattern of all the protons.

   (b) What is the difference in IR spectrum of pure ethanol and on dilution with CCl_4? Explain.

     P.T.O.

(c) What is an auxochrome? Explain how an auxochrome exerts a bathochromic shift on a chromophore with suitable example.

(d) In dilute alkaline solution phenolphthalein gives pink colour, however in excess of alkali, it gives a colourless solution. Explain.

(e) What are amphiphilic polymers? Discuss with an example.

(f) Curcumin, an important ingredient of Indian cooking, has immense medicinal values. Give the structure of its main constituent and discuss its use as medicine.   (5×2.5)

2. (a) α-Naphthyl amine on heating with sulphuric acid at 160°C gives compound (A). Benzidine on diazotization gives compound (B). Coupling reaction of compound (A) with Compound (B) produces compound (C), Compound (C) is a direct red dye and absorbs at 498nm in UV spectroscopy.

Write the complete sequence of reactions from (A) to (C) with all the reagents used in the reactions. Give the name of (C) and discuss the colour change of (C) in pH range of 3.1-4.5.

(b) Give synthesis of crystal violet. Label the structures that form the leuco base, colour base and the dye salt.

(c) Explain how the positions of two hydroxyls in Alizarin structure were established? Discuss with an example why Alizarin is known as mordant dye? (4.5,4,4)

3. (a) Identify A, B, C and D in the following reaction. Complete the reaction by giving all the structures

$$\text{Chloramphenicol} \xrightarrow{\text{Alkaline hydrolysis}} [A] \xrightarrow{\text{HIO}_4} [B] + [C] + [D]$$
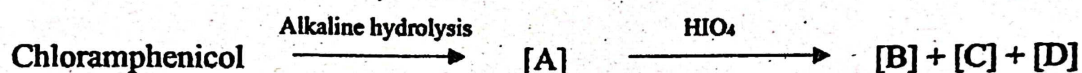
Give IUPAC name, biological active structure, and applications of chloramphenicol.

(b) Write the conventional synthesis of Ibuprofen.

(c) (i) Name the four species of plasmodium responsible for causing malaria.

(ii) Chloroquine is synthesized from a heterocyclic compound (A) and an amine (B). Give the name and synthesis of compound (A). (4.5,4,4)
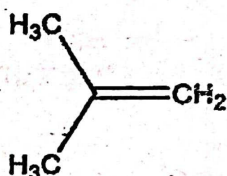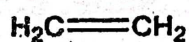
P.T.O.

4. (a) Identify the polymer from the structure given below and give its synthesis from its monomers and discuss its uses.
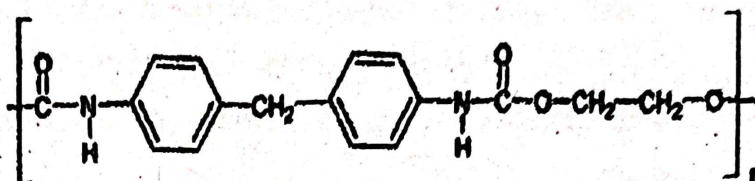
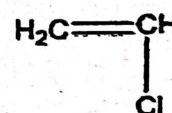(b) Arrange the following monomers in order of their decreasing ability to undergo cationic polymerization with reasons.

(A)   (B)   (C)

(c) Differentiate in chain growth and step growth polymerization with examples.   (4.5,4,4)

5. (a) In ^1H NMR chemical shift values of Acetylene protons, ethylenic protons, ethane protons are δ 1.9, 2.4, 0.9 respectively. Explain.

(b) How will you distinguish between *cis*- and *trans*-cinnamic acid on the basis of PMR spectroscopy?

(c) A and B are two isomers. Assign given peak values appropriately to two isomers of molecular formula C_3H_6O, give their structures and explain all peaks :

UV (in n-hexane)	IR (in KBr)	^1H NMR (CDCl$_3$)
A: 180 nm (ε max 9000)	1720 cm^{-1} (s)	$\delta 2.1$, s, 6H
B: 184 nm (ε max 10000)	2975,2827,	$\delta 9.8$ (t,1H);
	2725,1740 cm^{-1}	$\delta 2.4$ (m,2H);
		$\delta 1.2$ (t,2H)

(4.5,4,4)

6. (a) (i) What is Fermi resonance? Discuss with an example.

(ii) *cis*-1,2-Dichloroethane is IR active while trans-1,2-dichloroethane is IR inactive. Explain.

(b) Distinguish between the following pairs on the basis of IR spectroscopy.

(i) $CH_3CH_2CONH_2$ and $CH_3CH_2NH_2$

(ii) CH_3CH_2OH and $CH_3\text{-}O\text{-}CH_3$
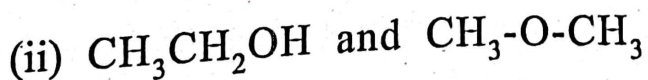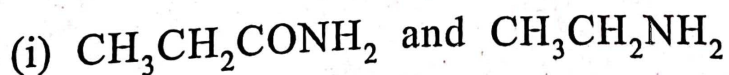
(c) The IR spectrum of ethyl acetoacetate exhibit peaks at 3050,1748,1724 and 1650 cm^{-1}. Assign these peaks with reason to the structural feature of the compound. (4.5,4,4)

7. (a) (i) A compound has λmax 296nm in dioxan but it shifts to 288nm in ethanol. Which transition π ⟶ π* or n ⟶ π* is responsible for this. Explain.

(ii) The wavelength as well as extinction coefficient increases with the increase in conjugation in the compound. Justify the statement.

(b) An unknown compound is believed to have either structure A or B.
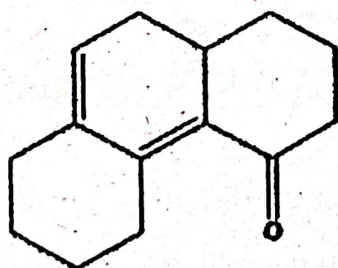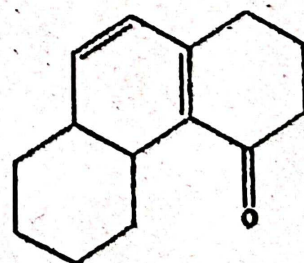
(A)   (B)

Its UV spectrum shows λmax (EtOH) at 330nm. What would be its most likely structure, (calculate λmax using Woodward Fieser rule).

(c) How will you use UV spectral data to distinguish among the following isomeric systems?
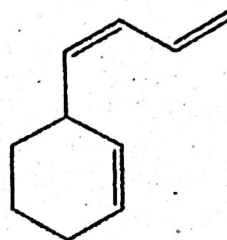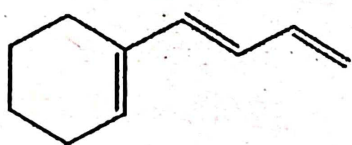
(calculate λmax using Woodward Fieser rule)

(4.5,4,4)

Base value for homoannular (cisoid) diene = 253 nm

Base value for heteroannular (transoid) diene = 214 nm

Base value for acyclic conjugated diene = 217 nm

Base value for Acyclic enone = 215 nm

Increment for:

Alkyl substituent or Ring residue attached to the parent diene = 5 nm

Double bond extending conjugation = 30 nm

Exocyclic double bonds = 5 nm

P.T.O.

Homoannular diene component = 39 nm

α-alkyl group or ring residue = 10 nm

β-alkyl group or ring residue = 12 nm

γ-and higher alkyl group or ring residue = 18 nm

8. (a) One of the constituent of famous antipyretic analgesic drug APC, has the molecular formula $C_{10}H_{13}NO_2$ and displays the following spectral characteristics IR (cm^{-1}): 3250,1650,1275,1050

NMR (δ): 1.4(t, 3H), 2.05(s, 3H), 3.9(q, 2H), 6.7(d,2H, J=8 Hz), 7.4 (d,2H, J=8Hz), 9.8(s,1H)

Calculate its DBE and assign all the peaks of spectral data and identify the structure of the compound.

