[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 1196 **F**

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: (3×5)

   (a) Graphite is a good conductor of electricity while diamond is not.

(b) Ionisation energy decreases from B to Al but increases from Al to Ga.

(c) Dilute solution of alkali metals in liquid ammonia is blue coloured and paramagnetic in nature.

(d) The bond angle in NH_3 is 107°C while in PH_3 is 93°C.

(e) Na_2CO_3 is more soluble than $NaHCO_3$ in water.

2. (a) Explain why most lines in the Ellingham diagram slope upward from left to right. What happens when line crosses $\Delta G = 0$? (5)

(b) Chemistry of Lithium is different from other alkali metals. Give examples in support of the statement. (5)

(c) Why is white phosphorous very reactive in comparison to red phosphorous? Phosphoric acid is syrupy and viscous. Explain. (5)

(a) Explain briefly the complex formation tendency of the alkali metals with special reference to crown ethers and cryptands. (5)

(b) When heated sulfur melts to a mobile liquid, but on further heating the viscosity increases sharply and then decreases again. Explain. Give the structure and oxidation state of sulfur in H_2SO_3. (5)

(c) What are clathrates compounds of noble gases? Why do helium and neon not form clathrates? (5)

4. (a) Write a short note on Hydrometallurgy and Zone Refining. (5)

(b) Complete and balance the following reactions:

(i) $XeF_4 + H_2O \longrightarrow$

(ii) $Mg\,(NO_3)_2\,(s)\ \Delta \longrightarrow$

(iii) $P_4 + HNO_3 \longrightarrow$

(iv) $B_2H_6 + H_2O \longrightarrow$

(v) $SiH_4 + AgNO_3 + H_2O \longrightarrow$

(5)

(c) What is the inert pair effect? $PbCl_4$ is a stronge oxidizing agent than $SnCl_4$. Explain. (5

5. (a) Among alkaline earth metals (except Beryllium which will be the softest metal and have the mo insoluble sulfate? Give reason. (

(b) Discuss the structure and bonding in Diborane. What are the products formed when diborane reacts with excess ammonia at low and at high temperatures? (5)

(c) Draw and explain the structure of the following compounds:

(i) ICl_3

(ii) Basic beryllium acetate. (5)

6. (a) What are interhalogen compounds? Why are they more reactive as compared to halogens? (5)

(b) Discuss the structure of XeF_2 using MOT. What are the advantages of this theory over V BT for XeF_2? (5)

(c) Give details of Electrolytic reduction and Van Arkel de Boer process. (5)

7. (a) Explain the following according to Ellingham Diagram:

   (i) For extraction of metals from HgO and Ag_2O, no need to add a reductant.

   (ii) Cr_2O_3 can be reduced by Al, but Al_2O_3 can not be reduced by Cr. (5)

(b) Arrange the following hydrides in increasing order of their boiling points and bond angle. Give reasons for the same H_2Se, H_2O, H_2Te, and H_2S. (5)

(c) Oxygen exists as an O_2 molecule while sulfur exists as an S_8 molecule. Explain. (5)

(a) Discuss briefly the following-

(i) Variation of the atomic radii and electronegativity among the elements of the main group.

(ii) Although the ionization energy of Li is maximum amongst alkali metals it is the strongest reducing agent in the aqueous solution. Why? (5)

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

(i) Allotropes of Carbon

(ii) Hydrides of elements of group 15

(iii) The oxo-acids of chlorine (5×2)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 1234 **F**

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 value of heat capacity at constant pressure greater than the value at constant volume?

(b) Reversible processes cannot be carried out in reality. Explain.

(c) Partial molar volume of a component in a solution depends on the nature as well as the amount of the other components. Explain qualitatively.

(d) Steam at 1 bar is converted to liquid water spontaneously at temperatures below 100°C although this results in decrease in its entropy. Explain.

(e) If Joule Thompson Coefficient is positive for a gas it indicates that attractive forces dominate between molecules of the gas. Is this statement true? Explain giving reason

(f) Why is the partial molar Gibbs free energy called as Chemical potential?

(g) Which of the following processes are spontaneous and why?

(i) Reversible isothermal expansion of ideal gas.

(ii) Vaporization of superheated water above 100°C.

(iii) Melting of ice at freezing point.

(5×3=15)

2. (a) If the equation of state of a gas is

$\left(P+\frac{a}{V^2}\right)V=RT$; Show that P is a state function.

Also prove that $\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T+1=0$.

(b) Show that isothermal reversible work of expansion of an ideal gas is greater than that of a van der Waals gas under similar conditions?.

(c) The value of $C_{p,m}$ for a sample of a perfect gas was found to vary with temperature as $C_{p,m}/JK^{-1}\ mol^{-1} = 20.17 + 0.3665(T/K)$. Calculate q, w, ΔU, and ΔH for one mole of the gas when the temperature is raised from 25°C to 200°C at constant pressure. (5,5,5)

3. (a) Using indicator diagram show that more work is done by the system during? expansion of an ideal gas in a reversible process than in an irreversible process.

(b) Show that chemical potential of a component in a mixture can be written in terms of enthalpy. Is this a partial molar quantity? Give reason.

(c) One mole of an ideal gas with $C_V = 3/2\ R$ undergoes adiabatic reversible expansion from 22.4 liters to 44.8 liters. If initial temperature is 27°C, calculate the final temperature and the work done in the process. (5,5,5)

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

(b) Show that dw is not an exact differential and hence w is not a state function.

(c) What is the difference between bond dissociation enthalpy and bond energy?

The value of $\Delta_r H°$ (298K) for the reaction $N_2H_4(g) \rightarrow N_2H_2(g) + H_2(g)$ is found to be 108.76 kJ mol^{-1}. Calculate the bond enthalpy of N = N bond assuming that the structure of N_2H_2 is HN = NH. Given the following bond enthalpies : ε_{N-N} = 163.18 kJ mol^{-1}, ε_{N-H} = 390.79 kJ mol^{-1} and ε_{H-H} = 435.89 kJ mol^{-1}. (5,5,5)

5. (a) Derive the thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T + P = T\left(\frac{\partial P}{\partial T}\right)_V$$

starting from $dU = dq + dw$

(b) What is residual entropy? Explain giving two examples.

(c) 5 g ice at 273 K is added to 30 g water at 323 K in a thermally insulated container. All the ice melts when equilibrium is achieved. What is the final temperature? What is the total entropy change? Given $\Delta_{fus}H = 334.72 \text{Jg}^{-1}$, $C_P(1,H_2O) = 4.184 \text{ JK}^{-1}\text{g}^{-1}$.

(5,5,5)

6. (a) Describe Joule's experiment and the result obtained from it. What are its shortcomings?

(b) What is inversion temperature? Starting from the definition of μ_{JT} show that $T_i = 1/\alpha_i$ where α_i is the isobaric expansivity of the gas at the temperature T_i.

