

8. (a) Derive the relation $\Delta S = C_v \ln \frac{T_f}{T_i} + \frac{\alpha}{\kappa} (V_f - V_i)$ starting from $dU = dq + dw$.
- (b) How are extremely low temperatures achieved? Why is it not possible to attain absolute zero in a finite number of steps?
- (c) A solution of 60 mole% ethanol in water has to be prepared. The partial molar volumes of ethanol and water in this solution are $57 \text{ cm}^3 \text{ mol}^{-1}$ & $16 \text{ cm}^3 \text{ mol}^{-1}$ respectively. The molar volumes for pure water and ethanol are 18.0 and $58 \text{ cm}^3 \text{ mol}^{-1}$ respectively. Calculate the volumes of ethanol and water that should be mixed to get 3 m^3 of this solution. (5,5,5)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 4151 H

Unique Paper Code : 2172011203

Name of the Paper : CHEMICAL
THERMODYNAMICS AND
ITS APPLICATIONS

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

Semester : II

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. Q. 1 is compulsory.
 4. Use of scientific calculators is allowed.
-
1. Attempt any five :
 - (a) Why is the Helmholtz free energy called as work function?

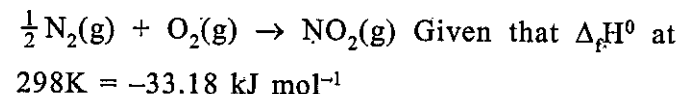
- (b) Freezing occurs spontaneously below the freezing point although it leads to a more ordered state. Explain.
- (c) Two liquids A and B are mixed in the ratio 1:2 in one solution and in the ratio 1: 3 in the second solution. Will the partial molar volume of A be same or different in the two solutions? Explain qualitatively.
- (d) Efficiency of Carnot engine cannot be one or more than one. Why? Explain the implication of this in terms of second law of thermodynamics.
- (e) Endothermic reactions are entropy driven processes. Explain.
- (f) Is Hess's Law valid for heat exchanged 'q' in a process? Is it valid for entropy change 'ΔS'? Give reason for your answer.
- (g) Why do gases diffuse spontaneously to form a homogeneous mixture? (5×3=15)

2. (a) Derive the relation $C_p - C_v = \left\{ V - \left(\frac{\partial H}{\partial P} \right)_T \right\} \left(\frac{\partial P}{\partial T} \right)_V$ starting from the relation $H = U + PV$.

- (c) Derive the relationship between $\Delta_r G^\circ$ and $\Delta_r A^\circ$ for a chemical reaction. At 298K ΔG for the reaction $C_6H_6(l) + \frac{15}{2} O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$ is $-9.26 \text{ kJ mol}^{-1}$. Find ΔA for the same reaction at 298K. (5,5,5)

7. (a) Derive the relation $\left\{ \frac{\partial \left(\frac{\Delta_r G}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right\}_p = \Delta_r H$.

- (b) The free energy change of a reaction, $\Delta_r G$ is positive. Is there any way by which this reaction can be made to proceed? Explain with examples.
- (c) Calculate $\Delta_r H^\circ$ at 373K for the reaction

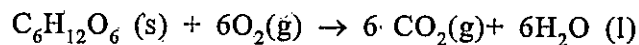


$$C_{p,m}(NO_2, g)/J \text{ K}^{-1} \text{ mol}^{-1} = 27.78 + 30.85 \times 10^{-3}(T/K)$$

$$C_{p,m}(N_2, g)/J \text{ K}^{-1} \text{ mol}^{-1} = 28.46 + 2.26 \times 10^{-3}(T/K)$$

$$C_{p,m}(O_2, g)/J \text{ K}^{-1} \text{ mol}^{-1} = 26.85 + 8.49 \times 10^{-3}(T/K) \quad (5,5,5)$$

Glucose is oxidized to CO_2 and water according to the equation:



In this process $\Delta U = -2810 \text{ kJmol}^{-1}$ and $\Delta S = 182.4 \text{ JK}^{-1}$ at 25°C . How much of this energy change can be extracted as (a) heat (b) work?

- (b) The enthalpy of neutralization of HCl with NaOH is -57.3 kJmol^{-1} ; enthalpy of neutralization of CH_3COOH with NaOH is $-49.86 \text{ kJmol}^{-1}$ and enthalpy of neutralization of NH_4OH with HCl is $-51.34 \text{ kJmol}^{-1}$.

(i) How much heat will be evolved when 50mL of 1N HCl is mixed with 50mL 0.9N NaOH ?

(ii) Calculate enthalpy of ionization of CH_3COOH and of NH_4OH .

(iii) What is the enthalpy of neutralization of NH_4OH with CH_3COOH ?

- (b) Show that the magnitude of work involved in a reversible adiabatic expansion of an ideal gas is less than in isothermal expansion when the expansion is carried out between same initial and final volumes.

- (c) An ideal gas at 30 Pa and 298K. is expanded reversibly and adiabatically from a volume of 1.43dm^3 to 2.86dm^3 . If $C_{p,m} = 29.1 \text{ JK}^{-1} \text{ mol}^{-1}$, calculate the final T and P of the gas and q, w and ΔU for the process. (5,5,5)

3. (a) Using an indicator diagram show that more work has to be done by the surroundings in compressing a gas in an irreversible process than in a reversible process.

- (b) Prove that the criterion of $\Delta G < 0$ for predicting the spontaneous nature of a process is completely equivalent with that of $\Delta S_{\text{total}} > 0$.

- (c) Define enthalpy of combustion.

Calculate the enthalpy of formation of methane from the given data :

Enthalpy of combustion of methane = $-890.36 \text{ kJ mol}^{-1}$, enthalpies of formation of carbon dioxide and water = $-393.13 \text{ kJ mol}^{-1}$ and $-285.58 \text{ kJ mol}^{-1}$ respectively. (5,5,5)

4. (a) For an isothermal reversible expansion of a van der Waals gas show that

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

- (b) Describe the Joule-Thomson experiment. Show that the expansion in this experiment is an isenthalpic process. Define Joule Thomson coefficient.

- (c) Using the given data, calculate the enthalpy of formation of acetic acid :

(i) Enthalpy of sublimation of graphite = 718.39 kJ mol⁻¹,

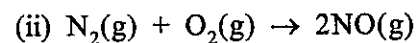
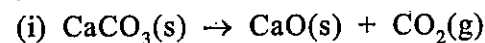
(ii) Enthalpy of dissociation of hydrogen gas = 435.97 kJ mol⁻¹

(iii) Enthalpy of dissociation of oxygen gas = 495.04 kJ mol⁻¹,

(iv) $\epsilon_{C-H} = 413.38$ kJ mol⁻¹, $\epsilon_{C-C} = 347.69$ kJ mol⁻¹, $\epsilon_{C=O} = 728.02$ kJ mol⁻¹, $\epsilon_{C-O} = 351.46$ kJ mol⁻¹, $\epsilon_{O-H} = 462.75$ kJ mol⁻¹.
(5,5,5)

5. (a) Show that ΔG_{mix} has minimum value and ΔS_{mix} has maximum value for a binary mixture of ideal gases when the mixture is equimolar.

- (b) Predict if ΔS_{sys} is positive, negative or zero in each of the following giving reason



(iii) Reversible adiabatic expansion of an ideal gas

(iv) Reversible isothermal expansion of ideal gas

(v) Stretching of a rubber band

- (c) Calculate ΔS for the transformation $\text{H}_2\text{O}(\text{s}, 0^\circ\text{C}, 1\text{bar}) \rightarrow \text{H}_2\text{O}(\text{g}, 100^\circ\text{C}, 1\text{bar})$ if $T_m = 0^\circ\text{C}$, $\Delta_{\text{fus}}H = 6.01 \text{ kJ mol}^{-1}$, $T_b = 100^\circ\text{C}$, $C_p(\text{H}_2\text{O}, \text{l}) = 75.24 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta H_{\text{vap}} = 40.65 \text{ kJ mol}^{-1}$. (5,5,5)

6. (a) Show that for an isothermal change in an ideal gas

$$\Delta G = nRT \ln \frac{p_2}{p_1} = nRT \ln \frac{V_1}{V_2}$$

2

May-2024

[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

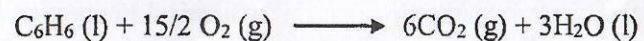
Instructions for Candidates

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 :

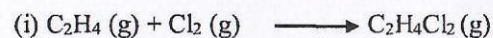


$$\Delta H^\circ = -3303 \text{ KJ}$$

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

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

- (b) Calculate the enthalpy change for the following reactions



$$\text{Given B.E. (C-C)} = 348 \text{ KJmol}^{-1}$$

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

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

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

$$\text{Given B.E. (H-Cl)} = 432 \text{ KJmol}^{-1}$$

- (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.

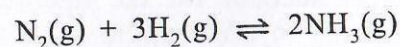
- (b) At a certain temperature, degree of dissociation of pure water is 1.81×10^{-9} . Calculate the ionic product of water at this temperature.

- (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.