(b) Give the mechanism of synthesis of polypropylene using BF$_3$ catalyst. (10,2.5)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 4056   **H**

Unique Paper Code   : 2172012401

Name of the Paper   : DSC 10 : Coordination Chemistry and Reaction Mechanism

Name of the Course   : **B.Sc. (Hons) Chemistry (NEP-UGCF-2022)**

Semester   : IV

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 **six** questions in all.

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

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P.T.O.

1. (a) Which is greater: Crystal field splitting in tetrahedral complex or in octahedral complex. Justify your answer giving reasons.

(b) Write the various steps involved in the formation of the complex $[Fe(bpy)_3]^{2+}$ from $[Fe(H_2O)_6]^{2+}$. Third equilibrium constant K_3 is observed to be greater than the second equilibrium constant K_2. Give reason for the same.

(c) Explain the factors affecting crystal field splitting in octahedral complex. (5,5,5)

2. (a) Write all the possible isomers of $[PtCl_2(NH_3)_2(py)_2]$. Predict which of the isomer is optically active? Justify your answer.

(b) Arrange the following complexes in order of anticipated decrease in molar conductance in aqueous solution. Give reason.

$[Pt(NH_3)_6]Cl_4, [Pt(NH_3)_3Cl_3]Cl, K_2[PtCl_6]$

(c) How does the Valence bond theory account for the fact that $[Ni(CN)_4]^{2-}$ is diamagnetic and square planar but $[NiCl_4]^{2-}$ is paramagnetic and tetrahedral.   (5,5,5)

3. (a) A solution containing 2.674 g of $Co(NH_3)_6Cl_3$ (Molar mass = 267.4) is passed through a cation exchange resin. The chloride ion solution thus obtained gave 4.305 g of AgCl (molar mass = 143.5) precipitate with $AgNO_3$ solution. Determine the correct formula of the complex.

(b) Name the type of isomerism in the following pairs of isomers. How will you distinguish the isomers?

     (i) $[Co(en)_2(H_2O)Cl]Cl_2$ and

         $[Co(en)_2Cl_2]Cl.H_2O$

     (ii) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

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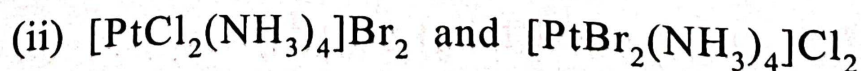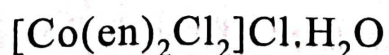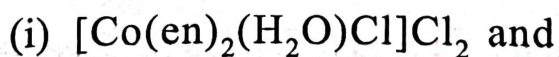
(c) Giving suitable reason explain which of the following in the given pair of complexes will have greater value of Δ_0:

(i) $[Co(NH_3)_6]^{3+}$ or $[Co(H_2O)_6]^{3+}$

(ii) $[Co(NH_3)_6]^{3+}$ or $[Ir(NH_3)_6]^{3+}$ (5,5,5)
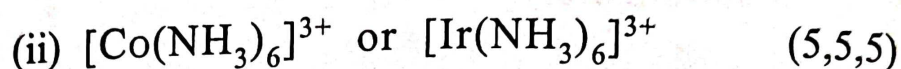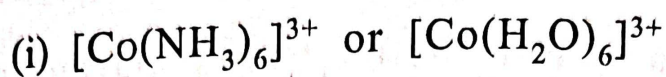
4. (a) Draw MO diagram for $[Co(NH_3)6]^{3+}$.

(b) Calculate the CFSE for d^7 complex in terms of Δ_0 for an octahedral complex, when the ligand is (i) iodide ion (ii) cyanide ion.

(c) What is trans effect? Using trans effect how would you distinguish between cis- and trans- $[PtCl_2(NH_3)_2]$ (5,5,5)

5. (a) Write IUPAC names of the following complexes :

(i) $[Co(NH_3)_5(N_3)]^{2+}$

(ii) $Na[PtBrCl(NH_3)(NO_2)]$

(iii) $[Co(NH_3)_6][Cr(CN)_6]$

(iv) $[(NH_3)_5Co - O_2 - Co(NH_3)_5](NO_3)_4$

(v) $K_4[Fe(CN)_6]$
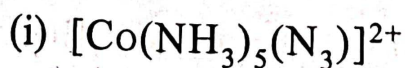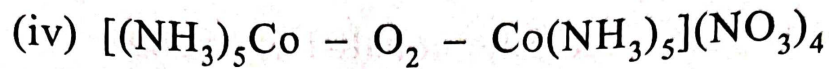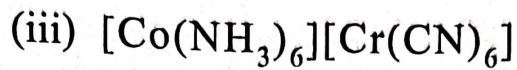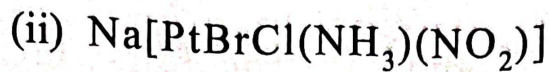
(b) What is meant by thermodynamic and kinetic stability of the complexes? Explain giving suitable examples.

(c) What is meant by chelate effect? Which of the following complexes has greater stability? Explain giving reasons.

$[Co(pn)_3]^{3+}$ or $[Co(tn)_3]^{3+}$ where pn is 1,2-diaminopropane and tn is 1,3-diaminopropane.

(5,5,5)

P.T.O.

6. (a) Write the formula for the following complexes according to the IUPAC system of nomenclature :

   (i) μ-amido-μ-superoxidobis[bis(ethane-1,2-diamine)cobalt(III)]nitrate

   (ii) tetraamminechloridonitrito-N-cobalt(III) ion

   (iii) triamminediaquachloridocobalt(III) sulphate

   (iv) tetrakis(triphenylphosphane)platinum(0)

   (v) sodium carbonylpentacyanido-C-ferrate(III)

   (b) Using Valence Bond theory identify the following as labile and inert complex :

   (i) $[V(NH_3)_6]^{3+}$

   (ii) $[Cr(CN)_6]^{3+}$

   (c) Write merits and demerits of crystal field theory.

   (5,5,5)

7. (a) Define Jahn - Teller theorem. In solid state CuF_2 is octahedrally surrounded by 6 F^- ions, with 2 Cu—F bond distances are 2.01 A^0 and 4 Cu—F bond distances are 1.85 A^0. Explain

(b) Draw and explain the crystal field splitting diagram for square planar complex.

(c) Give an example of the following ligands, write their structures and mention the donor atoms present in them :

    (i) bidentate ligand

    (ii) hexadentate ligand   (5,5,5)

8. Write short note on : **(Any three)**

(a) Structural isomerism

(b) Theories of Trans effect

                                       P.T.O.

(c) Inner and Outer orbital complex

(d) Spectrochemical series   (5,5,5)

9

[This question paper contains 8 printed pages.]

Sr. No. of Question Paper : 4094   **H**

Unique Paper Code   : 2172012402

Name of the Paper   : DSC: Carbohydrates, Lipids
                            and Heterocyclic Compounds

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

Semester   : IV

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 **six** questions in all.

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

P.T.O.

1. (a) Compound A, $C_6H_{12}O_6$, a monosaccharide reacts with HCN followed by acid hydrolysis to give B, $C_7H_{14}O_8$ (a hydroxy acid). B on reduction with HI/P gives 2-Methylhexanoic acid. Identify A and B. Give complete sequence of reaction with structures. What inference can be drawn from above sequence.

   (b) Write open chain structure for the aldaric acid obtained by Nitric acid oxidation of D-(+)-Mannose. Is the product optically active? Explain with the help of structure.

   (c) What are epimers and anomers? Suggest a method to convert D-(+)-Glucose to D-(+)-Mannose.

   (d) Explain Mutarotation taking Glucose as an example.   (4,4,4,3)

2. (a) Draw conformational structures of α-D-(+)-Glucopyranose and β-D-(+)- Glucopyranose. Which of the two is more stable, give reason.