(c) State Hess's law of constant heat summation. Calculate the enthalpy of formation of tungsten carbide (WC) from the following data :

$W(s) + 3/2\ O_2(g) \rightarrow WO_3(s)\ \Delta_r H^\circ_{298} = -837.47$ kJ mol^{-1} $WC(s) + 5/2\ O_2(g) \rightarrow WO_3(s) + CO_2(g)\ \Delta_r H^\circ_{298} = -1195.79$ kJ mol^{-1} C (graphite) + $O_2(g) \rightarrow CO_2(g)\ \Delta_r H^\circ_{298} = -393.51$ kJ mol^{-1}.

(5,5,5)

7. (a) Derive the relation $\left\{\dfrac{\partial\left(\dfrac{\Delta_r A}{T}\right)}{\partial T}\right\}_p = -\dfrac{\Delta_r U}{T^2}$.

(b) Define enthalpy of neutralization. Why is its value always negative? The value of enthalpy of neutralization of strong acid and strong base is same for all acids and bases. Explain. Will there be a change in the value of enthalpy of neutralization if the acid or the base is a weak electrolyte? Give reason for your answer.

(c) Compute $\Delta_r G$ for the process: H_2O (l, 2 atm, 373 K) → H_2O (g, 2 atm, 373 K). (5,5,5)

8. (a) Derive the relation $\Delta S = C_p \ln \frac{T_f}{T_i} - V\alpha(P_f - P_i)$ starting from $dH = TdS + VdP$.

(b) Absolute entropy of liquid water at 298K has to be calculated. Write all the steps involved. Also write the final expression for calculation of entropy.

(c) Calculate the entropy of separating the components in 100 g of air. The composition is 21% volume O_2, 78% volume N_2 & 1% volume Ar (Atomic Weight of Ar is 40). (5,5,5)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 4522 **E**

Unique Paper Code : 32171401

Name of the Paper : Inorganic Chemistry-III

Name of the Course : **B.Sc. (H) 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. **All** questions carry equal marks.

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

   (i) $[Co(NH_3)_6]Cl_3$

P.T.O.

(ii) $[Cu(NH_3)(H_2O)Br_2]$

(iii) $[Co(NH_3)_4(H_2O)Br](NO_3)_2$

(b) Write the formulae of the following coordination compounds :

(i) Dichloridobis (ethane-1, 2-diamine) platinum (IV) nitrate

(ii) Potassium tetra cynonickelate (II)

(iii) Tris(ethane-l, 2-diamine) chromium (III) chloride

(c) Calculate the oxidation state of central metal atom in the following :

(i) $[Co(NH_3)_5Cl]^{2+}$

(ii) $K_4[Fe(CN)_6]$

(iii) $[Co(NO_2)_2(py)_2(NH_3)_2]NO_3$

(d) Draw the structures of all geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$. (3,3,3,3.5)

2. (a) A complex ion having the composition $[TiL_6]^{3+}$, L = neutral ligand shows an absorption maxima at 500 nm (500×10^{-9} cm). Calculate the crystal field splitting, Δ_0 for this complex.

(b) What is chelate effect? Describe two factors that contribute to the stability of bis(dimethylglyoximato) nickel(II) complex.

(c) Transition elements normally shows variable oxidation states. Explain.

(d) Arrange the following in increasing order of stability :

$[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(dien)_3]^{3+}$

Where en = ethylene diamine, dien = diethyltriamine

(3,3,3,3.5)

3. (a) Potassium permanganate is stored in dark bottles. Why?

(b) Explain the order of Δ_0 for octahedral complexes for F^-, H_2O, CN^-.

(c) The complexes of Mn(II) are generally less stable than those of subsequently divalent 3d series of metal ions. Why?

(d) All the Cr-F bond lengths in $[CrF_6]^{3-}$ are equal but in $[CrF_6]^{4-}$ two Cr-F bond lengths are shorter than the remaining four. Explain. (3,3,3,3.5)

4. (a) The complex $[Pt(NH_3)_2(NO_2)_2]$ exists in two isomeric forms α and β. The a form reacts with one mole of oxalic acid whereas β form reacts with two moles of oxalic acid. Give the structure of α and β form.

(b) What are the drawbacks of crystal field theory?

(c) What are spinels? What kind of spinel is Fe_3O_4?

(d) Why do d-orbitals of the metal cation split when ligands approach towards it? (3,3,3,3.5)

5. (a) Why do lanthanides and actinides give very sharp bands in their electronic spectra?

(b) Calculate the magnetic moment of Europium(III). Explain discrepancy between observed and calculated magnetic moment. (Atomic number of Europium is 63).

(c) Cerium(III) ion with a $4f^1$ configuration is colourless while cerium(IV) ion with a $4f^0$ configuration is red. Why?

(d) Explain the ion exchange method used for separation of Lanthanides. (3,3,3,3.5)

6. Explain the following :

(a) Crystal field splitting in tetrahedral complexes(Δ_t) is only 4/9 of the corresponding splitting in octahedral complexes(Δ_0).

(b) $CuSO_4.5H_2O$ is blue but $CuSO_4$ is colourless.

(c) How variation of lattice energy of divalent metal halides of the first transition series can be taken as an evidence of crystal field stabilization.

(d) Inner and outer orbital complex. (3,3,3,3.5)

7. (a) Calculate the CFSE in terms of Δ_t of a d^7 metal ion placed in a tetrahedral crystal field. Predict the magnetic behaviour.

(b) Why is potassium dichromate intensely coloured?

(c) The $\{Ni(CN)_4]^{2-}$ is square planar and diamagnetic whereas $[NiCl_4]^{2-}$ is tetrahedral and paramagnetic. Explain.

(d) Explain hydrate isomerism with example.

(3,3,3,3.5)

8. (a) Explain the following properties of the transition elements

(i) Alloy formation

(ii) Complex formation

(b) Given below are the Latimer diagram for Cr in acidic medium :

$$Cr_2O_7 \xrightarrow{1.33} Cr^{3+} \xrightarrow{-0.41} Cr^{2+} \xrightarrow{-0.91} Cr$$

(i) Write half reaction for the conversion of $Cr_2O_7 \rightarrow Cr^{3+}$

(ii) Is there any tendency of Cr^{2+} to reduce to Cr? Give reasons.

(iii) Calculate skip step emf for $Cr^{3+} \rightarrow Cr$ change

(c) On adding a solution of potassium cyanide to an aqueous metal salt, a green precipitate, A is initially obtained which subsequently dissolves in excess of cyanide to give a yellow complex, B. Addition of iron (III) chloride solution to B gives a blue compound, C. On heating B with concentrated sulphuric acid, a poisonous gas D is evolved. Identify A, B, C, and D.

(4,4.5,4)

9. (a) How are the three isomers of $[Pt(Br)(NH_3)(Cl)(py)]$ prepared from $[PtCl_4]^{2-}$.

(b) Classify the following complex ions as labile or inert. Write the explanatory sentence on each.