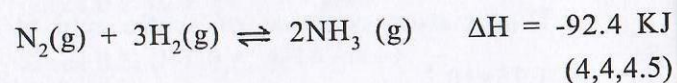
3. (a) For a reaction



$$K_p = 1.64 \times 10^{-4} \text{ at } 673 \text{ K.}$$

Calculate :

- (i) ΔG° 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 $\text{N}_2\text{O}(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$ at 300K, and 1 atm $K_p = 0.157$. Calculate K_c & K_r 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



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



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

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

$$\Delta H_f^\circ(\text{C}_2\text{H}_6) = -84.5 \text{ KJ}$$

$$\Delta H_f^\circ(\text{H}_2\text{O}) = 0$$

- (b) The equilibrium constant, K_p for the reaction :

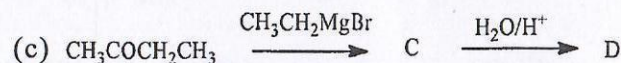
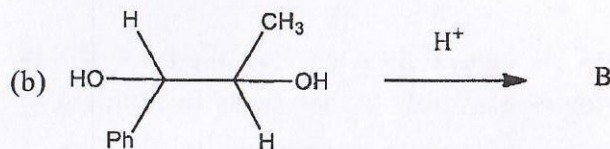
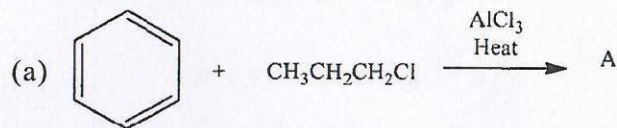
$$\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} \text{ is } 1 \times 10^{-12} \text{ at } 600 \text{ K and } 1 \times 10^{-7} \text{ at } 800 \text{ K. Calculate the heat of reaction.}$$

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

(4,4,4.5)

SECTION B

1. (i) Complete the following reactions :



- (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 $\text{C}_6\text{H}_5\text{CHO}$

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

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

(ii) Explain $\text{S}_{\text{N}}1$ 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

3354

8

(ii) Lucas test for alcohol

(iii) Reimer-Tiemann reaction

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

(500)

4
[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 4006

H

Unique Paper Code : 2172521201

Name of the Paper : DSC: Chemical Bonding and
Elements in Biological
System

Name of the Course : B.Sc. Life Science with
Chemistry

Semester : II

Duration : 2 Hours

Maximum Marks : 60

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **four** questions.
3. **All** questions carry equal marks.

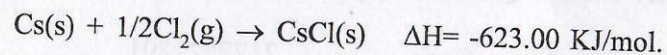
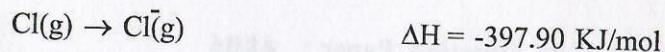
1. (a) Draw the Born Haber cycle and calculate the lattice energy of CsCl from the following data:



P.T.O.

4006

2



(b) How does Molecular Orbital Theory account for the following :

(i) Why Be_2 molecule does not exist?

(ii) Paramagnetic character in O_2 molecule.

(c) Write the toxic effects of Pb (II). Give the reasons for its toxicity. How can it be treated?

(5,5,5)

2. (a) Write down the main postulates of the Valence bond theory.

(b) (i) Explain, in spite of the same hybridization, H_2O is angular, whereas NH_3 is pyramidal.

(ii) Using the LCAO method, draw the shapes of molecular orbitals formed by the combination of p-p atomic orbitals, both axial as well as sideways.

4006

3

(c) How is the unequal concentration of Na^+ and K^+ ions in extracellular and intracellular fluid controlled in the human body? Give a diagrammatic representation of the process and explain the mechanism involved in it. (5,5,5)

3. (a) Draw the MO energy level diagram of CO. Calculate its bond angle and comment on its magnetic behaviour.

(b) Define resonance and resonance energy. Draw the possible structure of CO_3^{2-} .

(c) How is iron transported and stored in the human body? Where is it stored? (5,5,5)

4. (a) Arrange the following in the increasing order of their solubility in water and explain LiF, LiCl, LiBr, LiI.

(b) Write the differences between :

(i) Bonding orbitals and Anti bonding orbitals.

(ii) Sigma bonding and pi bonding.

(c) What do you understand by essential and toxic metal ions in the bio-system?

Draw the Dose-response curve for essential elements and toxic metal ions in a human body.

(5,5,5)

P.T.O.

5. (a) Write down the Born Lande equation to calculate the lattice energy of an ionic crystal and explain various terms involved in the equation.

- (b) (i) Arrange the following molecules in the decreasing order of X-P-X bond angle



- (ii) Why bond angle of CH_4 is higher than NH_3 ?

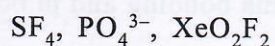
- (c) Describe the role of calcium in blood clotting?

(5,5,5)

6. (a) (i) BaSO_4 is ionic in nature but insoluble in water. Explain.

- (ii) The dipole moment of HI is 0.384D and the bond distance is 1.60Å. What will be the % of the ionic character in HI?

- (b) Give the hybridisation of the central atom and the shapes of the following molecules :



- (c) Describe the role of copper metal ion along with its impact in case of excess and deficiency of it in the human body?

(5,5,5)

(1000)

28

[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 4007

H

Unique Paper Code : 2172521202

Name of the Paper : DSC - Periodic Properties
and Chemical Bonding

Name of the Course : **Bachelor of Science in
Analytical / Industrial
Chemistry / PSC**

Semester : II

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** out of **six** questions.
3. Attempt **all** parts of question together.

1. (a) Which is more covalent in nature in the following and why?

P.T.O.

- (i) NaCl or LiCl
- (ii) H₂O or F₂O
- (b) Write salient features of VBT.
- (c) Draw the MO diagram of O₂, and predict the bond order of O₂, O₂⁻, O₂²⁻. (4,5,6)
2. (a) Draw and discuss the structure of PCI₃F₂ and PF₃Cl₂.
- (b) Why is the second ionization energy of alkali metals higher than the first ionization energy?
- (c) Draw the Born Haber cycle for MgF₂ formation and give expression also. (4,5,6)
3. (a) Define electron gain enthalpy. Explain its trends in halogens.
- (b) Explain the catalytic properties of elements of d-block elements.
- (c) Using VSEPR theory, explain the shapes and give the hybridization found in the following molecules: PCI₅, NH₃, XeF₄. (4,5,6)

4. (a) Calculate the lattice energy of MgO (in kJmol⁻¹):

Given : Madelung constant $A = 1.475$, $r(\text{Mg}^{2+}) = 0.65 \text{ \AA}$, $r(\text{O}^{2-}) = 1.40 \text{ \AA}$, $n=7$, $e = 4.8 \times 10^{-10} \text{ e.s.u.}$, $N = 6.02 \times 10^{23}$.

- (b) Write short note on shielding effect.
- (c) Define resonance. Draw and discuss the resonating structures of SO₄²⁻. (4,5,6)
5. (a) Explain enthalpy of atomization. How does it vary for d-block elements?
- (b) Write the difference between the Bonding molecular orbitals and anti bonding molecular orbitals.
- (c) Why first ionization energy of oxygen is lower than nitrogen? (4,5,6)
6. (a) Why the electronegativity of F is higher than Cl while the electron gain enthalpy is vice-versa?
- (b) Sizes of 4d and 5d series elements in a group are same. Explain.

4007

4

(c) Define Fajan's rule. Discuss the factor affecting Fajan's rule with examples. (4,5,6)

(1000)

2

[This question paper contains 4 printed pages.] ✓

Your Roll No.....

Sr. No. of Question Paper : 4075

H

Unique Paper Code : 2172011201

Name of the Paper : Chemistry of S- and P- Block Elements

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

Semester : II

Duration : 3 Hours

Maximum Marks : 90

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **Six** questions.
3. **All** questions carry equal marks.

1. Explain the following :

(5×3)

- (a) Silicon does not form analog to an alkene.
- (b) Alkali metals impart characteristic color to Bunsen flame.
- (c) BaSO_4 is insoluble whereas MgSO_4 is very soluble in water.
- (d) Nitrogen exists as N_2 whereas phosphorus exists as P_4 .
- (e) CO_2 is gas whereas SiO_2 is solid.

P.T.O.

2. (a) As alkali metals are added in liquid ammonia gradually, a blue coloured solution is obtained initially, but with more addition of alkali metal, a bronze-colored layer is formed which floats over blue colored solution. Explain. (5)
- (b) What is the Ellingham Diagram? In the Ellingham diagrams the slopes of lines change abruptly at the melting and boiling points of metals. Explain. (5)
- (c) Arrange the following in the increasing order of their acidic strength. Explain. (5)
- (i) HF, HCl, HBr, and HI
- (ii) H_2SO_3 and H_2SO_4
3. Write short notes on any **three** of the following : (3×5)
- (i) Pseudohalogens and Pseudohalides
- (ii) Zone refining process
- (iii) Inert pair effect.
- (iv) Clathrate Compounds.
4. (a) Describe the principle of hydrometallurgy with reference to the cyanide process. (5)
- (b) Explain the dissimilarities between the two allotropic forms of carbon, namely graphite, and diamond. (5)

- (c) Draw the structure of diborane and discuss the bonding involved. Also, give experimental evidence in support of the structure. (5)
5. (a) Give the principle of the electrolytic process of purification of metals with examples. (5)
- (b) Lithium forms predominantly the monoxide, sodium forms peroxide whereas potassium, rubidium, and cesium form superoxides. Comment. (5)
- (c) Name the hydrides of group 15 elements and discuss the variation in their properties with reference to : (5)
- (i) Basic character
- (ii) Thermal Stability
- (iii) Reducing character
6. (a) Draw and discuss the structure of the following: (5)
- (i) Mg-EDTA Complex
- (ii) Basic beryllium nitrate
- (b) What is the diagonal relationship? Give at least three examples to explain how boron resembles silicon. (5)
- (c) Carbon is a better reducing agent below 710°C while carbon monoxide is better reducing agent above 710°C . Explain using the Ellingham diagram. (5)

7. (a) Select the correct answer in each category with appropriate justification : (5)

(i) Highest solubility in water: He, Ne, and Xe.

(ii) Paramagnetic species: O^{2-} , O_2^{2-} and O_2^- .

(b) Comment on the following : (5)

(i) Chlorine has greater electron gain enthalpy than fluorine, yet fluorine is a stronger oxidizing agent.

(ii) Thallium does not exist in (III) oxidation state, yet TlI_3 exists.

(c) Name the different oxo-acids of chlorine. Draw their structures and arrange them in the increasing order of their acid strength, and give reason(s). (5)

8. (a) Explain the following : (5)

(i) Which has a greater bond angle? NH_3 or PH_3 .

(ii) P_4 molecule is stable while P_2 not.