(b) Explain Amadori rearrangement for the formation of Glucosazone from D-Glucose.

(c) How the ring size of Glucose was confirmed as pyranose ring with periodic acid method? Justify your answer.

(d) Why D-(-)-Fructose inspite of having a ketonic functional group gives positive test with Fehling's solution? Give the relevant reaction.   (4,4,4,3)

3. (a) How will you convert Pyrrole into 3-Chloropyridine? Give the reaction and the mechanism involved.

(b) Arrange the following compounds in increasing order of aromaticity. Draw the relevant resonating structures and explain.

Furan, Thiophene. Pyrrole

(c) Carry out the following conversions :

(i) Pyridine to 3-Aminopyridine

(ii) Pyrrole to N-Methyl pyrrole

(d) What happens when Quinoline reacts with sodamide in presence of ammonia followed by hydrolysis. What type of reaction is it.

(4,4,4,3)

4. (a) Pyrrole can act as a weak acid as well as a weak base. Give reason and reaction of Pyrrole with a strong acid and a strong base.

(b) Pyridine undergoes Nucleophilic substitution reaction preferably at C-2 position. Show the attack of nucleophile to justify the above statement.

(c) Electrophilic substitution in Indole occurs in the pyrrole ring but in Quinoline, benzene ring is more reactive towards electrophilic substitution. Give reason.

(d) What are phospholipids? Give one example and their biological importance. (4,4,4,3)

5. (a) Explain why Maltose reduces Fehling's solution. What are the products formed on hydrolysis of Maltose. Write down the Haworth projection of the hydrolysis product. What type of linkage is present in Maltose.

(b) What happens when Lactose reacts with

    (i) HCl/H_2O

    (ii) CH_3OH/HCl

Give the chemical reactions involved in both.

(c) Answer the following :

    (i) What is invert sugar? How is it formed?

    (ii) Give Haworth projection of Sucrose. Also give its systematic name.

(d) What are polysaccharides? Give two differences between starch and cellulose? (4,4,4,3)

6. (a) Define acid value and iodine value of oils and fats. Give their significance.

(b) In Skraup synthesis, violent reaction occurs when Aniline reacts with glycerol and conc. sulfuric acid in the presence of Nitrobenzene. Give the reaction and its mechanism. What is the role of Nitrobenzene in this reaction. How can this reaction be controlled.

(c) Explain why Pyridine is more basic than Pyrrole but less basic than aliphatic amine.

(d) Give one example each of ω - 3 & ω - 6 fatty acids with their structures. (4,4,4,3)

7. (a) Write the complete reaction and the product formed :

   (i) 2,5-Hexadione is heated with NH_3

   (ii) Pyrrole is reacted with Benzenediazonium chloride in presence of dil. alkali

(iii) Furan on heating with Maleic anhydride

(iv) Thiophene on hydrogenation in presence of Raney Ni

(v) Indole reacts with $CH_3COCl/SnCl_4$

(vi) Quinoline reacts with conc. H_2SO_4 at 220°C

(b) Quinoline on oxidation with $KMnO_4$ gives a dicarboxylic acid A ($C_7H_5O_4N$). A on heating with Se/H_2SO_4 undergoes selective decarboxylation to give B which on further treatment with PCl_5 and NH_3 gives C. C on Hoffmann bromamide reaction gives 3-Aminopyridine. Complete the sequence of reaction giving structures of A, B and C.

(6×2,3)

8. (a) Write short notes on **(Any three)** :

(i) Hantzsch synthesis for Pyrrole

(ii) Fischer Indole synthesis

P.T.O.

(iii) Killiani-Fischer synthesis

(iv) Friedlander synthesis of Quinoline

(b) Write the structure of Glyceryl trioleate. Give the products obtained on its hydrolysis and hydrogenation. (4,4,4,3)

Sr. No. of Question Paper: 4183   Your Roll No. ....

Unique Paper Code: 2173012011

Name of the Paper: DSE: Reactions, Reagents and Chemical Process

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

Semester: IV

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. All parts of a question should be attempted together.

3. Each question carries 15 marks.

1. Explain the following reaction with suitable mechanism. (5, 5, 5)

 (a) Bischler-Napieralski Reaction

 (b) Darzens reaction

 (c) Demjanov rearrangement

2. (a) The most suitable reagents for performing the following transformation are? (1x5, 2x5)

i)

ii)

iii)

iv) H_3C—CH=CH—COOEt ⟶ H_3C—CH$_2$—CH$_2$—CH$_2$OH

v)
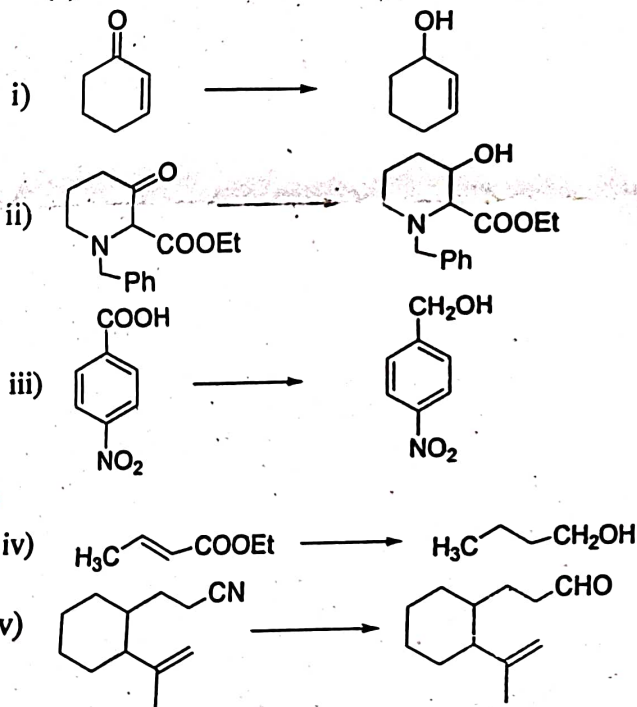
(b) Write the structure of following reagents

    (i) Tebbe's reagent

    (ii) TPAP reagent

    (iii) ABNO reagent

    (iv) PMHS reagent

    (v) DEAP reagent

3 (a) What is synthetic utility of DAIBAL-H and LAH in organic synthesis explain with suitable example. (10, 5)

 (b) Write the structure and synthetic application of following reagents

    (i) Swern Reagent

    (ii) Jones Reagent

4. (a) What is Wacker oxidation. Explain role of catalyst and co-catalyst used in Wacker oxidation with suitable example. (5, 5, 5)

(b) Which reagent/ catalyst used in the following reactions
    (i) Wittig reaction
    (ii) Corey Kim Oxidation reaction
    (iii) Prevost Reaction

(c) Explain the Heck reaction with suitable mechanism.

5. (a). Complete the following reaction by giving major product. (12, 3)

i)

C_6H_5O —≡ $\xrightarrow[\Delta]{C_6H_5CH_2N_3}$

ii)

COOH (on benzene ring) $\xrightarrow{Na/ NH_3 (l)}$

iii)

(benzene)–NHCOCH$_3$ $\xrightarrow[\text{Toluene / Reflux}]{POCl_3}$
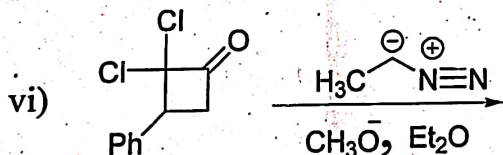
iv)

Cl—CH$_2$—C(=O)—OEt $\xrightarrow[^tBuOH]{^tBuO^-}$

v)

(epoxide)—COOEt $\xrightarrow{\text{1. NaOH} \quad \text{2. HCl}}$

vi)

Cl, Cl–(cyclobutanone)–Ph + $H_3C\overset{\ominus}{C}\overset{\oplus}{-}N≡N$ $\xrightarrow{CH_3\bar{O},\ Et_2O}$
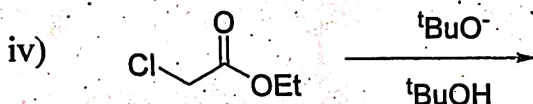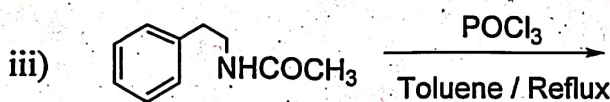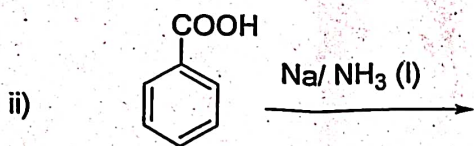
(b) What is Birch reduction? Explain with suitable example.