(i) $[V(H_2O)]^{3+}$

(ii) $[Cr(H_2O)]^{2+}$

(iii) $[Fe(H_2O)]^{2+}$

(c) The trans isomer of diamminedichloroplatinum(II) complex, is more stable than the cis isomer. Explain. (6,3,3.5)

[This question paper contains 8 printed pages.]

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

E

Sr. No. of Question Paper : 4678

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_4H_9NO) on treatment with bromine and aqueous NaOH forms compound B (C_3H_9N). B on treatment with $NaNO_2$ and dil. HCl gives C (C_3H_8O) 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 reactions involved. Name the reaction involved in conversion of A to B with mechanism.

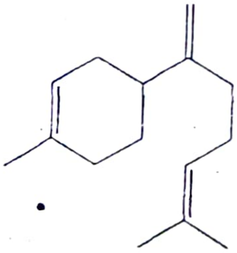
(b) How will you show that Naphthalene consists of two benzene rings fused together? Explain giving the complete sequence of reactions.

(c) Arrange the following in increasing order of basicity. Give reason.

Pyridine, Pyrrole, Pyrrolidine

(d) Define ‘Isoprene rule’. Indicate the isoprene units in the following compounds with the dotted lines :

(i)



(ii)

(6,3,3,3)

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

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

(c) Comment on the fact that Anthracene undergoes Diels - Alder reaction. Support your answer by giving an example.

(d) All bond lengths in Naphthalene are not equal. Explain with the help of suitable structures.

(3,3,3,3)

3\. (a) How will you distinguish between Aniline, N-methylaniline and N,N-dimethylaniline using Hinsberg's method? Give reactions.

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

m-methoxy aniline; p-methoxy aniline; aniline

(c) N-ethyl-N-methylaniline is chiral but non-resolvable. However, 2-aminopentane is resolvable. Explain.

(d) Write the final product formed in the reaction of nitrobenzene under the following conditions :

(i) Sn/HCl

(ii) Zn/NH_4Cl

(iii) Electrolytic reduction (3,3,3,3)

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

(i) Aniline into benzonitrile

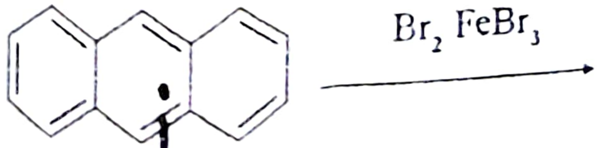
(ii) Benzyl chloride into anthracene

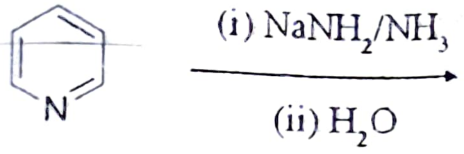
(iii) Aniline into 1,3,5-tribromobenzene

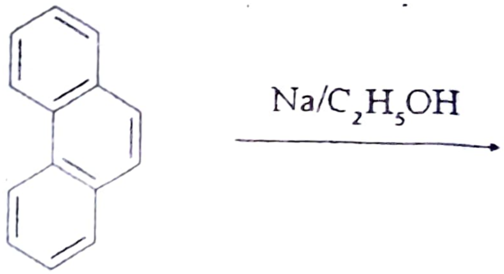
(iv) Pyrrole into 3-chloropyridine

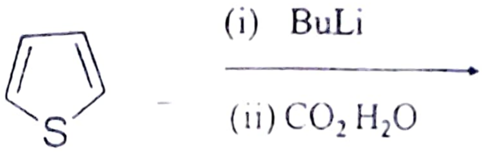
(b) Write the mechanism of acid catalysed hydrolysis of alkyl nitriles. (3,3,3,3)

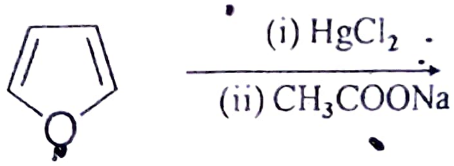
5. Complete the Reactions : **(any 12)** (12×1=12)

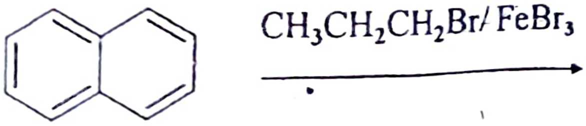
(i) 

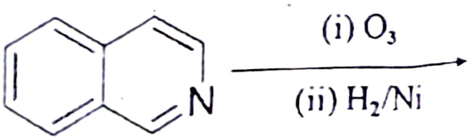
(ii) 

(iii) 

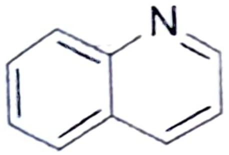
(iv) 

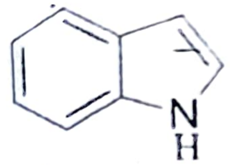
(v) 

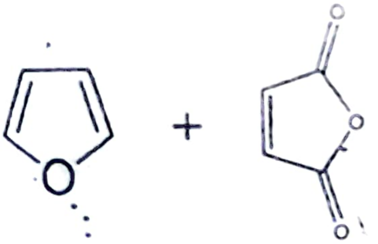
(vi) 

(vii) 

(viii) $CH_3CN \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } CH_3CH_2MgI}$

(ix)  $\xrightarrow{KMnO_4}$

(x)  $\xrightarrow[NaOC_2H_5]{\text{ethyl nitrate}}$

(xi)  $\xrightarrow[30\ °C]{\text{xylene}}$

(xii) $CH_3CH_2NO_2 + HONO \longrightarrow$

(xiii) $CH_3NC + S \longrightarrow$

(xiv) $C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow$

6. (a) Citral contains an α, β-unsaturated carbonyl group. Justify giving the relevant reaction.

(b) Discuss the reaction which indicate the position of linkage between pyridine and N-methyl pyrrolidine in nicotine.

(c) How will you show the presence of the following in an alkaloid :

(i) o-methyl group

(ii) phenolic group

(d) Give the synthesis of citral from methylheptenone using Reformatsky reaction. (3,3,3,3)

7. (a) Thiophene undergoes electrophilic substitution reaction at 2-position. Explain giving suitable structures.

(b) The reactions of pyrrole cannot be done in strongly acidic medium. Give reason and the reaction involved.

(c) Pyridine undergoes nucleophilic substitution reactions also. Justify the statement by providing suitable resonating structures.

P.T.O.

(d) Discuss the aromatic character of furan based on resonance. On catalytic hydrogenation, furan loses its aromaticity. Give the reaction and explain.

(3,3,3,3)

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

(i) Pomeranz-Fritsch synthesis of Isoquinoline

(ii) Fischer-Indole synthesis

(iii) Mannich reaction

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

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : **4802** **E**

Unique Paper Code : 32171403

Name of the Paper : Physical Chemistry – IV

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

Semester : IV

Duration : 3 Hours Maximum Marks : 75

<u>Instructions for Candidates</u>

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **six** questions in all.
3. Use of scientific calculator is permitted.

1. (i) (a) Distinguish between order and molecularity.