(b) Discuss the structure of graphite and explain its lubricating and electrical properties. (5)

(c) Silanes are more reactive than alkanes. Give reactions in support of your comment with an explanation. (5)

(2000)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 971

H

Unique Paper Code : 32175902

Name of the Paper : Chemical Energetics, Equilibria
and Functional Group Organic
Chemistry – 1

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

Semester : II / 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 any **three** questions from **Section A** and **three** questions from **Section B**.
3. Use separate Answer booklet for **Section A** and **Section B**.
4. Scientific Calculators and log tables may be used.

P.T.O.

SECTION A

Attempt any **three** questions from this section.

1. (a) Define

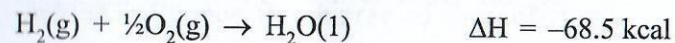
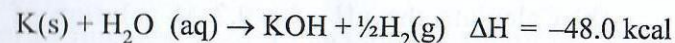
- (i) Third law of thermodynamics
- (ii) Absolute entropies of substances
- (iii) What is buffer solution? Give examples.
- (iv) Explain the buffer action of an acidic buffer.

(b) (i) Define Bond energies.

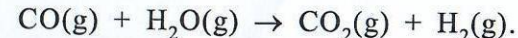
- (ii) Bond energies of F_2 and Cl_2 are 36.6 and 580 kcal/mol respectively. Heat liberated in the reaction $F_2 + Cl_2 \rightarrow 2FCl$ is 36.6 kcal. Find the bond energy of F—Cl bond.

(c) State first and second law of thermodynamics and explain their significance? (4,4,4.5)

2. (a) Calculate heat of formation of potassium hydroxide from the following data :



(b) Calculate ΔG° and K_p for the following reaction at 298 K.



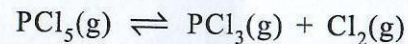
Given that ΔG° for $CO(g)$, $CO_2(g)$ and $H_2O(g)$ are -32.807, -97.26 and -54.64 kcal/mol respectively.

(c) (i) State the principle of solubility product. How is the solubility of a salt affected by the presence of a common ion?

(ii) Discuss the application of solubility product in cation analysis. (4,4,4.5)

2. (a) Derive Kirchoff's equation for variation of enthalpy of reaction with temperature.
- (b) Calculate the pH of a 0.2 M solution of NaCN? K_a for HCN is 4.0×10^{-10} .
- (c) (i) Define state function and path function.
- (ii) Derive the relation between hydrolysis constant and degree of hydrolysis for a salt of weak acid and strong base. (4,4,4.5)
3. (a) The heat of reaction $N_2 + 3H_2 \rightarrow 2NH_3$ at $27^\circ C$ was found to be -21.976 kcal. What will be the heat of reaction at $50^\circ C$? The molar capacities at constant pressure and at $27^\circ C$ for nitrogen, hydrogen and ammonia are 6.8, 6.77 and 8.66 cal $mol^{-1} degree^{-1}$ respectively.

- (b) Consider the reaction



How would the equilibrium be affected by

- (i) The addition of Cl_2
- (ii) Decrease in the volume of container.
- (c) Define degree of dissociation. Explain the factors which influence the degree of dissociation? (4,4,4.5)

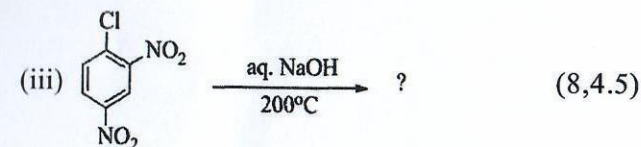
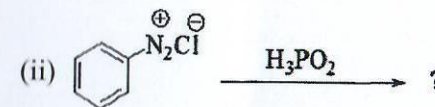
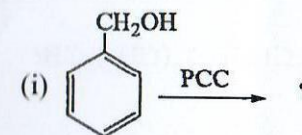
SECTION B

Attempt any three questions from this section.

4. (a) Explain S_Ni mechanism with a suitable example.
- (b) Distinguish the following pairs with suitable chemical tests :
- (i) benzaldehyde and acetone
- (ii) methanol and phenol
- (c) Explain why phenol is more acidic than most of the aliphatic alcohols.

- (d) Explain why n-propyl benzene cannot be prepared by Friedel-Craft's alkylation of benzene with propyl chloride. (4,4,2,2.5)
5. (a) What is ambident ion? How can you prepare the following from alkyl halides?
- nitrite and nitro
 - nitrile and isonitrile
- (b) Differentiate between Aldol and Cannizzaro reaction by giving suitable examples and mechanism.
- (c) Write down any four differences between S_N1 and S_N2 mechanisms. (4,4,4.5)
6. (a) Write a short note (including example and mechanism) on any two of the following :
- Reimer-Tiemann Reaction
 - Sulphonation of benzene
 - Benzyne mechanism

(b) Complete the following reactions :



7. (a) Carry out the following conversions :

- isopropanol from acetaldehyde
- nitrobenzene from acetylene

(b) Write and explain the mechanism of Pinacol-Pinacolone rearrangement.

(c) Explain why addition of ammonia derivative to carbonyl compounds is carried out at optimum pH of 4 to 5.5.

- (d) Explain why reactivity of the following towards nucleophilic substitution reaction follows the order:



(4,4,2,2.5)

Unique Paper Code

: 32175913

Name of the Paper

: GE-Chemistry of s & p Block elements,
States of Matter and Chemical Kinetics

Name of the Course

: B. Sc. (Hons.) Chemistry

Semester

: II/IV

Duration

: 3 hours

Maximum Marks

: 75

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

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

Use separate answer-sheets for Section A and Section B and do not intermix the sections.

Section A

(Inorganic Chemistry)

Attempt any three questions.

Question No. 1 is compulsory.

1. Explain

- Differentiate between mineral and ore.
- CCl_4 is not hydrolyzed but SiCl_4 is hydrolyzed by water.
- Graphite is a good conductor of heat and electricity.
- At room temperature Oxygen exists as a diatomic gas but Sulphur exists as S_8 solid molecule.
- The chemical and physical properties of Li and Mg are similar.
- Diamond is hard but graphite is soft and slippery in nature.
- The chemical reactivity of noble gases is very low.

(2,2,2,2,2,1.5)

2. a) Arrange the following Boron trihalides in increasing order of their acidity:

BF_3 , BCl_3 , BBr_3

- Give the names of oxy acids of chlorine in various oxidation states and arrange them in increasing order of acidic strength. Justify your answer.
- Explain the multicentered bonding in diborane. Write its any one chemical property.
- Write short notes on Electrolytic refining.

(3,3,3,3)

3. a) What are Ellingham diagrams? explain its significance.

- b) Why first member of each group of p block shows abnormal behaviour? Justify with examples.
- c) Write the structure of hydroxyl amine and comment on its reducing behaviour with example.
- d) Draw the structure of PCl_3 and PCl_5 molecules. Also discuss their any two chemical properties.

(3,3,3,3)

4. a) What is Hydrometallurgy? Explain its steps with reference to cyanide process.
- b) Why viscosity of sulphur first increases and then decreases?
 - c) What is Allotropy? Discuss allotropy of Sulphur.
 - d) Discuss the difference in the geometry of XeF_4 and XeO_2F_2 .

(3,3,3,3)

Section B

(Physical Chemistry)

Attempt any three questions.

5. a) Write the mathematical expression for the Maxwell distribution of molecular speeds of a gas. Briefly explain the terms involved. How does the change in temperature influence the distribution of molecular speed?
- b) Calculate the most probable speed, average speed and root mean square speed of O_2 at 300 K.
 - c) Derive the expression of collision frequency Z_{11} of a gas.

(4,4,4.5)

6. a) Describe the drop number method for the determination of surface tension of a liquid.
- b) At 20°C time taken by equal volumes of water and toluene to flow through a capillary tube is 109 and 62 seconds respectively. Density of water and toluene are 998 and 866 Kg m^{-3} respectively. Viscosity of water at this temperature is $1 \times 10^{-3} \text{ Nm}^{-2} \text{ s}$. What is the value of absolute viscosity of toluene?

- c) Derive the Arrhenius equation for showing the effect of temperature on the reaction rate.

(4,4,4.5)

7. a) What are crystalline and amorphous solids?

- b) Calculate the Miller indices of the crystal plane which cuts through the crystal axis at:

(i) (2a, 3b, 4c)

(ii) (a, -3b, -3c)

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

(i) Law of rational indices

(ii) Schottky and Frenkel defect

(iii) Law of constancy of interfacial angles

(4.5,4,4)

8. a) Derive the integrated rate law equation for the first order reaction.

- b) Calculate the activation energy of a reaction whose rate constant is tripled by a 10°C rise in temperature in the vicinity of 27°C . ($R=8.314\text{ JK}^{-1}\text{mol}^{-1}$)

- c) Differentiate between order and molecularity of a reaction.

(4.5,4,4)

(d) Differentiate between edgeoscopy and poroscopy.

(4,5,3,3)

4. (a) Explain the role of a forensic chemist at a fire scene. What evidences can be collected from the fire scene?

(b) Explain scope and significance of explosive analysis in forensic science.

(c) Give the chemical composition of various fractions of petroleum products. (5,5,5)

[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 4736

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.

1. Attempt (any **three**) questions :-

(a) What is Forensic science? Give different branches of forensic science.

(b) Write short note on TLC and its application.

(c) What is arson and explain different motives of Arson?

(d) Discuss different types of alcoholic beverages. Give examples. (5,5,5)

2. (a) What are latent fingerprints? Describe any one powder method for developing the latent fingerprints from curved or rough surfaces.

(b) Differentiate between detonation and deflagration. Give any two examples of explosives.

(c) Define the elements of fire tetrahedron.

(d) Fill in the following blanks :-

(i) Iodine vapours interact with _____ content of fingerprints.

(ii) _____ can be used as an adulterant in petrol/ diesel. (5,5,5)

(iii) The full form of AFIS is _____. (4,4,4,3)

3. (a) Define drugs of abuse? Discuss the harmful effects of drugs of abuse.

(b) Identify the fingerprint patterns of the following : (any 5)



i)



ii)



iii)



iv)



v)



vii)

(c) Explain the role of phenolphthalein as a detective dye.