6. (a) What is Suzuki coupling reaction? Write the steps involves in the mechanism of involves in Suzuki coupling reaction. (5, 5, 5)

(b) Write the reaction and mechanism of Julia olefination reaction?

(c) Which reactant and reagent is used in Chugaev Reaction. (5, 5, 5)

7. (a) Explain large scale process with at least two suitable examples?

(b) Explain validation of large-scale process with suitable examples?

(c) Explain the stages of scale up process with suitable examples? (5, 5, 5)

8. Write short notes on following

(a) Halogenation & types of halogenations

(b) Swern Oxidation.

(c) Fenton's reagent.

/ /

[This question paper contains 8 printed pages.]

Instructions for Candidates

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

2. Attempt any Six questions in all including Q. No. 1, which is compulsory.

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

1. Attempt **any five** of the following:

(a) Explain the basic principle of pH metric titrations. Give name and explain any one indicator electrode.

(b) "Multistep extraction is more efficient as compared to single step extraction". Justify it

(c) How Adsorption chromatography differs from Partition chromatography.

(d) Explain the origin of spectra. How molecular spectra differs from atomic spectra.

(e) How Furnace heating rate and Furnace atmosphere affect the thermo gravimetric results? Explain it.

(f) Explain how tests of significance are helpful in the statistical quantitative analysis.

(g) What are the variables that affect the column efficiency? How column efficiency can be increased?   (5x3)

2.   Attempt **any three** from the following:

    (a) Classify electro-analytical methods or thermal methods of analysis.

    (b) What are the various methods of *introduction of sample* in atomic absorption spectroscopy (AAS)?

    (c) What are different types of wavelength selectors used in UV-VIS spectrophotometer. Explain any one.

    (d) Define Thermo Gravimetric Analysis (TGA)? Discuss decomposition analysis of $CuSO_4.5H_2O$ using TGA curve.   (3x4)

3.   **Attempt the following:**

    (a) Explain the various processes involved in Flame Emission Spectroscopy (FES).

                                 P.T.O.

(b) Explain redox potentiometric titration with electrode system with suitable example.

(c) Explain the preparation of TLC plates and give its analytical applications. (3x4)

4. Attempt **any three** of the following:

(a) Prove that A=2-log % T. Why absorptivity remains same while absorbance changes within the Beer's law. What is the absorbance range of Beer's law?

(b) Define determinate errors? What are the sources of determinate errors?

(c) Define background absorption. Explain any one background correction method..

(d) State and explain Nernst Distribution law and give two limitations of the law. (3x4)

5. **Attempt the following:**

   (a) Define Accuracy and Precision. What are the various ways of expressing accuracy and precision?

   (b) Define ion exchange chromatography? Explain the action of cation exchange resin.

   (c) Write the difference between line source and continuous source with examples of each. (3x4)

6. Attempt any three of the following:

   (a) How Refractory compound formation affects the results in AAS/AES. How can we avoid such situation in analysis.

   (b) What is meant by the term sampling. Define Grab sample and Gross sample.

P.T.O.

(c) Draw and explain the Conductometric Titration Curve of the following:

(i) Strong Acid vs Strong Base

(ii) Weak Acid vs Strong Base

(iii) Mixture of Acids vs Strong Base

(d) Explain classical methods of analysis. Describe the terms:

(i) Proximate analysis,

(ii) Partial analysis,

(iii) Complete analysis (3x4)

7. Distinguish between the followings (any three):

(a) Batch extraction and continuous extraction

(b) Single beam spectrophotometer and double beam spectrophotometer

(c) Plate number and plate height

(d) Standard deviation of mean and relative standard deviation

(e) Prism and Gratings (3x4)

8. **Attempt the following:**

(a) The mean $\bar{x}$ of four deviations of the copper content of a sample of an alloy was 8.27% with standard deviation s= 0.17%. Calculate the 95% confidence limit for the true value. (t for 95% confidence for 3 degrees of freedom is 3.18).

(b) Discuss the various burner designs used in AAS and FES? Why turbulent flow burners never strike back?

P.T.O.

(c) Discuss the frontal, elution and displacement methods of the development of chromatograms.

(3x4)

Sr. No of the question paper : **3140**
Name of the Course : B.Sc. (H) Chemistry
Semester : VI
Name of the paper : DSE-8: Green Chemistry
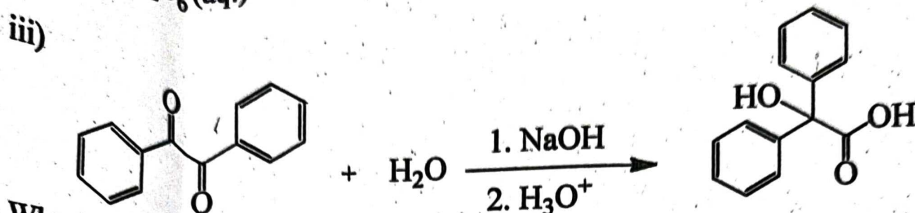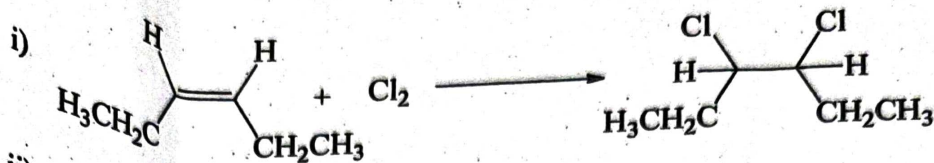Unique Paper Code : 32177908

Duration: 3 hrs   Maximum Marks: 75

Instruction for the candidates
1   Write your Roll no. on the top immediately on the receipt of the question paper.
2   Attempt *Six* questions. All parts of a question should be attempted together.
3   Each question carries 12.5 marks.

1   (a) ISD stands for ....: Discuss the concept of ISD. Name the chemical involved for Flixborough tragedy. How it was responsible for the tragedy?
    (b) Why catalytic amount of reagent is favoured over the stoichiometric amount of the same reagent? Explain with suitable examples.
    (c) Write an account on the terms used in the Pollution Prevention Act 1990 by US Environmental Protection Agency (EPA).
                                                                                (4.5, 4, 4)

2   (a) Name the green chemistry principle involved in the synthesis of Poly lactic acid (PLA). Write the efficient green synthesis of PLA from corn. Discuss its merits and demerits.
    (b) Discuss the merits of microwave assisted reactions over conventional reactions in water (*Any two*):
        i)   Oxidation of toluene
        ii) Saponification
        iii) Hydrolysis of benzyl chloride
    (c) Fill in the blanks (*Any four*):
        i)   Chlorofluoro carbon causes .... of ozone layer.
        ii) Addition reactions have .... percent atom economy.
        iii) .... is extracted from orange peel using supercritical CO_2.
        iv) E-factor is ....
        v)   .... is the Father of green chemistry.
                                                                                (4.5, 4, 4)

3   (a) Define cradle to cradle carpeting. Why EcoWox carpeting produced by Shaw industries is preferred over PVC backed carpeting.
    (b) How does the use of protecting/deprotecting group(s) affect the atom economy of the reaction? Explain using appropriate example.
    (c) Write short notes on (*Any two*):
        i)   Combinatorial chemistry
        ii) Environmentally advanced wood preservatives
        iii) Solventless reactions
                                                                                (4.5, 4, 4)

4 (a) Define atom economy. Calculate the atom economy of the reactions given below (*Any two*):

i)

$$H_3CH_2C-CH=CH-CH_2CH_3 + Cl_2 \longrightarrow H_3CH_2C-CHCl-CHCl-CH_2CH_3$$

ii)

$$C_6H_{12}O_6 \text{(aq.)} \longrightarrow 2C_2H_5OH\text{(aq.)} + 2CO_2\text{(g)}$$

iii)

$$+ H_2O \xrightarrow[\text{2. } H_3O^+]{\text{1. NaOH}}$$

(b) Why ionic liquids are called "Designer solvents"? What are their structural characteristics?