(b) Can the activation energy of a reaction be zero or negative? (2+2)

(ii) The rate law for the reaction described by

$$N_2O_{2(g)} \longrightarrow 2\ NO_{(g)}$$

P.T.O.

is first order in the concentration of $N_2O_{2(g)}$. Derive an expression for the time-dependent behavior of [NO], the product concentration. (4)

(iii) The reaction between carbon disulfide and ozone

$$CS_{2(g)} + 2\ O_{3(g)} \longrightarrow CO_{2(g)} + 2\ SO_{2(g)}$$

was studied using a large excess of $CS_{2(g)}$. The pressure of ozone as a function of time is given in the following table :

Time /s	0	30	60	120	180	240
Ozone pressure / torr	1.76	1.04	0.79	0.52	0.37	0.29

Is the reaction first order or second order with respect to ozone? (4.5)

2. (i) The half-life period of a reactant is 50 minutes at a certain concentration is reduced to one half of the initial concentration, the half-life period becomes 25 minutes. What is the order of the reaction? (4)

(ii) Give reason : **(Any two)**

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

(b) The value of steric factor p is usually less than one.

(c) Higher the activation energy of a reaction, slower is the rate of reaction. (2+2)

(iii) The mechanism proposed for the decomposition of N_2O_5 is :

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$$

$$NO + NO_3 \xrightarrow{k_2} N_2O_5$$

$$NO_2 + NO_3 \xrightarrow{k_3} NO + O_2 + NO_2$$

$$NO + NO_3 \xrightarrow{k_4} 2NO_2$$

Derive the expression for the rate of disappearance of N_2O_5. (4.5)

3. (i) Discuss Collision Theory of bimolecular gaseous reactions. (4)

(ii) A first order reaction has rate constant 2.2×10^{-5} min^{-1} at 458 K and 3.07×10^{-3} min^{-1} at 510 K respectively. Calculate the energy of activation. (4)

(iii) The rate constant for the dissociation of ethane

$$C_2H_6 \longrightarrow 2\ CH_3$$

P.T.O.

is given by : $k = 5 \times 10^6 \exp\left(\frac{-368\ \text{kJ}}{RT}\right)$

Calculate the enthalpy and entropy of activation for this reaction at 850 K. (4.5)

4. (i) The decomposition of phosphine, PH_3, on tungsten is first order at low pressures and zeroth order at high pressures. Account for these observations. (2)

(ii) For the reaction :

$$A \xrightarrow{k_1} B \xrightarrow{k_1'} C$$

Show that :

$$[C]_t = [A]_0 \left[1 - \frac{1}{(k1' - k1)} \{k_1' \exp(-k_1 t) - k_1 \exp(-k_1' t)\}\right]$$

Further plot the graph illustrating the variations of [A], [B], [C] with time 't', considering $k_1' >> k_1$. (6)

(iii) The enzyme catalase catalyzes the decomposition of H_2O_2. The data are :

$[H_2O_2]$ / (mol/L)	0.001	0.002	0.005
Initial rate / (mol/L s)	1.38×10^{-3}	2.67×10^{-3}	6.00×10^{-3}

If the concentration of catalase is 4.0×10^{-9} mol/L, plot the data to determine r_{max}, the constant K_M, and the turnover number, k_2. (4.5)

5. (i) Draw and discuss the titration curves obtained during the conductometric titration of :

(a) An aqueous solution of CH_3COOH with aqueous solution of NaOH.

(b) An aqueous solution of HCl with aqueous solution of NH_4OH. (2+2)

(ii) Discuss the asymmetric effect and electrophoretic effect. How these effects can be minimized? (4)

(iii) At 25°C, the specific conductance of distilled water is 58.0×10^{-7} Sm^{-1} and the λ°_{m} values of H^+ and OH^- ions are 349.8×10^{-4} and 198.5×10^{-4} $Sm^2 mol^{-1}$, respectively. Assuming that λ_m differs very little from λ°_{m}, calculate the ionic product of water at 25°C. (4.5)

6. (i) What is Walden's rule? Explain, why Walden's rule is not applicable to cations of small sizes. (4)

(ii) Calculate the transport numbers of H^+ and Cl^- from the following date obtained by moving boundary method using $CdCl_2$ as the indicator electrolyte: concentration of HCl solution = 0.1 M, mass of Ag deposited in the coulometer = 0.1209 g; movement of boundary = 7.50 cm and cross-sectional area of the tube = 1.24 cm². (4)

(iii) Describe Hittorf' s method for determination of transport number. (4.5)

7. (i) Attempt any **two** :

(a) Transport number of Cl^- ion in aqueous solution of HCl is 0.16 and it is 0.62 in aqueous solution of NaCl. Explain the difference.

(b) Define ionic mobility. How does it differ from ionic speed?

(c) Explain why conductivity decreases on dilution whereas molar conductivity increases? (2+2)

(ii) The specific conductivity of a saturated solution of CaF_2 was found to be 4.2×10^{-5} ohm^{-1} cm^{-1}. The specific conductivity of water used to make the solution was 2.0×10^{-6} ohm 1 cm^{-1}. The equivalent conductivities of Ca^{2+} and F^- ions are 52.0 and 48.0 ohm^{-1} cm^2 equiv^{-1}. Calculate the solubility of CaF_2 in water. (4)

(iii) State and explain Kohlrausch's law of independent migration of ions. If the molar conductivities at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 426.1 and 91.0 ohm^{-1} cm^2 mol^{-1} respectively, what will be the molar conductivity of Acetic acid? (4.5)

8. (i) Define quantum yield. How it is determined experimentally using a uranyl oxalate actinometer? Give reasons for high and low quantum yield. (4)

(ii) In a given cell, solution 'A' transmits 42% and solution 'B' 85% of radiation having a certain wavelength. What is the transmittance at the same wavelength of a solution made by mixing 35 mL solution 'A' and 55 mL solution 'B' if no reaction occurs? (4)

(iii) Formaldehyde can be synthesized by irradiating a mixture of CO and H_2 containing a trace of Hg with light of wavelength 253.7 nm. Show that the given reaction mechanism

$$Hg \xrightarrow{I_a} Hg^*$$

$$Hg^* + H_2 \xrightarrow{k_2} 2H + Hg$$

$$H + CO \xrightarrow{k_3} HCO$$

$$HCO + H_2 \xrightarrow{k_4} HCHO + H$$

$$2HCO \xrightarrow{k_5} HCHO + CO$$

$$2HCO \xrightarrow{k_6} HCOCHO \text{ (glyoxal)}$$

confirms the following rate law

$$\frac{d[HCHO]}{dt} = \frac{k_5 I_a}{k_5 + k_6} + k_4[H_2]\left(\frac{I_a}{k_5 + k_6}\right)^{1/2}$$ (4.5)

9. (i) Adsorption of UV radiations decomposes acetone according to the reaction :

$$(CH_3)_2CO \xrightarrow{h\nu} C_6H_6 + CO$$

The quantum yield of the reaction at 280 nm is 0.2. A sample of acetone absorbs monochromatic radiation at 280 nm at the rate of 7.5×10^{-3} J s^{-1}. Calculate the rate of formation of CO. (3.5)

(ii) Write short notes : (Attempt any **three**)

(a) Phosphorescence and Fluorescence

(b) Photosensitized reactions

(c) Van't Hoff Differential Method for determination of order of reaction.