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- (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)

(2000)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 4113

H

Unique Paper Code : 2172011202

Name of the Paper : Haloalkanes, Arenes,
Haloarenes, Alcohols, Phenols,
Ethers and Epoxides

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

Semester : II

Duration : 2 Hours

Maximum Marks : 60

Instructions for Candidates

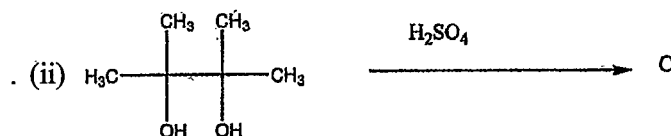
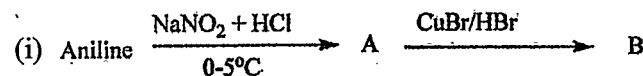
1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt all parts of a question together.
3. Attempt any four questions in all.
4. Question no. 1 is compulsory.
5. Each question carries 15 marks.

P.T.O.

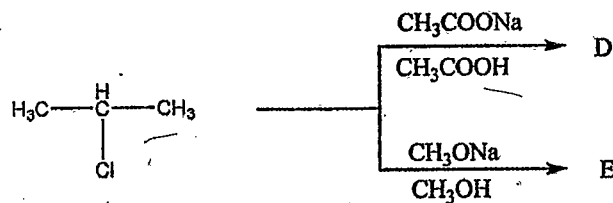
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1. (a) Complete the following reaction as indicated, identify and write their names-



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



- (c) Write various steps in the reaction of given epoxide in the given conditions :

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- (b) Out of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and $(\text{C}_6\text{H}_5)_2\text{CHCl}$ which is more easily hydrolyzed by aqueous sodium hydroxide under $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ 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

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6

(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 .

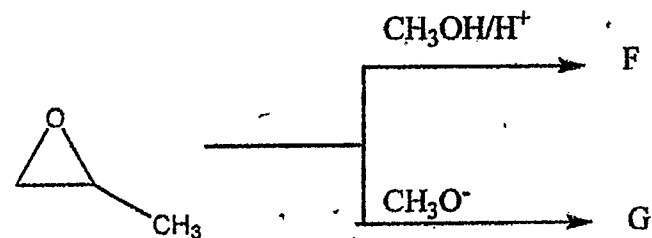
(d) A compound 'A' reacts with CH_3MgBr to give Ethanol which upon oxidation with PCC gets converted to 'B'. Identify A and B. Write all the steps involved in the given reaction.

(5×3=15)

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

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3



(5×3=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.

(5×3=15)

P.T.O.

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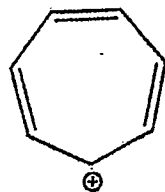
3. (a) Giving reasons arrange the following compounds as mentioned in parentheses

(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)



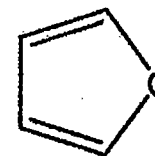
(ii)



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(iii)



(iv)



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

(i) Benzene to m-Dinitrobenzene

(ii) Methyl chloride to Ethanoic acid

(5×3=15)

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

P.T.O.

9

[This question paper contains 8 printed pages.]

Your Roll No.....

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.

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2

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) $\text{H}_4\text{P}_2\text{O}_7$
 - (ii) HClO_4
- (b) In contrast to diamond graphite conduct electricity? Explain

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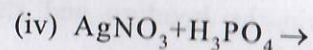
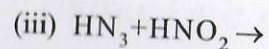
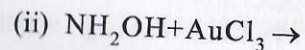
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- (c) Explain electrolytic refining with suitable examples.
- (d) Draw and explain the bonding and structure in diborane?
(4,4,2,2.5)
3. (a) Discuss the slope of CO gas in Ellingham diagram.
- (b) What is oxidative refining? Explain tossing and puddling.
- (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) $\text{N}_2\text{H}_4 + \text{O}_3 \rightarrow$

P.T.O.

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4



(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.

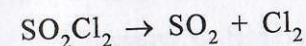
5. (a) (i) Show that for a first order reaction the half life period is -

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

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5

- (ii) The half life of the homogeneous gaseous reaction



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

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

- (ii) The rate constant of a second order reaction is $5.70 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C and $1.64 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 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
- (2a,3b,c)
 - (a, ∞ ,c)
 - (∞ ,3b,3c)
- (2+2,4,4.5)
7. (a) Write short notes on the any **two** of the following :
- Viscosity of gases and its dependence on temperature and pressure.
 - Frenkel defect
 - 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 $A + A \rightarrow$ 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 $a = 5.5 \text{ L}^2 \text{ atm mol}^{-1}$, $b = 63.8 \text{ cm}^3 \text{ mol}^{-1}$, $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$.
- (b) (i) Explain law of rational indices.
- (ii) Show that effective volume is four times the volume of the gas.

(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)

3

[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

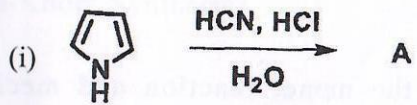
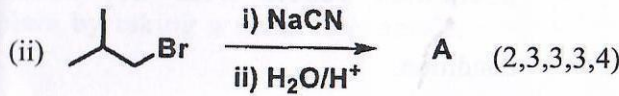
Instructions for Candidates

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.

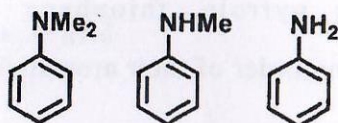
P.T.O.

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
2. (a) Write the reaction for the synthesis of Tribromobenzene from aniline.
- (b) Write the reaction of Diazotization and explain the mechanism.

(3,3,3,3,3)

- (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)  (i) c1cc[nH]1 $\xrightarrow[\text{H}_2\text{O}]{\text{HCN, HCl}}$ A
- (ii)  (ii) CC(C)C(Br)C $\xrightarrow[\text{ii) H}_2\text{O/H}^+]{\text{i) NaCN}}$ 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 :

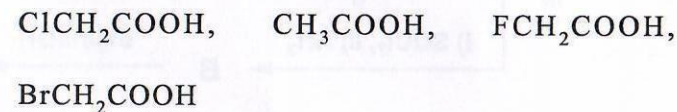


(c) Write the reaction involved when Furan treated with maleic anhydride and name the reaction.

(d) Write the name, reaction and mechanism for the synthesis of primary amines when acetamide reacts with Br₂ under alkaline condition.

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

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

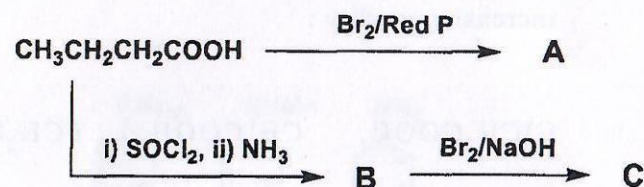


(b) Explain Chichibabin reaction with suitable example.

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

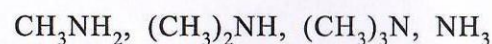
(d) Why tertiary amines with three different groups to nitrogen atoms do not show optical activity? Explain by taking a suitable example.

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



(2,3,3,3,4)

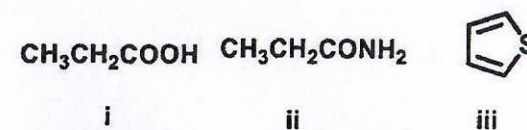
5. (a) Put the amines in their increasing order of basicity under gas phase :



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

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

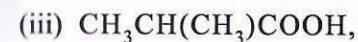
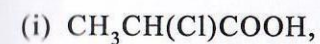
- (d) Write the IUPAC name of the following heterocyclic compounds :



- (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.



(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 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 4045

H

Unique Paper Code : 2173522006

Name of the Paper : DSE : Biomolecules – I

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

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** questions carry equal marks.
4. Attempt **all** parts of a question together.

1. (a) Give the mechanism of osazone formation for D-glucose. D-Glucose and D- Fructose give the same osazone. Explain.

P.T.O.

4045

2

- (b) Distinguish between reducing and non-reducing sugars. Draw the Fischer projection and Haworth projection structure of anomers of glucose and fructose.
- (c) Give the biological functions of lipids? (5,5,5)
2. (a) Convert the following :
- (i) D-Fructose to D-Glucose
- (ii) D-Glucose to D-Arabinose
- (b) What are nucleotide and nucleoside? Give the name and draw the structure of nucleotide & nucleoside having adenine as a base found in DNA.
- (c) Write a short note on oil and fats.
- (d) What are biochemical functions of steroid hormones? (4,3,4,4)
3. (a) Outline a sequence of reaction by which Maltose can be converted into 2,3,4,6- Tetra-O-methyl-D-glucose and 2,3,5,6-Tetra-O-methyl-D-gluconic acid. Draw all the configurational structures.

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3

- (b) What is RNA? Briefly explain the three functional types of RNA.
- (c) What is rancidity? Differentiate between oxidative and hydrolytic rancidity. (5,5,5)
4. (a) What product will be formed when glucose is
- (i) reacted with HCN.
- (ii) reacted with phenyl hydrazine.
- (iii) reacted with dil. HNO_3 .
- (iv) heated with HI in presence of phosphorus.
- (v) reduced with sodium-alcohol.
- (b) What are epimers? Explain using suitable examples. Suggest a method to convert D-(+)-Glucose to D-(+)-Mannose.
- (c) Define iodine number. What is its significance. Calculate the iodine number of triolein whose molecular weight is 884.
- (d) What are liposomes and how are they utilized in various fields? (5,3,3,4)

P.T.O.

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

(b) Briefly explain the various components present in nucleic acids.

(b) Write a note on hydrogenation of oil. (5,5,5)

6. (a) Draw the structures of disaccharide sucrose and lactose. How is the nature of linkages between 2 monosaccharide units established?

(b) Write short note on :

(i) Cellulose

(ii) Omega-3 and Omega-6 fatty acids

(iii) Lipid Membranes

(c) Give the biological importance of triglycerides.