(c) Give green synthesis of the following (*Any two*):
i) Hoffmann elimination reaction using microwave
ii) Disodium iminodiacetate
iii) Catechol

(4.5, 4, 4)

5 (a) What is interesterification of oils? Differentiate between chemical interesterification and enzymatic interesterification.

(b) What is cocrystal control solid state synthesis? Give one example.

(c) Percentage yield is different from atom economy. Explain.

(4.5, 4, 4)

6 (a) Plastic waste imposes a great problem in today's World. How an environmentalist and green chemist deals to get rid of plastic from the environment? Enlist the points of differentiation between environmental chemistry and green chemistry.

(b) What is waste or pollution prevention hierarchy? Explain.

(c) Provide the green alternative to Simmons-Smith reaction and how it is a better alternative to conventional method.

(4.5, 4, 4)

7 (a) Which gas was responsible for the "Bhopal gas tragedy"? Give the conventional and green method for the synthesis of carbaryl.

(b) Although CO_2 is a green house gas but still supercritical CO_2 is considered as green solvent. Justify.

(c) What is naturally occurring plant growth stimulators. Give its advantages.

(4.5, 4, 4)

8 (a) Explain microwave assisted synthesis of copper(II) complex of phthalocyanine. What are its advantages over conventional synthesis. Also name the green chemistry principle involved in its synthesis.

(b) What are photocatalysts? How photocatalytic reactions are different from photochemical reactions?

c) What is biodiesel? How is it prepared and give the reaction involved? What is the composition of B20?

(4.5, 4, 4)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 3354   **H**

Unique Paper Code   : 42171205

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

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

Semester   : II

Duration : 3 Hours   Maximum Marks : 75
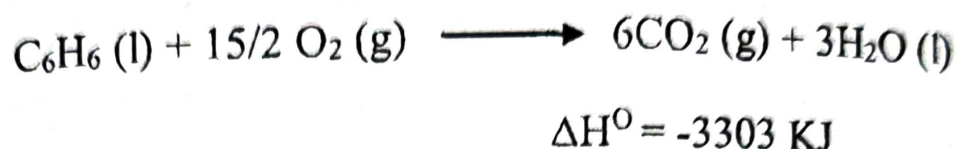
Instructions for Candidates

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

2. **Section A** and **B** are **two** parts given in question paper, students should be asked to attempt separately.

3. Attempt any **THREE** questions each from **Section A** and **Section B**.

4. **All** questions carry **12.5** marks each.

5. Attempt all parts of a question together.

    P.T.O.

SECTION A

1. (a) Calculate the heat of formation of benzene from the following data :

$$C_6H_6 \text{ (l)} + 15/2 \text{ } O_2 \text{ (g)} \longrightarrow 6CO_2 \text{ (g)} + 3H_2O \text{ (l)}$$

$$\Delta H^O = -3303 \text{ KJ}$$

$$\Delta H_f^O \text{ (CO}_2\text{)} = -393.5 \text{ KJ}$$

$$\Delta H_f^O \text{ (H}_2\text{O)} = -285.8 \text{ KJ}$$

(b) Calculate the enthalpy change for the following reactions

(i) C_2H_4 (g) + Cl_2 (g) $\longrightarrow$ $C_2H_4Cl_2$ (g)

(ii) C_2H_6 (g) + $2Cl_2$ (g) $\longrightarrow$ $C_2H_2Cl_2$ (g) + 2HCl (g)
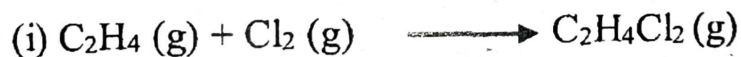
Given B.E. (C-C) = 348 KJmol^{-1}

Given B.E. (C-H) = 413 KJmol^{-1}

Given B.E. (Cl-Cl) = 242 KJmol^{-1}

Given B.E. (C-Cl) = 328 KJmol^{-1}

Given B.E. (H-Cl) = 432 KJmol-1

(c) Derive Kirchhoff s equation thermodynamically. Given the brief account for the importance of Kirchhoff s equation in thermodynamic studies.

(4,4,4.5)

2. (a) What is meant by 'degree of hydrolysis' and 'hydrolysis constant'?

Describe the relationship between hydrolysis constant and the dissociation constant of the base for the hydrolysis of a salt of strong acid and a weak base.

(b) At a certain temperature, degree of dissociation of pure water is 1.81×10^{-9}. Calculate the ionic product of water at this temperature.

(c) Calculate the pH of a solution obtained by mixing 5 gm of acetic acid and 7.5 gm of sodium acetate and making the volume equal to 500 ml? Dissociation constant of acetic acid at 25°C is 1.75×10^{-5}.

(4,4.4.5)

P.T.O.

3.   (a) For a rection

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
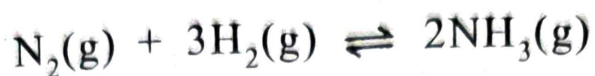
$$Kp = 1.64 \times 10^{-4} \text{ at } 673 \text{ K.}$$

Calculate :

    (i) $\Delta G°$ and

    (ii) ΔG when the pressure of N_2 and H_2 are maintained at 10 and 30 atm, respectively and NH_3 is removed at a partial pressure of 3 atm.

    (iii) Is this process spontaneous?

(b) For the reaction $N_2O(g) \longrightarrow 2NO_2(g)$ at 300K, and 1 atm Kp = 0.157. Calculate Kc & Kr for this reaction.

(c) State & explain Le Chatelier's Principle. Apply this principle to study the effect of temperature, pressure and concentration for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4 \text{ KJ}$$

                                                                  (4,4,4.5)
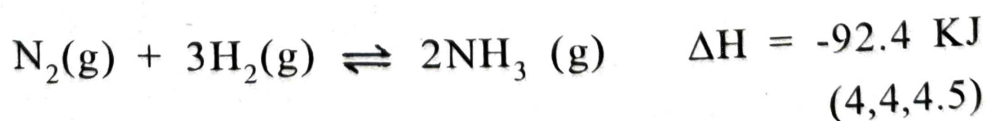
4. (a) Calculate the enthalpy change for the following reaction at 25°

$$C_2H_6 (g) + 7/2\ O_2(g) \longrightarrow 2CO_2 (g) + 3H_2O (1)$$

$\Delta H_f^{\circ} (CO_2) = -393.5\ KJ$

$\Delta H_f^{\circ} (H_2O) = -285.8\ KJ$

$\Delta H_f^{\circ} (C_2H_6) = -84.5\ KJ$

$\Delta H_f^{\circ} (H_2O) = 0$

(b) The equilibrium constant, Kp for the reaction :

$A + B \rightleftharpoons C + D$ is 1×10^{-12} at 600 K and 1×10^{-7} at 800 K. Calculate the heat of reaction.

(c) The solubility product of magnesium hydroxide $Mg(OH)_2$ at 25°C is 1.24×10^{-11}. Calculate the solubility of magnesium hydroxide in grams per litre? (Mg = 24, O = 16, H = 1).