(d) Stationary and non-stationary chain reactions.

(e) Ostwald's dilution law. (3+3+3)

(500)

[This question paper contains 6 printed pages.]

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

Sr. No. of Question Paper : 4505 **E**

Unique Paper Code : 32171601

Name of the Paper : Inorganic Chemistry IV : Organometallic Chemistry and Bio-inorganic 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 out of **nine**.

3. **All** questions carry equal marks **(12.5)**.

1. (i) The cyclopentadienyl rings in ferrocene have aromatic character but cyclopentadiene itself has no such character explain. Give two reactions of ferrocene which show it is more reactive than benzene.

(ii) Give the complete cycle describing each step to outline the working of the Ziegler-Natta catalyst for the polymerization of ethene.

(iii) Mn^{2+} ions are not precipitated as MnS on passing H_2S gas in group II but precipitate as MnS on passing H_2S gas in Group IV of qualitative analysis. Explain.

(5,5,2.5)

2. (i) What is meant by synergic effect? How does it account for the formation and stability of carbonyl complexes of transition metals in low oxidation states?

(ii) Why is it necessary to remove interfering ions before Group III analysis? Explain.

(iii) Name an important biomolecule containing cobalt and its function?

(5,5,2.5)

3. (i) Draw the structure of methyl lithium. In which category of organometallic compounds will you place it? What are the coordination numbers of Li and C in the tetramer?

(ii) What is the difference between active and passive transport? Why is the sodium – potassium pump considered to be a case of active transport? Explain giving the working of sodium-potassium pump.

(iii) Name the reagent used to separate Group IIA and IIB cations. Explain its role. (5,5,2.5)

4. (i) A mixture of salts, when heated with ethanol and conc. H_2SO_4 gave a gas A 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 gave 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 name the ions present.

(ii) Using the MO diagram of CO explain-

(a) CO acts as an electron pair donor and acceptor through carbon and not through oxygen and formation of both sigma and pi bond involve carbon.

(b) CO has negligible donor properties to Lewis acids like BF_3 but binds to transition metals

(c) CO is referred to as a π acid ligand.

(iii) Name the storehouse and transporter of iron. In which part of human body are they found?

(5,5,2.5)

5. (i) What is Fischer Tropsch process? How is synthetic gasoline prepared using this process?

(ii) How do you rationalize the increase in the C-C bond length from 133.7 pm in ethene to 137.5 pm in Zeise's salt, accompanied by a decrease in C-C stretching frequency from 1623 cm^{-1} to 1526 cm^{-1}?

(iii) Name the metal which plays an important role in the enzymes: Carbonic anhydrase and Carboxypeptidase A. Why this metal is considered to be excellent biocatalyst? (5,5,2.5)

6. (i) Describe the Perutz mechanism of oxygenation of haemoglobin. What is the trigger for this mechanism?

(ii) Differentiate between homogenous and heterogeneous catalysis giving examples of each and mention one advantage and one disadvantage of each.

(iii) Which is more stable and why:

$[Fe(\eta^5\text{-}C_5H_5)_2]$ or $[Co(\eta^5\text{-}C_5H_5)_2]$? (5,5,2.5)

7. (i) What do you understand by essential and non-essential metal ions in the biosystem? Give an example of each type.

(ii) Explain why is sodium carbonate extract prepared to perform confirmatory test for anions in qualitative analysis? Why is the extract acidified before adding any reagent?

(iii) Why is cis-platin active in cancer therapy in contrast to the trans-form? (5,5,2.5)

8. (i) Arrange the following in the increasing order of CO stretching frequencies in the IR spectrum and Explain the order: $[Mn(CO)_6]^+$, $[Cr(CO)_6]$, $[V(CO)_6]^-$, $[Fe(CO)_6]^{2+}$, $[Ti(CO)_6]^{2-}$

P.T.O.

(ii) Why is it necessary to test Group V ions in the order Ba^{2+}, Sr^{2+} Ca^{2+}?

(iii) Why are iron and copper essential in the human body? What are the diseases associated with excess of these metals?

(5,5,2.5)

9. (i) What are the toxic effects of arsenic? Give the reasons for its toxicity. How can it be treated?

(ii) Compare die synergic effect of Zeise's salt with that in metal carbonyls. Which one will have higher Fe-C bond order among $Fe(CO)_5$ and $[Fe(CO)_4]^{2-}$. Justify your answer.

(iii) State the formula of the rhodium complex used as Wilkinson's catalyst and the oxidation state of rhodium in it.

(5,5,2.5)

[This question paper contains 4 printed pages.]

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

Sr. No. of Question Paper : 4706 **E**

Unique Paper Code : 32177904

Name of the Paper : 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 a total of 6 questions.
3. **Three** questions to be attempted from **section A** and **three** from **section B**.
4. **All** questions are equal marks.
5. Log tables to be provide to the candidates.
6. Use of scientific calculator is allowed

SECTION – A

Attempt any 3 questions from this section

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

(a) Explain electroanalytical methods.

(b) What are the advantages of continuous drying over the batch drying?

(c) Explain the sample injection system in GC?

(d) What is *Electro Osmotic flow*?

(e) Discuss the principle and one application of DSC?

(f) Differentiate between partition chromatography and adsorption chromatography. (5×2.5)

2. (a) What is thermal gravimetric analysis (TGA)? Discuss decomposition analysis of $CaC_2O_4.2H_2O$ using TGA.

(b) What are redox titrations? Explain with one example.

(c) Explain the preparation of TLC plates and give applications of TLC. (4,4,4.5)

3. Write short notes on the following :

   (a) Analytical applications of *thermogravimetry*.

   (b) Chromatogram

   (c) Cyclic voltammetry (4,4,4.5)

4. (a) Explain column chromatography and its applications.

   (b) What are the criteria for a good thermobalance?

   (c) Lead was determined in a sample of dust by eight different methods and the results are 9.11,9.14,9.21,9.12,9.08,9.09,9.14 and 9.16 Calculate the arithmetic mean and standard deviation. (4,4,4.5)

SECTION – B

Attempt any 3 questions from this section

5. (a) Give a schematic diagram of a glass electrode and explain its function. Why is the glass electrode stored in water?

   (b) How is potentiometry used to find E_{eq} in an *redox process*?

(c) What are mobile phase and a stationary phase in a Thin Layer chromatography with examples?

(4,4,4.5)

6. Distinguish between the following :

(a) standard deviation and average deviation.

(b) Batch extraction and continuous extraction.

(c) accuracy and precision. (4,4,4.5)

7. (a) What is the principle of paper chromatography? Explain the procedure of paper chromatography.