(4,6,5)

(500)

[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

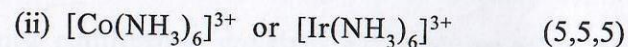
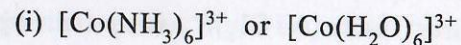
1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt six questions in all.
3. All Questions carry equal marks.

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 $[\text{Fe}(\text{bpy})_3]^{2+}$ from $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$. 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 $[\text{PtCl}_2(\text{NH}_3)_2(\text{py})_2]$. 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.

- $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$, $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$, $\text{K}_2[\text{PtCl}_6]$
- (c) How does the Valence bond theory account for the fact that $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic and square planar but $[\text{NiCl}_4]^{2-}$ is paramagnetic and tetrahedral. (5,5,5)
 3. (a) A solution containing 2.674 g of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ (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) $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$
 - (ii) $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$

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

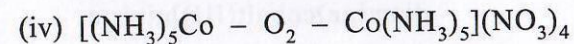
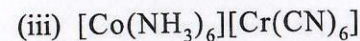
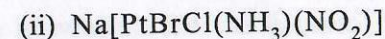
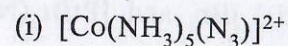


4. (a) Draw MO diagram for $[\text{Co}(\text{NH}_3)_6]^{3+}$.

(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- $[\text{PtCl}_2(\text{NH}_3)_2]$ (5,5,5)

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



(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.

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

(5,5,5)

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) $[\text{V}(\text{NH}_3)_6]^{3+}$

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

(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 $2.01 \text{ \AA}$ and 4 Cu—F bond distances are $1.85 \text{ \AA}$. 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

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(c) Inner and Outer orbital complex

(d) Spectrochemical series

(5,5,5)

(1000)

1
[This question paper contains 8 printed pages.] ✓

Your Roll No.....

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) $\text{HCl}/\text{H}_2\text{O}$

(ii) $\text{CH}_3\text{OH}/\text{HCl}$

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 $\text{CH}_3\text{COCl}/\text{SnCl}_4$
- (vi) Quinoline reacts with conc. H_2SO_4 at 220°C
- (b) Quinoline on oxidation with KMnO_4 gives a dicarboxylic acid A ($\text{C}_7\text{H}_5\text{O}_4\text{N}$). A on heating with $\text{Se}/\text{H}_2\text{SO}_4$ 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

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(iii) Killiani-Fischer synthesis

(iv) Friedlander synthesis of Quinoline

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

(1200)

[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 4269

H

Unique Paper Code : 2173542003

Name of the Paper : DSE : Conductance,
Electrochemistry and
Chemical Kinetics

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

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 **four** questions in all. Question No. 1 is compulsory.
3. **All** questions carry equal marks.
4. Attempt all parts of a question together.
5. Use of non-programmable scientific calculator is allowed.

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

(a) What is the role of salt bridge in galvanic cells?

P.T.O.

- (b) Can a solution of 1M copper sulphate be stored in a vessel made of Nickel metal? Given that $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$ and $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$.
- (c) Metallic conductance decreases while electrolytic conductance increases with temperature.
- (d) Reactions of third and higher order are not very common.
- (e) Higher the activation energy of a reaction, slower is the rate of a reaction.
- (f) Define the term ionic mobility? Give its unit.
(5×3)
2. (a) (i) Write the integrated rate law equation for a second order reaction when the initial concentrations of both the reactants are same.
- (ii) Show that for a first order reaction the time required for 99.9% completion of the reaction is 10 times that required for 50% completion.
- (b) Give the mathematical expression of the Arrhenius equation and explain the terms involved.
- (c) Briefly describe any one method to determine the order of the reaction.
(6,5,4)

3. (a) What is meant by transference number of an ion? The molar conductance at infinite dilution of KCl is $130.1 \text{ Scm}^2\text{mol}^{-1}$. The Hittorf number, t_- of Cl^- in very dilute solution is 0.505. Calculate the mobilities in of K^+ and Cl^- ions (Faraday's constant $F = 96500 \text{ C mol}^{-1}$).
- (b) How does molar conductivity vary with dilution for strong and weak electrolytes?
- (c) Discuss the titration curves obtained in the conductometric titration of CH_3COOH versus NaOH aqueous solutions.
(5,5,5)
4. (a) For the following electrochemical cell
 $\text{Fe}/\text{Fe}^{2+}(0.1\text{M})//\text{Cd}^{2+}(0.01\text{M})/\text{Cd}$
Write down the cell reaction and determine the EMF of the cell.
Also indicate the direction of spontaneous cell reaction.
(The standard electrode potential of Fe^{2+}/Fe half-cell is -0.44 V and that of Cd^{2+}/Cd is -0.40 V).
- (b) State the principal underlying the potentiometric titrations. What are the advantages of potentiometric titrations over volumetric titrations. Draw the potentiometric titration curve involving strong acid and strong base.

- (c) If the molar conductivities at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 426.1 and $91.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively, what will be the molar conductivity of acetic acid? (6,5,4)
5. (a) Derive an equation to determine the pH of a solution using glass electrode.
- (b) Give the expression of the free energy change (ΔG) accompanying a cell reaction using the EMF of a cell. Also derive the expressions of the enthalpy change (ΔH) and the entropy change (ΔS).
- (c) The rate constant of a second-order reaction is $5.70 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C and $1.64 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 40°C . Calculate the activation energy and the Arrhenius pre-exponential factor. ($R=8.314 \text{ J K}^{-1}\text{mol}^{-1}$) (5,5,5)
6. Write short notes on any **three** of the following :
- (i) Reversible and irreversible galvanic cells
 - (ii) Role of catalyst on the rate of a reaction
 - (iii) Standard Hydrogen Electrode
 - (iv) Michaelis-Menten mechanism of enzyme catalysis (5,5,5)

[This question paper contains 4 printed pages.] ✓

Your Roll No.....

Sr. No. of Question Paper : 2822

H

Unique Paper Code : 42173922 / 32173907

Name of the Paper : SEC – Analytical Clinical
Biochemistry

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

Semester : IV / VI

Duration : 2 Hours

Maximum Marks : 38

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **four** questions.
3. **All** questions carry equal marks.

1. (a) Explain the Structure activity relationships of drug molecules with suitable example.
(b) Explain the effect of temperature and pH on the activity of enzymes.

P.T.O.

- (c) What is the fate of pyruvate during carbohydrate metabolism? (3.5,3,3)
2. Differentiate between the following :
- (a) DNA and RNA
- (b) Competitive and Non-Competitive enzyme inhibition
- (c) Anabolism and Catabolism (3.5,3,3)
3. (a) Give a brief classification of lipoproteins and discuss their major functions.
- (b) How cholesterol is estimated by Libermann-Burchard method and mention the factors that affect colour formation during the reaction.
- (c) Explain "induced fit model" of enzyme action. (3.5,3,3)
4. Answer the following : (3,3,3.5)
- (i) Describe the binding role of double bond and aromatic ring groups in structure activity relationship.

- (ii) Which sugar present in RNA? What are the 3 types and functions of RNA? Write the chemical structure of two bases present in the RNA.
- (iii) (a) What is the Blood? Explain the function of blood.
- (b) Define the replication process.
5. (a) Differentiate any **three** the following : (3,3,3,0.5)
- (i) Anabolism and Catabolism
- (ii) Transcription and Translation.
- (iii) Polynucleotide and Polynucleoside
- (iv) Coenzyme and Cofactor
- (b) Write the full form of ADP.
6. (a) Write short notes on any **three** of the following : (3,3,3,0.5)
- (i) Biological importance of Protein
- (ii) Application of Liposome

(iii) Transcription

(iv) Factors affecting the action of Enzyme

(b) Write the structure of Thymine.

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[This question paper contains 4 printed pages.] ✓

Your Roll No.....

Sr. No. of Question Paper : 3271

H

Unique Paper Code : 32173901

Name of the Paper : SEC : IT Skills for Chemists

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

Semester : IV / VI

Duration : 2 Hours

Maximum Marks : 38

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **four** questions in all.
3. Use of non-programmable scientific calculator and logarithmic table is allowed.

1. (a) Simplify : $\frac{\sqrt[3]{ab^3}(ac^4)^2}{a^{\frac{4}{3}}b}$

(b) Using the van der Waal's equation at critical point,

$$\left(P_c + \frac{a}{V_c^2}\right)(V_c - b) = RT_c$$

Obtain P_c , given $V_c = 3b$ and $T_c = \frac{8a}{27Rb}$.

P.T.O.

- (c) Differentiate between accuracy and precision, giving relevant examples from chemical sciences. (3,3.5,3)
2. (a) The molar enthalpy change ΔH associated with a change of temperature from T_1 to T_2 can be found from the equation,

$$\Delta H = \int_{T_1}^{T_2} C_{p,m} dT$$

Using the trapezoidal rule, calculate ΔH over the temperature range 300 K to 1100 K. Given :

T/K	$C_{p,m}/\text{JK}^{-1}\text{mol}^{-1}$
300	39.9
500	46.5
700	50.8
900	53.4
1100	54.9

- (b) The natural logarithm of $1+x$ is expanded as :

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

Using $\frac{d \ln x}{dx} = \frac{1}{x}$ find the series to represent $1/(1+x)$.

(5,4.5)

3. (a) Eadie Hofstee plot is used to study the kinetics of enzyme catalysis based on the Michaelis-Menten equation for the rate ' v ' of the reaction as :

$$\frac{v}{[E_0][S]} = \frac{k_{cat}}{K_M} - \frac{v}{K_M[E_0]}$$

Obtain the expression for K_M and k_{cat} by constructing a linear plot using the above expression.

- (b) Find the velocity at which the fraction is maximum ($P(v)/dv = 0$) in Maxwell- Boltzmann distribution

$$P(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi v^2 \exp\left(-\frac{mv^2}{2kT}\right)$$

For He gas at 300 K. ($k = 1.38 \times 10^{-23} \text{ JK}^{-1}$)

(4.5,5)

4. (a) Find the mean and the standard deviation and coefficient of variance of the set of observations:

32.41, 33.76, 32.91, 33.04, 32.75, 33.23.