(4,4,4.5)

P.T.O.

SECTION B
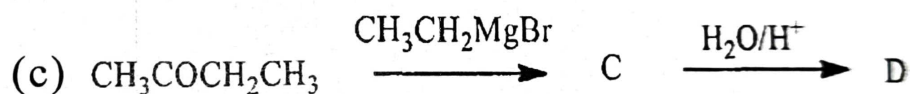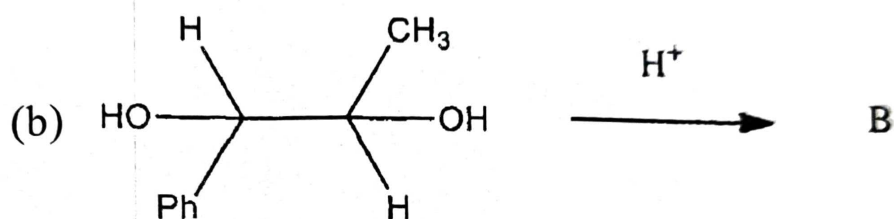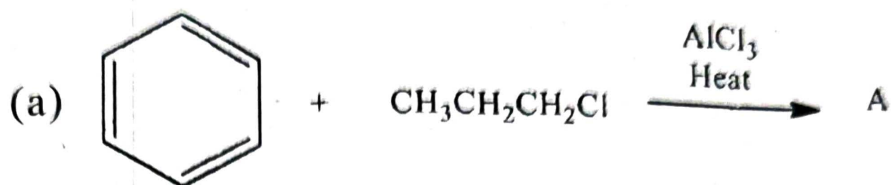
1. (i) Complete the following reactions :

(a) + $CH_3CH_2CH_2Cl$ $\xrightarrow{\text{AlCl}_3 \ \text{Heat}}$ A

(b) $\xrightarrow{H^+}$ B

(c) $CH_3COCH_2CH_3$ $\xrightarrow{CH_3CH_2MgBr}$ C $\xrightarrow{H_2O/H^+}$ D

(ii) Carry out following conversion:

(a) Cumene to Phenol

(b) Toluene to Benzaldehyde

(iii) Write a suitable test to distinguish following pair of compounds :

(a) CH_3CHO and C_6H_5CHO

(b) Ethanol and Phenol   (4,4,4.5)

2. (i) Explain Williamson's synthesis of t-Butyl ethyl ether.

    (ii) Explain S$_N$I mechanism with suitable example.

    (iii) Which one is more reactive in nucleophilic addition reaction, Benzaldehyde or Propanol. Explain your answer.   (4,4,4.5)

3. (i) Explain the effect of nitro substituent on reactivity of haloarenes.

    (ii) Why phenols are more acidic than aliphatic alcohols. Compare the acidity of nitrophenol with phenol.

    (iii) Differentiate between Aldol and Cannizzaro reaction by suitable examples and mechanism.

                                              (4,4,4.5)

4. Write short notes on any **three** of the following :

    (i) Benzoin condensation

                                                    P.T.O.

(ii) Lucas test for alcohol

(iii) Reimer-Tiemann reaction

(iv) Wolff Kishner reduction   (4,4,4.5)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 4002   H

Unique Paper Code	: 2172512401
Name of the Paper	: DSC : Chemistry of Carboxylic Acids & their Derivatives, Amines and Heterocycles
Name of the Course	: **B.Sc. (Prog.) LS/PS/IC/ Electronic Sciences**
Semester	: IV

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 out of **SIX**.

3. All parts of a question should be attempted together.

4. Each question carries **15 marks**.

P.T.O.

1. Write the synthesis of any **five** of the following compounds using Ethyl Acetoacetate.

   (a) *n*-Butanoic acid

   (b) Butanone-2

   (c) Succinic acid

   (d) Adipic acid

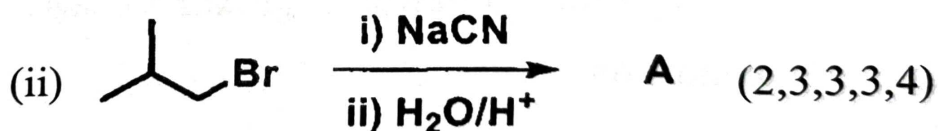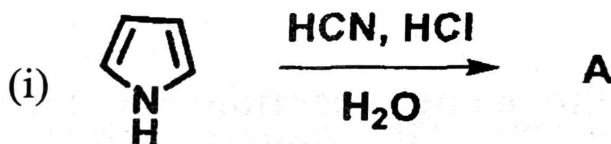   (e) Methyl ketone

   (f) Crotonic acid   (3,3,3,3,3)

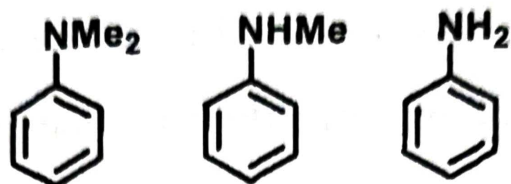2. (a) Write the reaction for the synthesis of Tribromobenzene from aniline.

   (b) Write the reaction of Diazotization and explain the mechanism.

(c) Explain, why Pyrrole behaves as both weak acid and weak base?

(d) Arrange pyrrole, thiophene and furan in decreasing order of their aromaticity. Justify your answer.

(e) Complete the following reactions and specify A?

(i) $\xrightarrow[\textbf{H}_2\textbf{O}]{\textbf{HCN, HCl}}$ **A**

(ii) Br $\xrightarrow[\text{ii) H}_2\text{O/H}^+]{\text{i) NaCN}}$ **A** (2,3,3,3,4)

3. (a) Pyridine undergoes nucleophilic substitution at position 2 and 4, explain.

(b) Explain basicity order of following amines :

NMe$_2$ NHMe   NH$_2$

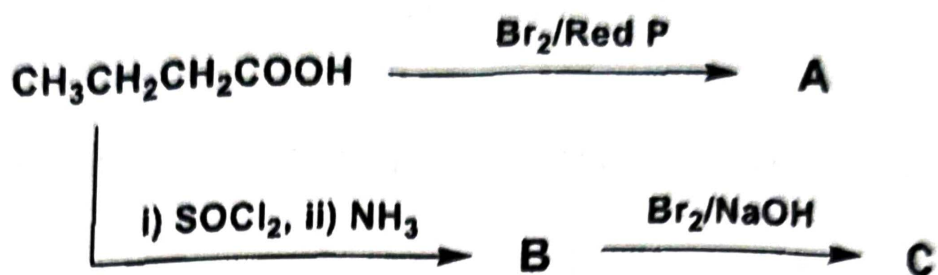(c) Write the reaction involved when Furan treated with maleic anhydride and name the reaction.

(d) Write the name, reaction and mechanism for the synthesis of primary amines when acetamide reacts with Br$_2$ under alkaline condition.

(e) Distinguish between primary, secondary and tertiary amines by using benzene sulfonyl chloride. (3,3,3,3,3)

4002

4. (a) Arrange the following compounds in order of their increasing acidity :

$ClCH_2COOH$, CH_3COOH, FCH_2COOH, $BrCH_2COOH$
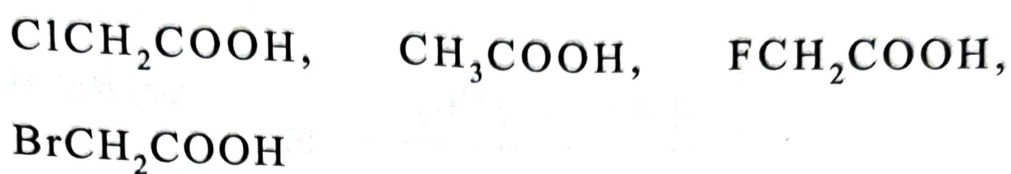
(b) Explain Chichibabin reaction with suitable example.