(b) Explain the conductometric titration of a weak acid with a strong base.

(c) Explain the types of Polarography with their applications. (4,4,4.5)

8. (a) Define the following terms and give the mathematical expression for each of the following :

(i) Retardation factor

(ii) Partition coefficient

(b) Write short notes on batch extraction and counter current extraction.

(c) Define the following :

(i) (AAS) Atomic absorption spectroscopy

(ii) Flame photometry (4,4,4.5)

(500)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 4785 **E**

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) The PMR spectrum of dimethyl formamide shows two signals at 52.84 and 83.0 for the methyl protons at room temperature but a single sharp peak appears at high temperature (165°C). Explain.

(b) In IR spectroscopy, o-nitrophenol shows a band at 3200 cm^{-1} in KBr pellet as well as in chloroform solution, whereas in p-nitrophenol the values are different in two media (3330cm^{-1} in KBr pellets and 3520 cm^{-1} in chloroform). Explain.

(c) λmax for aniline shifts from 230 nm in neutral solution to 203 nm in acidic medium. Name the effect and explain.

(d) What arc edible dyes? Give name and structure of two edible dyes.

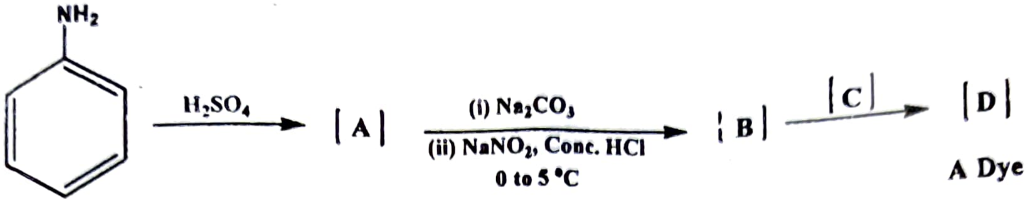
(e) Identify the class of following polymers and give two uses of each.

(i) Polyacetylene

(ii) poly (L-lactic acid)

(f) Azadirachtin has a bitter taste but a wonder drug. Comment. (5×2.5)

2. (a) Compound C is an aromatic amine which shows no peak in the region 3100 to 3600 cm^{-1}. Compound D absorbs at 465 nm and is red at pH below 3.1 and yellow above pH 4.4.



Identify compounds A, B, C and D and explain all the reactions involved. Discuss the use of compound D.

(b) Outline the synthesis of Malachite Green. Label the structures that form the leuco base, colour base and the dye salt.

(c) How is Indigotin obtained from Indigofera plants and why is it called Vat Dye? (4.5,4,4)

3. (a) Complete the following reaction by giving all the structures involved.

Heterocyclic compound (A) + An amine (B) $\longrightarrow$ An antimalarial drug (C)

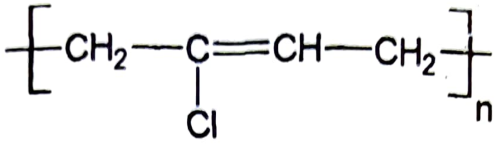
Give IUPAC name of compound (C). Discuss its uses and side effects.

(b) Give the name and one synthesis of a drug used for the treatment of typhoid.

(c) What is the active principle of Zantac? Discuss its medicinal values. (4.5,4,4)

P.T.O.

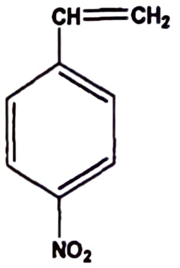
4. (a) Identify the following polymer.



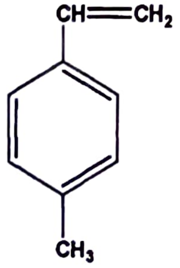
$$\left[\mathrm{CH_2 - \underset{Cl}{\underset{|}{C}} = CH - CH_2} \right]_n$$

Give the synthesis of polymer and its monomer.

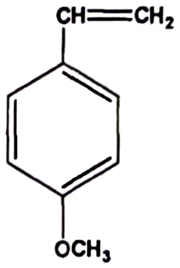
(b) Arrange the following monomers in order of their decreasing ability to undergo anionic polymerization with reasons.



(A)



(B)



(C)

(c) Discuss the uses of plasticized PVC and unplasticized PVC. Give the name and structure of two plasticizers. (4.5,4,4)

5. (a) In PMR spectroscopy, what information can be obtained from the following :

(i) Number of signals

(ii) Chemical shift

(iii) Area under peaks

(iv) Splitting of signals

(v) Coupling constant

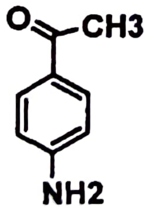
(b) A compound with molecular formula C_2H_2BrCl exhibits two doublets (J=16 Hz) in PMR spectra. Suggest a structure with explanation.

(c) Explain why the aldehydic protons appear much downfield in PMR spectrum. (4.5,4,4)

6. (a) IR spectrum of methyl salicylate exhibit peaks at 3300,2990,3050,1590 and 1540 cm^{-1}. Assign these peaks with reasons.

(b) Distinguish the following pairs of compounds by IR spectroscopy

(i)



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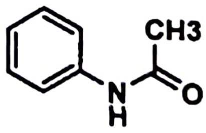
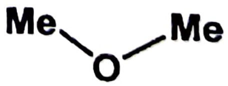
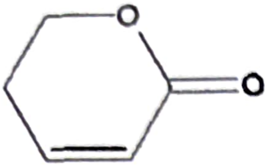


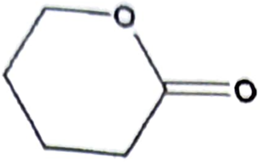
(ii)

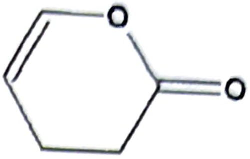
and



(c) The carbonyl stretching absorption for the following lactones are 1720,1745 and 1760 cm^{-1}. Match the absorption with the appropriate structure and give a reason for each choice.





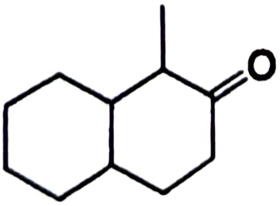


(4.5,4,4)

7. (a) (i) An organic compound in hexane exhibit λmax = 305nm and in ethanol shows λmax = 307nm. What should be the nature of transition and why?

(ii) Discuss the effect of steric hinderance to coplanarity in UV spectra by taking an example of cis and trans stilbene.

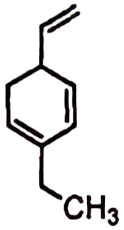
(b) Compound A has formula $C_{11}H_{16}O$ and be reduced to B, $C_{11}H_{18}O$ with hydrogen in presence of palladium. Compound B was found to have the following structure.