- (b) Find the pH and uncertainty associated with its measurement, given,

$$[H^+] = 6.2(\pm 0.04) \times 10^{-6} \text{M.} \quad (4.5,5)$$

3271

4

5. (a) Carry out linear least squares fit on the following data and find out the slope and the intercept of the fitted equation

x	0	1	2	3	4	5
y	0.10	0.98	2.00	2.99	4.02	4.98

You may use the following formulae :

$$\text{slope} = \frac{N \sum xy - \sum x \sum y}{N \sum x^2 - (\sum x)^2} \text{ and } \text{intercept} = \frac{\sum x^2 \sum y - \sum x \sum xy}{N \sum x^2 - (\sum x)^2}$$

- (b) Using the Newton-Raphson Method, find the pH of Benzoic acid (0.01 M) solution (ignoring the auto-ionization). Given $K_a(\text{C}_6\text{H}_5\text{COOH}) = 6.5 \times 10^{-5}$ and $K_w = 1.0 \times 10^{-14}$. Assume 5% dissociation of benzoic acid initially. (4.5,5)

(1000)

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 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, $A \rightarrow$ products, has a rate of reaction of 0.00250 M s^{-1} when $[A] = 0.484 \text{ M}$.

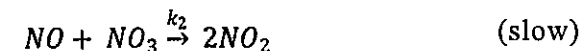
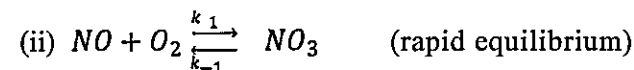
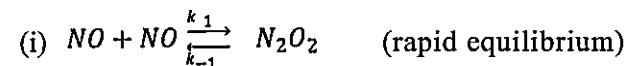
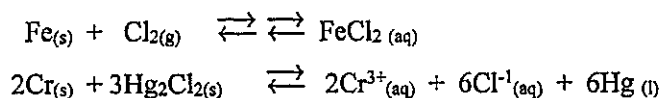
(i) What is the rate constant, k , for this reaction?

(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:



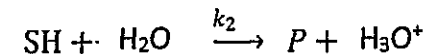
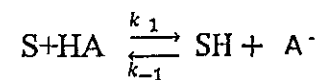
Show that both the mechanisms lead to the same rate law.

(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



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

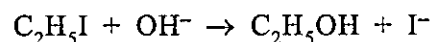


Show that it leads to

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

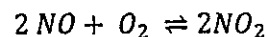
Under what conditions will the order of the reaction be equal to one? (3×5)

7. (a) For the reaction



The rate constant was found to have a value of $5.03 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 289 K and $6.71 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 333K. What is the activation energy of reaction. What is the rate constant at 305K.

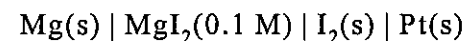
- (b) For the reaction :



Two mechanisms have been proposed:

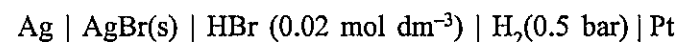
- (g) What is the difference between the Turnover Number (k_{cat}) and the Michaelis constant (K_M)? (5×3)

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



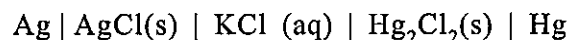
Given that : $E^\circ_{I^-|I_2} = 0.535 \text{ V}$ and $E^\circ_{Mg^{2+}|Mg} = -2.363 \text{ V}$

- (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



$E^\circ_{Br^- \mid AgBr \mid Ag} = 0.0713 \text{ V}$

- (b) The emf of the cell

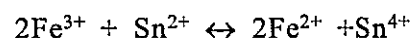


is 0.0455V at 298 K and the temperature coefficient is $3.38 \times 10^{-4} \text{ VK}^{-1}$. What is the reaction taking place in the cell and what are the free energy, enthalpy and entropy changes at 298 K?

- (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.



Given, $E^\circ_{\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}} = 0.771 \text{ V}$ and $E^\circ_{\text{Sn}^{4+}, \text{Sn}^{2+} | \text{Pt}} = 0.150 \text{ V}$

- (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

$$r = p \left\{ \pi \sigma_{AB}^2 \left(\frac{8KT}{\pi \mu} \right)^{1/2} N_A \cdot N_B \right\} \exp\left(\frac{-E_a}{RT}\right)$$

- (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 :

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

[This question paper contains 8 printed pages.]

Your Roll No.....

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

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.

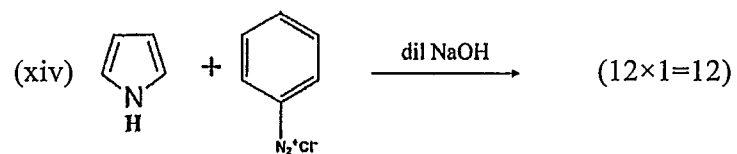
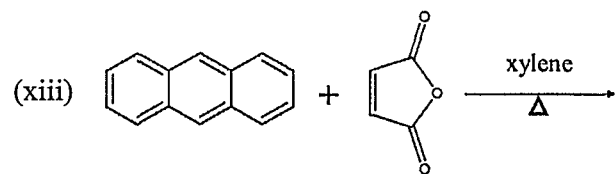
(c) Give synthesis of nicotine from nicotinonitrile.

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

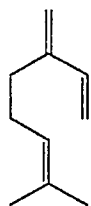
7. (a) Explain the fact that pyridine reacts with electrophiles as well as nucleophiles with the help of resonating structures.
- (b) Electrophilic substitution reaction in Indole occurs at C-3. Explain by drawing suitable resonating structures.
- (c) Pyrrole undergoes ring expansion with $CHCl_3$ and 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

2997

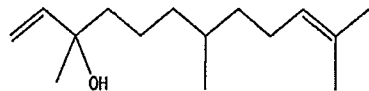
6



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.

2997

3

- (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

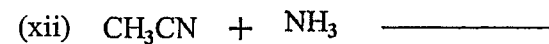
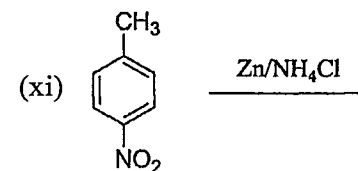
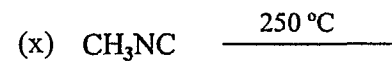
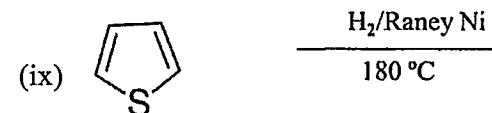
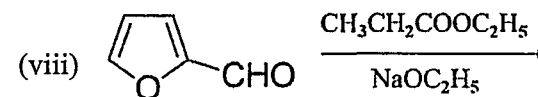
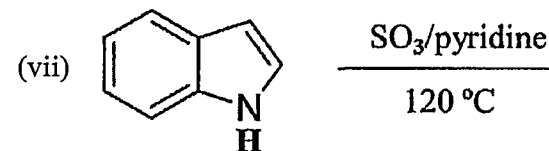
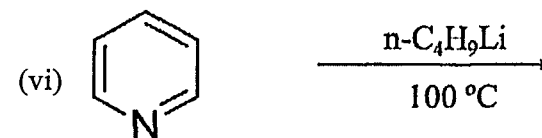
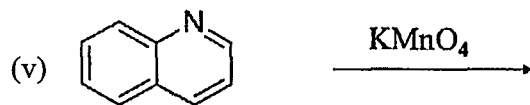
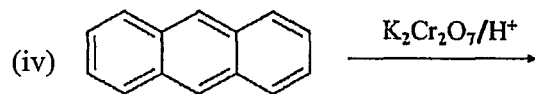
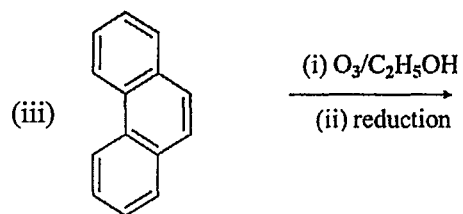
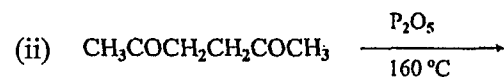
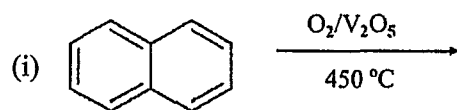
(iii) Aniline into p-bromoaniline

(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)



[This question paper contains 3 printed pages.]

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)

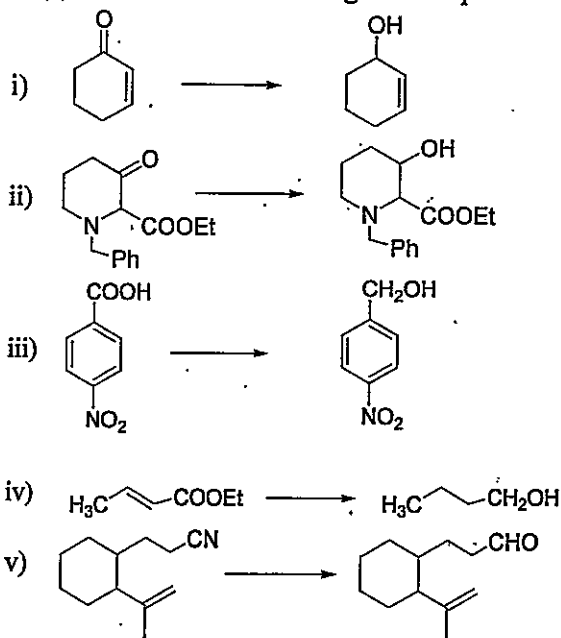
(a) Bischler-Napieralski Reaction

(b) Darzens reaction

(c) Demjanov rearrangement

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

(1x5, 2x5)



(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

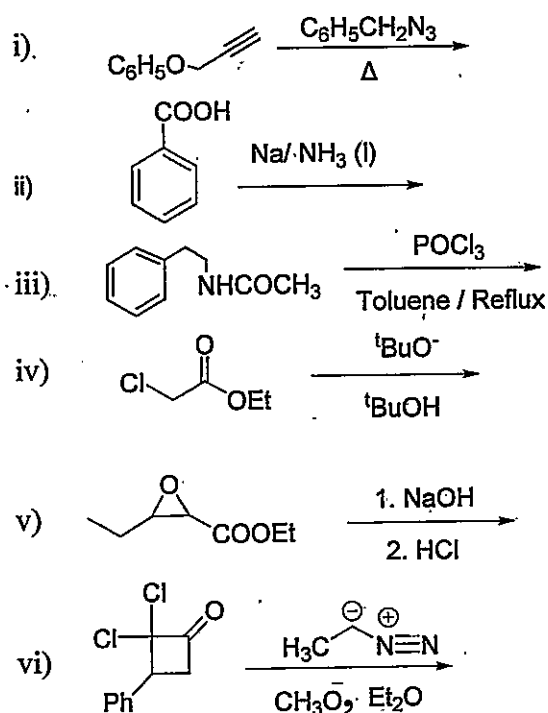
(i) Wittig reaction

(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)



(b) What is Birch reduction? Explain with suitable example.