(c) How do you synthesize 2,5-dimethyl pyrrole using Paal-Knorr Synthesis?

(d) Why tertiary amines with three different groups to nitrogen atoms do not show optical activity? Explain by taking a suitable example.

(e) Complete the following sequence of reactions giving structures of A, B and C. Also give the name of reaction.

P.T.O.

$$CH_3CH_2CH_2COOH \xrightarrow{\quad Br_2/Red\ P \quad} A$$

I) $SOCl_2$, II) NH_3

$$B \xrightarrow{\quad Br_2/NaOH \quad} C$$

(2,3,3,3,4)

5. (a) Put the amines in their increasing order of basicity under gas phase :

CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, NH_3

(b) Explain, why trichloroacetic acid is stronger acid than acetic acid?

(c) How will you synthesize phenol from benzenediazonium chloride.

(d) Write the IUPAC name of the following heterocyclic compounds :

CH_3CH_2COOH $CH_3CH_2CONH_2$

      i   ii   iii
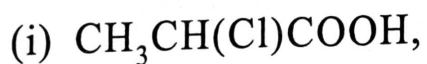
(e) Explain, acidic hydrolysis of furan led to the formation of furan hydrochloride salt which turns into brown resin in presence of O_2.

(2,3,3,3,4)

6. (a) Arrange the following in increasing order of their acidic Strength.

      (i) $CH_3CH(Cl)COOH$,

      (ii) $CH_3CH(NO_2)COOH$,

      (iii) $CH_3CH(CH_3)COOH$,

      (iv) $CH_3CH(Br)COOH$

P.T.O.

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

   (i) Alkaline Ester Hydrolysis

   (ii) Hell-Volhard Zelinsky Reaction

   (iii) Claisen Condensation

   (iv) Reformatsky Reaction

(c) Explain, why acid halides are more reactive than acid anhydrides.   (2,3,3,3,4)

[This question paper contains 8 printed pages.]

Sr. No. of Question Paper : 3358   **H**

Unique Paper Code   : 42174404

Name of the Paper   : DSC-Chemistry of s- and 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 **Section A** and **Section B** on separate sheets.

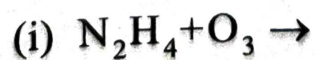3. Use of scientific calculator and log table is allowed.
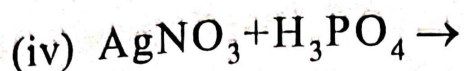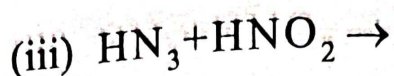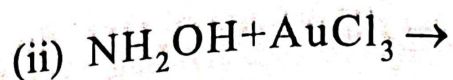
P.T.O.

SECTION A

(INORGANIC CHEMISTRY)

Attempt any **three** *questions.*

1. (a) Define Ionization energy. What are the factors effecting it?

   (b) Give the names and structure of the oxoacids of sulphur.

   (c) N-N bond is weaker than P-P single bond. Explain.

   (d) Which is stronger reducing agent, NH_3 or PH_3 and why?   (4,4,2,2.5)

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

      (i) $H_4P_2O_7$

      (ii) $HClO_4$

   (b) In contrast to diamond graphite conduct electricity? Explain

(c) Explain electrolytic refining with suitable examples.

(d) Draw and explain the bonding and structure in diborane? (4,4,2,2.5)

3. (a) Discuss the slope of CO gas in Ellingham diagram.

(b) What is oxidative refining? Explain tossing and puddling.

(c) Write short note on following :

(i) Mond's Process

(ii) Van Arkel-De Boer process

(iii) Calcination and roasting (4,4,4.5)

4. (a) Complete the following reactions :

(i) $N_2H_4 + O_3 \rightarrow$

(ii) $NH_2OH + AuCl_3 \rightarrow$

(iii) $HN_3 + HNO_2 \rightarrow$

(iv) $AgNO_3 + H_3PO_4 \rightarrow$

(b) Explain the reducing behaviour of both hydrazine and hydroxylamine with iron (III) chloride, also give the balance reactions in both cases.

(c) Explain the followings :

   (i) Hydrometallurgy

   (ii) Which reducing Sn^{2+} or Sn^{4+} and why?
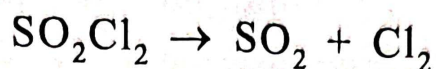
   (4,4,4.5)

SECTION - B

(PHYSICAL CHEMISTRY)

Attempt any **three** *questions.*

5. (a) (i) Show that for a first order reaction the half life period is –

$$t_{1/2} = \frac{0.693}{k}$$

      (ii) The half life of the homogeneous gaseous reaction

$$SO_2Cl_2 \rightarrow SO_2 + Cl_2$$

which obeys first order kinetics is 8 min. How long will it take for concentration of SO_2Cl_2 to reduce to 1% of the initial value?

(b) What do we mean by order of reaction? Describe the half-life method for determination of order.

(c) Explain the Maxwell Law for distribution of molecular velocities with a diagram showing the distribution at three different temperatures.

                                              (2+2,4,4.5)

6. (a) (i) Show that

$$ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

                                              P.T.O.

(ii) The rate constant of a second order reaction is 5.70×10^{-5} dm^3 mol^{-1}s^{-1} at 25°C and 1.64×10^{-4} dm^3 mol^{-1}s^{-1} at 40°C. Calculate the activation energy for the reaction.

(b) Define the surface tension of a liquid and describe in detail its determination using a stalagmometer.

(c) What are Miller Indices? Calculate the miller indices of crystal planes which cut through the crystal axes at

   (i) (2a,3b,c)

   (ii) (a,∞,c)

   (iii) (∞,3b,3c)   (2+2,4,4.5)

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

   (i) Viscosity of gases and its dependence on temperature and pressure.

   (ii) Frenkel defect

   (iii) Structure of NaCl

(b) Calculate the average, root mean square and most probable speeds for oxygen molecules at 298K.

(c) Show that for a second order reaction A + A → products, with 'a' as initial concentration of each reactant and 'a-x' as concentration at time t,

$$k = \frac{1}{t}\left(\frac{1}{(a-x)} - \frac{1}{a}\right)$$

For such a reaction, what is the slope of the plot of x/a(a – x) vs t?   (2+2,4,4.5)

8. (a) Calculate the pressure exerted by one mole of Oxygen gas at 298K, contained in a container of volume 5 litres, if the gas is a) ideal b) Van der Waals gas. Given a = 5.5 L^2 atm mol^{-1}, b = 63.8 cm^3 mol^{-1}, R = 0.082 L atm K^{-1} mol^{-1}.

(b) (i) Explain law of rational indices.

(ii) Show that effective volume is four times the volume of the gas.

P.T.O.

8

(c) (i) Explain elements of symmetry present in NaCl crystal?

(ii) Write a short note on X-ray diffraction.

(4,2+2,2+2.5)

(500)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 3455   **H**

Unique Paper Code   : 42177926

Name of the Paper   : DSE: Organometallics, Bio-Inorganic Chemistry, Polynuclear Hydrocarbons and UV, IR

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

Semester   : VI

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. Students should attempt **Section A** and **Section B** separately.

P.T.O.

Section A :

## Organometallics, Bio-inorganic Chemistry

(Attempt any **three** *questions)*

1. (a) Which of the following are organometallics compounds: $Ti(OEt)_4$, $B(OMe)_3$, $(\eta^5\text{-}C_5H_5)_2$ fe and $K[PtCl_3(C_2H_4)]$? Give reason.

   (b) Draw MO diagram of CO and explain how CO acts as an electron pair donor and acceptor through carbon and not through oxygen.

   (c) Give one method of synthesis of ferrocene and discuss its structures in solid and gaseous states.