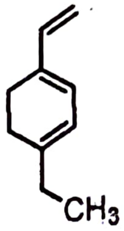


B

The UV spectrum of A showed strong absorption with λmax at 225nm and this absorption was not present in UV spectrum of B. What is the structure of A? (Use Woodward Fieser Rule)

(c) Distinguish among the following isomeric system by UV spectroscopy. (Use Woodward Fieser Rule)





Base value for homoannular (cisoid) diene = 253 nm

Base value for heteroannular (transoid) diene = 214 nm

Base value for Acyclic conjugated diene = 217 nm

Acyclic enone base value = 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

P.T.O.

β-alkyl group or ring residue = 12 nm

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

(4.5,4,4)

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

UV (in n-hexane)	**IR (in KBr)**	**^{1}H NMR ($CDCl_3$)**
A: 184 nm (ε max 10000)	2975,2827, 2725,1740 cm^{-1}	δ9.8(t,1H); δ2.47(m,2H); δ1.2 (t , 2H)
B: transparent above 180 nm	980-1010cm^{-1}(s)	δ3.5(m , 2H);δ4.5 (t, 4H)

(12.5)

OR

$$\underset{\substack{\textbf{A}\ (100\ \text{moles})\\ \bar{\nu}:\ 1710\ cm^{-1}}}{C_6H_{10}O} \xrightarrow[\text{(ii) } HNO_3]{\text{(i) Air liquid phase}} \underset{\substack{\textbf{B}\ (100\ \text{moles})\\ \bar{\nu}:\ 2500\text{-}2350\ cm^{-1}\ (br)}}{C_6H_{10}O_4} \xrightarrow[\substack{2.\ P_2O_5\\ 3.\ H_2/Ni}]{1.\ NH_3/Heat} \underset{\substack{\textbf{C}\ (100\ \text{moles})\\ \bar{\nu}:\ 3300\text{-}3450\ cm^{-1}\ (d)}}{C_6H_{16}N_2}$$

$$\textbf{B} + \textbf{C} \longrightarrow \text{-}[NH(CH_2)_6NH\text{-}\overset{O}{\overset{\|}{C}}(CH_2)_6\text{-}\overset{O}{\overset{\|}{C}}\text{-}]\text{-}_{100}$$

D

Identify A, B, C, D. Give their structures, names. Explain all peak of absorption of IR stretching frequencies. Give name of D and its uses. In D how much is the DP (degree of polymerization)?

(12.5)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 4832 **E**

Unique Paper Code : 32177908

Name of the Paper : DSE-4: Green 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 **six** questions.
3. All parts of a question should be attempted together.
4. Each question carries **12.5** marks.

1\. (a) Explain briefly each level of Waste Prevention Hierarchy,

P.T.O.

(b) Fill in the blanks (attempt any **four**)

(i) Sonochemistry is the process of organic synthesis under ______ irradiation.

(ii) ______ is a good alternative for dry cleaning of clothes.

(iii) Risk = (function) ______ X exposure.

(iv) Ionic liquids are also known as ______ solvents.

(v) The critical pressure and critical temperature of $ScCO_2$ ______

(c) Match the following :

I	Flixborough Disaster	i	Barry M. Trost
II	Adipic acid	ii	MIC
III	Atom Economy	iii	Cyclohexanol
IV	Bhopal Gas Tragedy	iv	D-Glucose

(4.5,4,4)

2. (a) Provide green route for the synthesis of the following compounds (attempt any **three**) :

(i) Catechol

(ii) Adipic Acid

(iii) Disodium iminodiacetate

(iv) Methylmethacrylate

(b) "What you don't have cannot harm you" is referred to which principle of green chemistry? Explain.

(c) An act was set up in 1990 to reduce or eliminate the toxicity of wastes. Name and elaborate it.

(4.5,4,4)

3. (a) What is atom economy? Consider the following acid promoted nucleophilic substitution reaction.

$$CH_3CH_2CH_2CH_2OH + NaBr + H_2SO_4 \longrightarrow CH_3CH_2CH_2CH_2Br + NaHSO_4$$

This reaction begins with dissolving 1.33 g of sodium bromide in 1.5 mL of water, followed by the addition of 0.80 mL (1.6 g) of 1-butanol and 1.1 mL (2.0 g) of concentrated sulfuric acid. On completion of the reaction, only 1.0 g of the product was obtained. Calculate the percentage yield of the reaction and also calculate the atom economy of the above reaction. Also compare the percentage yield and atom economy.

(b) Give an example of :

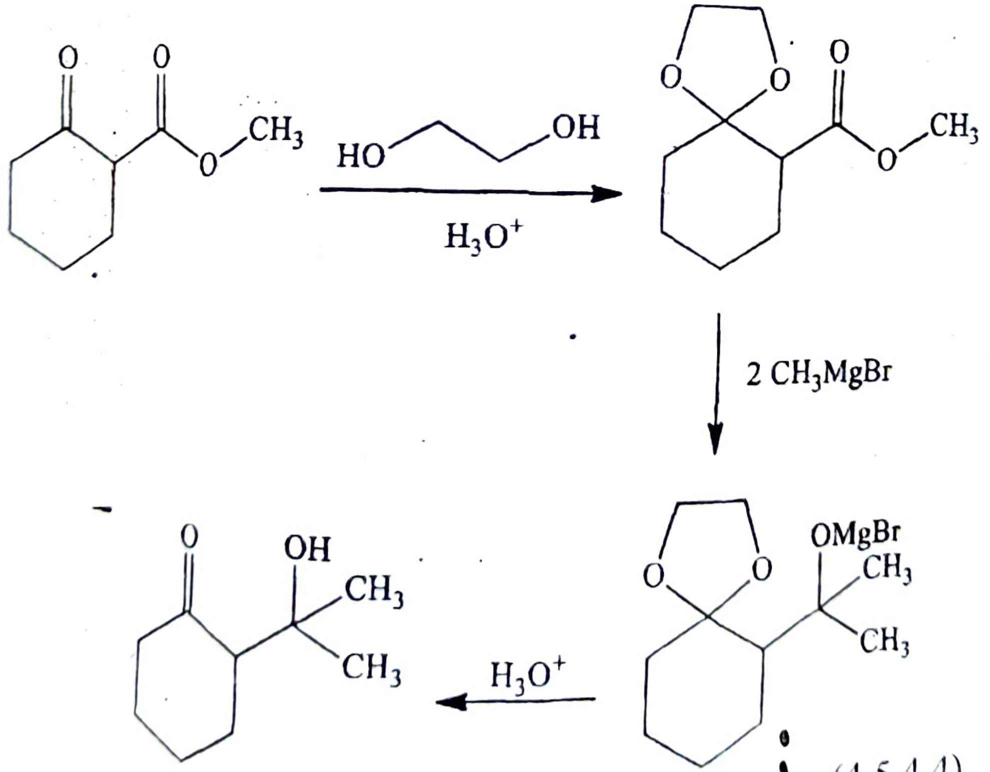
(i) Biocatalyst

(ii) Solvent less process

(iii) Photocatalyst

(iv) Green Plastics

(c) Explain, whether the following chemical synthesis can be considered as "Green"?