6. (a) What is Suzuki coupling reaction? Write the steps involved in the mechanism of 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:

7. (a) Explain large scale process with at least two suitable examples? (5, 5, 5)

(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.

3027

8

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

(3x4)

(1200)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 3027

H

Unique Paper Code : 32177904

Name of the Paper : DSE: Analytical Methods in 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 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.

P.T.O.

- (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)

- (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?

3027

6

(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

3027

3

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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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.

- (iii) Write a program to calculate $\sin(x)$ given by the series

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} \dots \quad (4,4,4.5)$$

[This question paper contains 12 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 3138

H

Unique Paper Code : 32177903

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

Name of the Course : **B.Sc. (H) 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 **(12.5)**.
4. Attempt all parts of a question together.

1. (i) Fill in the blanks :

(a) BASIC is _____ level language.

(b) Point of intersection of a row and a column in a graphic screen is known as _____ .

(c) _____ command allows the numeric data to be printed in decimal format.

(d) 2 Kilo Byte = _____ Byte

(e) A loop within another loop, in BASIC, is termed as _____ .

(f) _____ command is used to see a selected portion of the screen in graphics.

(g) _____ is a non-executable statement.

(h) _____ statement allows the same data to be reused for various variables.

(iii) Write a program in BASIC to calculate the pH of a 10^{-6} M acetic acid solution by Bisection method. Use the following equation for hydrogen ion concentration $[H^+]$ for a weak acid :

$$[H^+]^3 + K_a [H^+]^2 - (C K_a + K_w) [H^+] - K_a K_w$$

$$\text{Given } K_a = .8 \times 10^{-5} \text{ and } K_w = 10^{-14}$$

(4,4,4.5)

8. (i) Write the following mathematical expressions in BASIC :

$$(a) y = e^{(x \sin \beta t + x \cos \beta t)}$$

$$(b) \psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{l}\right)$$

(ii) Write a program in BASIC to generate a rectangle with diagonal coordinates (10, 20) and (180, 150).

3138

10

(a) FIX(X)

(b) INT(X)

(c) CINT(X)

(d) SGN(X)

(ii) Give the output of the following program :

10 LET X = 1

20 LET Y = 2

30 IF (2*X+Y^2) > Y+3 THEN PRINT "TRUE"
ELSE PRINT "FALSE"

40 IF X > Y OR X = 0 AND Y = 0 THEN PRINT
"T" ELSE PRINT "F"

50 IF NOT(NOT(X = 0) AND Y = 0)) THEN PRINT
"T" ELSE PRINT "F"

60 END

3138

3

(ii) Write a user friendly program in BASIC to read
(READ....DATA) text and count and print how
many times letters 'A' and 'a' occur in this
text. (8,4.5)

2. (i) Write the full form of the following :

(a) ASCII

(b) VIRUS

(c) ALU

(d) HTML

(ii) Give the syntax and functions of the following
commands :

(a) LEFTS

(b) LOCATE

P.T.O.

- (iii) Write a program to READ two matrices A(MxN) and B(NxP) using (READ-----DATA) and find their product. The matrices 'A' and 'B' and their product 'C' should be printed in matrix form. (4,4,4.5)

3. (i) Explain the following terms giving examples :

(a) Subscripted Variable

(b) Operating System

(ii) Convert the following as asked, show working too.

$$(a) (229.25)_{10} = (\quad)_2$$

$$(b) (1110110.1)_2 = (\quad)_{16}$$

(iii) Using following data, which were collected as part of a quality control study for the analysis of sodium in serum; results obtained were concentrations of Na^+ in mmol/L, write a

(b) 90 GOTO 90

(c) ON C\$ GOTO 100,200,300

(d) DATA, 10, 12, 30, 14, 25

(iii) Write a program in BASIC, Using Simpson's method, to determine the change in molar enthalpy of Oxygen gas when heated between 298 K and 373 K

$$\text{Given : } C_{p,m} = a + bT + c/T^2$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT$$

$$a = 29.96; b = 4.18 \times 10^{-3}; c = -1.67 \times 10^5$$

(4,4,4.5)

7. (i) What are the values given by the following functions when $X = -5.78$

P.T.O.

$b = 0.0429 \text{ dm}^3 \text{ mol}^{-1}$ in the volume range from 0.06 to 0.55 dm^3 at the difference of 0.005 using the Van der Waals equation for temperatures between 290 K and 350 K, at intervals of 20 K. ($R = 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$). (4,4,4.5)

6. (i) Identify the errors in the following BASIC constants and correct them.

(a) 6.6E^{23}

(b) COMPUTER "APPLICATIONS"

(c) $4.0 \times 10^{(-34)}$

(d) $9.4\text{E}2.5$

- (ii) Find errors in the following BASIC statements and correct them.

(a) FOR A\$ = B\$ TO C\$

program to estimate the mean, variance and standard deviation of the following data set of 10 samples.

[Na ⁺]mmol/L	140	143	141	137	132	157	143	149	118	145
--------------------------	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

$$\text{Mean} = \frac{1}{n} \sum_{i=1}^n x_i$$

$$\text{Variance} = \frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})^2$$

$$\text{Standard deviation} = \sqrt{\text{variance}} \quad (4,4,4.5)$$

4. (i) Differentiate between the following, explaining functions :

(a) Library functions and User defined functions

(b) RAM and ROM

- (ii) Which of the following are valid BASIC variables? Correct the invalid ones.

(a) X\$Y\$

(b) "VOLUME"

(c) NEWTON-RAPHSON

(d) LOG

- (iii) The following data for Concentration and Absorbance of a coloured solution is given. If the solution follows Lambert Beer's law, $A = \epsilon cl$, find the molar extinction coefficient using least square curve fitting method. Assume $l = 1$.

Concentration	0	1.0	2.0	3.0	4.0	5.0
Absorbance (at 515 nm)	0.234	0.365	0.479	0.521	0.664	0.802

$$\text{Given slope} = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{n \sum x_i^2 - (\sum x_i)^2} \quad (4,4,4.5)$$

5. (i) Write the output of the following program :

```
10 FOR I = 1 TO 3
```

```
20 SUM = 0
```

```
30 FOR J = 1 TO 2
```

```
40 SUM = SUM + I + J
```

```
50 NEXT J
```

```
60 PRINT SUM
```

```
70 NEXT I
```

```
80 END
```

- (ii) Write a program in BASIC to print first 'N' members of FIBONACCI series, N is to be input by the user.
- (iii) Write a Program to plot Van der Waals isotherms in BASIC GRAPHICS for CO₂ gas molecule having $a = 3.610 \text{ dm}^6 \text{ atm mol}^{-2}$ and

(17)

[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 ν_{CO} stretching frequencies in isoelectronic series of $[\text{V}(\text{CO})_6]^-$, $\text{Cr}(\text{CO})_6$ and $[\text{Mn}(\text{CO})_6]^+$ 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 dimeric trialkyl 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?

- (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)

(1000)

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[This question paper contains 8 printed pages.]

Your Roll No.....

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.

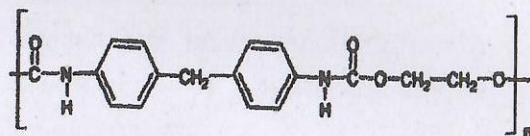
Write the complete sequence of reactions from (A) to (C) with all the reagents used in the reactions. Give the name of (C) and discuss the colour change of (C) in pH range of 3.1-4.5.

- (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
- 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)

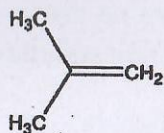
2979

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4. (a) Identify the polymer from the structure given below and give its synthesis from its monomers and discuss its uses.



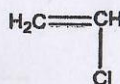
- (b) Arrange the following monomers in order of their decreasing ability to undergo cationic polymerization with reasons.



(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.

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- (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 $\text{C}_3\text{H}_6\text{O}$, 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) δ 2.1, s, 6HB: 184 nm (ϵ max 10000)

2975, 2827,

 δ 9.8 (t, 1H);2725, 1740 cm^{-1} δ 2.4 (m, 2H); δ 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) $\text{CH}_3\text{CH}_2\text{CONH}_2$ and $\text{CH}_3\text{CH}_2\text{NH}_2$ (ii) $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{-O-CH}_3$

P.T.O.

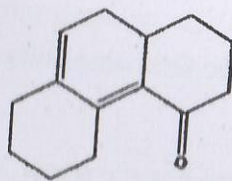
- (c) The IR spectrum of ethyl acetoacetate exhibit peaks at 3050, 1748, 1724 and 1650 cm^{-1} . Assign these peaks with reason to the structural feature of the compound.

(4.5,4,4)

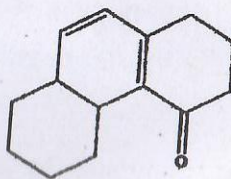
7. (a) (i) A compound has λ_{max} 296nm in dioxan but it shifts to 288nm in ethanol. Which transition $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ is responsible for this. Explain.

- (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.