                                                  (4,5,3.5)

2. (a) The CO stretching frequency in IR spectra are as follows: $[Mn(CO)_6]^+$ - 2090 cm^{-1}, $Cr(CO)_6$ - 2000 cm^{-1}, $[V(CO)_6]'$ - 1860 cm^{-1}, $[Ti(CO)_6]^{2-}$ - 1750 cm^{-1}. The value for CO(g) is 2143 cm^{-1}. Discuss.

   (b) What are the functions of haemoglobin and myoglobin? Explain why haem group cannot act as biological oxygen carrier in the absence of globin chain.

(c) Using the 18 electron rule as a guide. Find :

    (i) the number of CO ligands, in

$$[W(\eta^6\text{-}C_6H_6)(CO)_n]$$
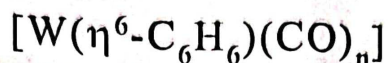
    (ii) the number of CO ligands in $[Co(\eta^5\text{-}C_5H_5)(CO)_n]$ (4,4.5,4)

3. (a) Explain the term "active transport" w.r.t action of sodium potassium pump in animal cells. Give systematic diagram for it.

  (b) What are the toxic metals for biological system? Explain the toxicity of one such metal.

  (c) Write a short note on :

    (i) Toxicity of Hg^{2+} ion

    (ii) Zeise's salt.   (4,4,4.5)

4. (a) What's the geometry, hybridization and oxidation no. of Mn in $KMnO_4$? Explain the reason for its color.

                                                      P.T.O.

(b) What happens when :

     (i) $K_2Cr_2O_7$ is treated with oxalic acid in acidic medium

     (ii) $KMnO_4$ is treated with mohr's salt in acidic medium

(c) Why transition elements show different oxidation states? Despite being a 17 electron species, $V(CO)_6$ does not dimerise. Give reason.

                                          (4,4,4.5)

Section B :

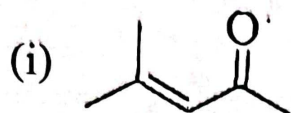### Polynuclear Hydrocarbons and UV, IR

(Attempt any three Questions)

5.   (a) Explain the following :

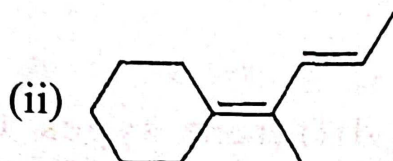   (i) Pyridine is less reactive towards electrophiles than pyrrole.

     (ii) Electrophilic substitution in naphthalene is more favoured at α-position than β-positions

3455   **5**

(b) Calculate the λ_{max} of the following compounds :
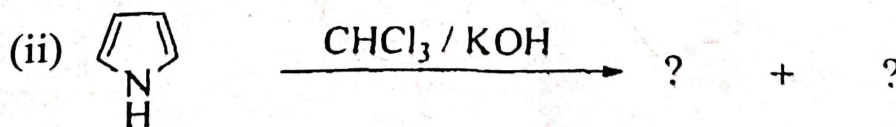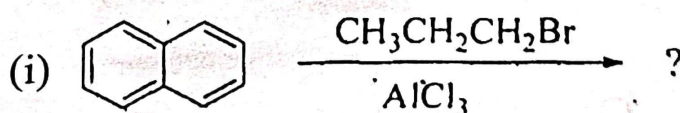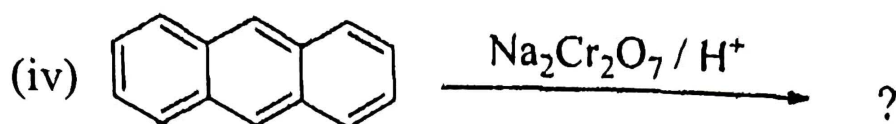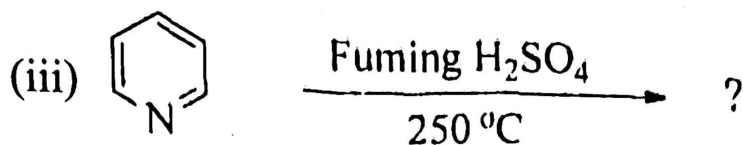
(i)   Base value = 215 nm

(ii)   Base value = 217 nm

(c) Give the aromaticity order of Pyrrole. Thiophene, Furan, and Benzene. Give reason.

(d) What is keto-enol tautomerism. Explain taking example of ethyl acetoacetate.   (4,4,2.5,2)

6.   (a) Complete the following reactions :

(i) $\xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}}$?

(ii) $\xrightarrow{\text{CHCl}_3 \ / \ \text{KOH}}$? + ?

   P.T.O.

(iii) [pyridine structure] $\xrightarrow[\text{250 °C}]{\text{Fuming H}_2\text{SO}_4}$?

(iv) [anthracene structure] $\xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7 / \text{H}^+}$?

(b) (i) Explain the different types of bending vibration in IR spectroscopy.

    (ii) How can you distinguish between *cis*-stilbene and *trans*-stilbene using UV spectroscopy?

(c) Discuss the mechanism of Claisen ester condensation.

(d) Arrange the following compounds in increasing $v_{C=O}$ stretching absorption. Give reason.

[structures: cyclopentanone, cyclohexanone, cyclopropanone, cyclobutanone]
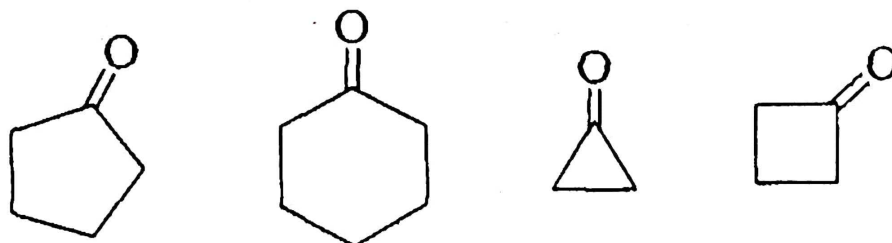
(4,4,2.5,2)

7. (a) Synthesis the following compounds using ethyl acetoacetate **(Any two)**

    (i) Succinic acid

    (ii) 3-methyl pentan-2-one

    (iii) Crotonic acid

(b) Write short notes :

    (i) Chichibabin reaction

    (ii) Charge transfer complex

(c) Furan is the only 5-membered heterocyclic aromatic compounds which undergoes Diels-Alder reactions. Explain

(d) Calculate the fundamental vibrational modes in H_2O and CO_2.   (4,4,2.5,2)

8. (a) (i) Anthracene on catalytic reduction gives dihydroanthracene, justify.

    (ii) Why λ_{max} of aniline shift from 230 nm in neutral medium to 203 nm in acidic medium.

P.T.O.

(b) Deduce the structures A, B, C, D
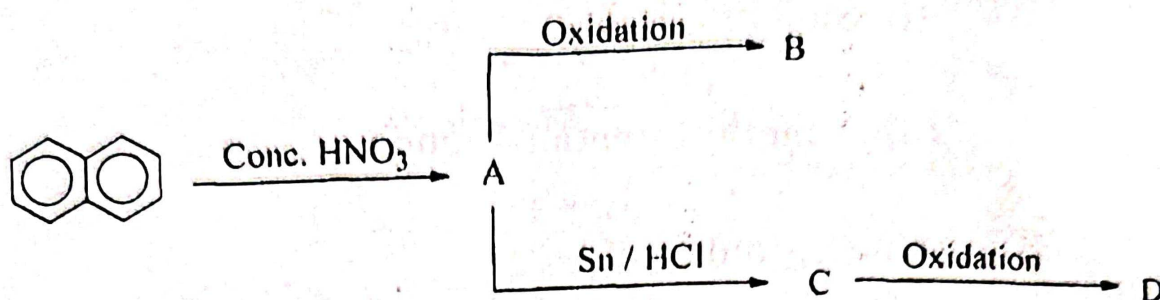
(c) Give the reaction for ketonic hydrolysis of ethylacetoacetate.

(d) What do you understand by bathochromic shift and hypsochromic shift?   (4,4,2.5,2)