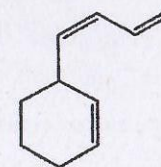
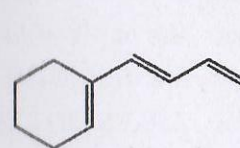
(A)



(B)

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

- (c) How will you use UV spectral data to distinguish among the following isomeric systems?



(calculate λ_{max} 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

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, $J=8$ Hz), 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)

Your Roll No.....

Sr. No. of Question Paper : 3517 H

Unique Paper Code : 42177926

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

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

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. Use separate sheets for **Section A** and **Section B**.
3. Attempt **three** questions from each section.
4. Do not intermix the sections and attempt all parts of a question paper together.
5. **All** questions carries equal marks.

P.T.O.

Section A

Attempt any **three** questions.

1. (a) How is Potassium dichromate prepared from chromite ore? Write two important uses of $K_2Cr_2O_7$.

(b) Write down the balanced chemical equation for the following reactions :

(i) $KMnO_4$ is added to $FeSO_4$ in acidic medium.

(ii) $K_2Cr_2O_7$ solution is treated KOH .

(iii) $K_4[Fe(CN)_6]$ is added into $CuSO_4$ solution.

(iv) H_2S is passed through $KMnO_4$ solution in acidic medium.

(c) Explain the hybridisation, magnetic behaviour and structure of Potassium ferrocyanide on the basis of VBT. (4,4,4.5)

2. (a) Define 18 electron rule. Using this rule as a guide, find the value of x :

(i) $Fe_3(CO)_x$

(ii) identify 3d metal in $[M(CO)_6]^-$

(iii) $Mn_2(CO)_x$

(b) Ni forms a mononuclear carbonyl but the cobalt carbonyl is dimeric. Explain.

(c) With reference to MO diagram of CO, explain why does CO act as both a Lewis acid and base? Which atom carbon or oxygen is involved in both the cases. (4,4,4.5)

3. (a) Which disease is caused due to toxicity of Hg. What are the symptoms. Give reasons for its toxicity.

(b) Discuss the role of magnesium ion in chlorophyll.

(c) Explain cooperative effect of four heme group in a hemoglobin molecule. Why are shapes of the oxygen saturation curves of hemoglobin and myoglobin different? (4,4,4.5)

4. (a) Give one method for the preparation of Ni(CO)_4 .
Using VBT explain the structure of Ni(CO)_4 and predict its magnetic behaviour.

- (b) The CO stretching frequency in IR spectra are as follows :



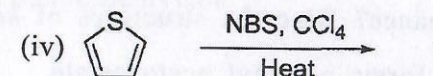
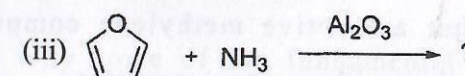
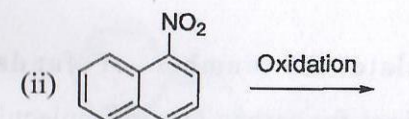
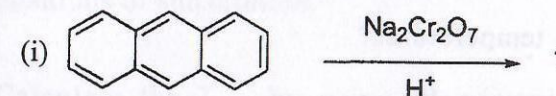
The value for free CO (2143 cm^{-1}). Explain giving reasons.

- (c) Explain the role of Na-K pump in controlling the concentration of Na^+ ions and K^+ ions inside and outside the cell. (4,4,4.5)

SECTION B

Attempt any **three** questions.

5. (a) Write the products formed in the following chemical reactions :



(b) Explain why butadiene has a higher value of $\lambda_{\max}$ than ethylene. 1,3-butadiene absorbs at 217 nm but 1,5-hexadiene absorbs below 200 nm. Explain.

(c) Why does the sulphonation of naphthalene yield different products at low and high temperatures? (4,4,4.5)

6. (a) (i) Why electrophilic attack on anthracene is favored at C-9?

(ii) Calculate the number of fundamental vibrations for carbon dioxide molecules in IR spectroscopy.

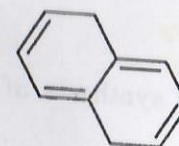
(b) (i) What are active methylene compounds? Explain with any two examples.

(ii) Differentiate between tautomerism and resonance? Give the structures of *keto* and *enol* forms of ethyl acetoacetate.

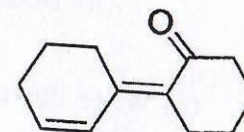
(c) What is a Bathochromic shift? Explain with the help of suitable example, the effect of extended conjugation on the π to π^* transition of dienes? (4,4,4.5)

7. (a) Explain the nucleophilic and electrophilic substitution in pyridine and discuss the favorable positions of substitution.

(b) Calculate the $\lambda_{\max}$ by using Woodward-Fieser Rules.



Base value = 253 nm



215 nm

(c) Why some of the fundamental vibrations are infrared active whereas the others are not. Discuss by using the example of *cis* and *trans*-1,2-dichloroethylene. (4,4,4.5)

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

(i) Hantzsch pyridine synthesis

(ii) Auxochromes and Chromophores

(iii) Lambert's Beer Law

(b) Write down the chemical reactions for the synthesis of the following compounds using ethyl acetoacetate.

(i) Succinic acid

(ii) Butanone

(c) Write down Paal-Knorr synthesis of furan. Give mechanism.

(4,4,4.5)

8. (a) Furan is not stable to acids, although it has aromatic character. Why?
- (b) How will you synthesize β -ketoesters by Claisen condensation. Write the mechanism.
- (c) Write the two methods of preparation of Thiophene.
- (d) Write the short note on any two –
- (i) Bathochromic shift or red shift
 - (ii) Rocking and Wagging vibrations
 - (iii) Knorr-Pyrrole synthesis (3,3,2.5,4)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 3398

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.

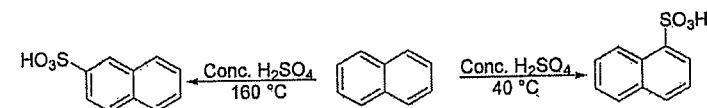
Section A :

Organometallics, Bio-inorganic Chemistry

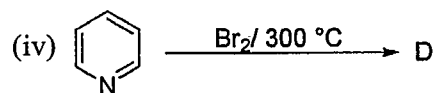
(Attempt any three questions)

1. (a) Write an essential feature for a compound to be termed as organometallic compound. How organometallic compounds are classified on the basis of bonding? Give one example of each.
- (b) What is meant by the term hapticity? How it is denoted for a ligand. Give an example where the same ligand can show varying hapticity.
- (c) Define the following terms giving one example each :
 - (i) Essential metal ions
 - (ii) Trace metals
 - (iii) Non-essential metal ions. (4,4,4.5)

- (c) Explain why pyrrole tend to polymerise in presence of strong acids but pyridine remains unaffected?
- (d) Discuss the aromaticity of furan, thiophene and pyrrole. Arrange them in increasing order of aromatic character and reactivity towards electrophilic aromatic substitution. (4,3,2.5,3)
7. (a) When naphthalene is treated with conc. Sulfuric acid the following products were obtained, why?



- (b) Discuss the origin of UV-visible spectra and arrange the following electronic excitations in order of their decreasing energy: $\sigma\text{-}\sigma^*$, $n\text{-}\sigma^*$, $\pi\text{-}\pi^*$, $n\text{-}\pi^*$.
- (c) Explain with suitable example why pyridine undergoes electrophilic substitution with great difficulty in acidic solution? Write the suitable examples.
- (d) Discuss the Elbs reaction. (3,3.5,3,3)



(c) Give evidence to show that acetoacetic ester exists in keto and enol forms.

(d) How will you distinguish *o*-hydroxybenzaldehyde (salicylaldehyde) and *m*-hydroxybenzaldehyde on the basis of IR spectroscopy? (3,4,2,3.5)

6. (a) Write a short note on any two of the following :

(i) Method of preparation of pyridine

(ii) Aromatic character of pyridine

(iii) Establish the structure of anthracene.

(b) Establish the structure and Howarth synthesis of naphthalene.

2. (a) Arrange the following species in increasing order of the property mentioned and give reason :

(i) $\text{Ni}(\text{CO})_4$, $[\text{Co}(\text{CO})_4]^-$ - C - O bond length

(ii) $\text{Fe}(\text{CO})_5$, $[\text{Fe}(\text{CO})_4]^{2-}$ - Fe - C bond order

(b) What is synergic effect? How does it account for the formation of carbonyls with transition metals in low oxidation states?

(c) Draw structures of KMnO_4 and $\text{K}_4[\text{Fe}(\text{CN})_6]$.

(d) Define 18 electron rule. (3,3,4,2.5)

3. (a) Give a diagrammatic representation of sodium potassium pump and explain its working. Why is the pump considered to be a case of active transport?

(b) What is the function of haemoglobin? Explain why haem group cannot act as biological oxygen carrier in the absence of globin chain?

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4

(c) Write the toxic effects of Hg(II) poisoning. Give reason for toxicity. (4.5,4,4)

4. (a) What's the geometry, hybridization and oxidation no. of Cr in $K_2Cr_2O_7$? Explain the reason for its color.

(b) Will the C-O bond length in metal carbonyls be longer or shorter than that in free CO? Justify your answer.

(c) Write a short note on :

(i) Zeise's salt

(ii) Role of Magnesium in chlorophyll

(4,2.5,6)

3398

5

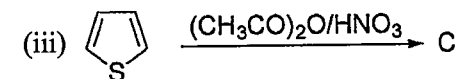
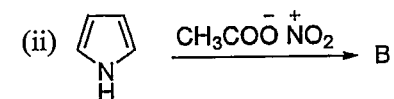
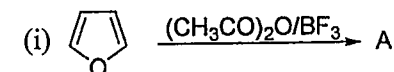
Section B :

Polynuclear Hydrocarbons and UV, IR

(Attempt any three Questions)

5. (a) Discuss and arrange the reactivity of Benzene, naphthalene and anthracene towards electrophilic aromatic substitution.

(b) Complete the following reactions-



P.T.O.