(4.5,4,4)

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

(b) What are trans fats? Describe the innovation by Novozyme in the production of non-trans fats and oils. Under what category in Presidential Challenge award, was this innovation accredited?

(c) Write the full name of the following (attempt any **four**) :

(i) EPA

(ii) TAML

(iii) TEMPO

(iv) FAME

(v) DSIDA

(vi) PEG (4.5,4,4)

5. (a) ______ is the most versatile, biodegradable thermoplastic polyester. How is it synthesized in a greener way?

(b) What is cradle to cradle (C_2C) approach? Draw a labeled diagram of C_2C approach.

(c) What are fluorous biphasic solvents? Discuss the limitations and one valuable applications of the solvent system.

(4.5,4,4)

6. (a) With the help of a labeled phase diagram, show all the phases of CO_2? How the supercritical phase is different from liquid phase? Write the advantages of using $ScCO_2$ over PERC in dry cleaning of garments?

(b) Explain, how green chemistry and sustainable development are inter-related to each other.

(c) Ultrasound assisted reaction is a step towards a greener environment. Justify giving example.

(4.5,4,4)

7. (a) Define ionic liquids. Why they are considered as green? Give any one application of ionic liquids being used as a green solvent.

   (b) Why catalytic amount of reagent is favoured over the stoichiometric amount of the same reagent? Explain with suitable examples.

   (c) What are the advantages of thiamine catalysed benzoin condensation over the conventional benzoin condensation? Write down the reaction involved, shedding light on the principles involved.

   (4.5,4,4)

8. (a) What is ozone layer? Discuss its role. Name the chemicals which cause depletion of ozone layer and explain the various reactions involved.

   (b) Write an account on environmentally advanced wood preservatives.

   (c) Avoidance of unnecessary derivatization and careful use of blocking/protecting groups is necessary in green chemistry practice. Explain with two suitable examples. (4.5,4,4)

9. (a) Write down the reaction involved in the carbaryl synthesis at UCIL factory. Also, suggest a greener alternative to the synthesis.

(b) Differentiate between :

(i) Homogenous and Heterogenous catalyst

(ii) Renewable and Nonrenewable Feedstock

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

(i) Bio-pesticides (Harpin)

(ii) Oxidation reagents and catalysts

(iii) Phase Transfer Catalyst (PTC)

(4.5,4,4)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 5805 **E**

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. (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. Attempt **three** questions from **Section A** and **three** from **Section B**.
3. Use separate sheets for **Section A** and **Section B**.

SECTION A

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

1. (a) Discuss different oxidation states displayed by Cr and Fe.

(b) Discuss eclipsed and staggered structure of Ferrocene. Give physical properties of Ferrocene.

(c) Explain the structure of haemoglobin and its functions in biological system. (4,4,4.5)

2. (a) What happens when (Write the balanced chemical equation)

(i) $KMnO_4$ is added to $MnSO_4$ solution.

(ii) $K_4[Fe(CN)_6]$ reacts with $FeCl_3$

(b) Draw the structure of chlorophyll and discuss the role of Mg^{+2} in energy production.

(c) Define Organometallic Compounds. Classify the organometallic compounds based on nature of metal-carbon bond with an example of each. (4,4,4.5)

3. (a) When an alkali is added to an orange red solution of compound A, yellow solution of compound B results which on acidifying gives back the orange red colour due to the formation of compound A. Identify compounds A and B and write the chemical reactions involved.

(b) Explain the concept of back bonding in metal carbonyls with the help of molecular orbital diagram of CO.

(c) Write short note on the followings :

(i) Na^+-K^+ pump

(ii) Toxicity of Hg^{+2} and Cd^{+2} (4,4,4.5)

4. (a) With reference to biological system define essential metal ions, trace metals and non-essential metal ions with an example of each.

(b) The CO stretching vibrations in IR spectra of $[Mn(CO)_6]^+$, $[Cr(CO)_6]$ and $[V(CO)_6]^-$ are 2090 cm^{-1}, 2000 cm^{-1} and 1860 cm^{-1}. The wavenumber for free CO is 2143 cm^{-1}. Explain the trend.

(c) Describe the preparation of $K_2Cr_2O_7$. What happens when $K_2Cr_2O_7$ is heated with conc. H_2SO_4 and NaCl? Write the chemical reaction involved and name the test. (4,4,4.5)

SECTION B

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

5\. (a) Write the products formed in the following reaction conditions :

(i) Naphthalene is treated with Conc. H_2SO_4 at 40°C and at 165°C.

(ii) Anthracene is oxidised with alkali $KMnO_4$ and $Na_2Cr_2O_7/H_2SO_4$.

(b) Five membered heterocyclic compounds give electrophilic substitution reaction predominantly at 2-position. Explain by taking furan as an example.

(c) Explain the observation. Concentrated solution of ethanol and ethylene glycol (Dihydroxy compound) shows broad O-H stretching frequency near 3350 cm^{-1}. On dilution with CCl_4, the spectrum of glycol does not change but that of alcohol shows at 3600 cm^{-1} replacing broad band at 3350 cm^{-1}.

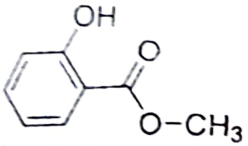
(d) How will you carry out?

(i) Synthesis of succinic acid from ethyl acetoacetate.

(ii) Conversion of ethyl acetoacetate to crotonic acid.

(e) Which absorption shift takes place on addition of acid in aniline? Explain. (2,2,2.5,4,2)

6. (a) Methyl salicylate (structure given below) shows following absorption peaks in IR spectrum: 3300, 1680, 3050, 1540, 2950, 1590 cm^{-1}. Which of these peaks belongs to the following segments?

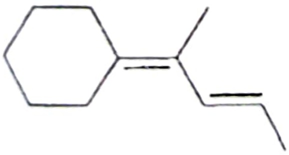


Methyl salicylate

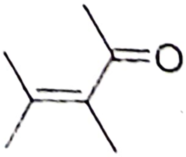
i. C-H stretching peak of methyl group
ii. C=O stretching peak
iii. C-H stretching peak of benzene ring
iv. C=C stretching peak of benzene ring
v. Hydrogen bonded O-H stretching peak

(b) Calculate the absorption maximum (λ_{max}) for $\pi \rightarrow \pi^*$ transition in the following compounds using Woodward-fieser rules.

i.



ii.



P.T.O.

Parental/Base values	λ_{max} (nm)
Acyclic/ Heteroannular dienes	214
Homoannular dienes	253
α, β unsaturated Acyclic ketones	215
α, β unsaturated Aldehydes	210

Increments	(nm)
Alkyl substitution/ Ring residue	+5
Additional conjugation	+30
Exocyclic double bond	+5
α-alkyl substituent	+10
β-alkyl substituent	+12

(c) Write notes on: Chromophores and Auxochromes.

(d) Assign the following C=O stretching frequencies in decreasing order for formaldehyde, acetaldehyde and acetone with valid explanation.

C=O stretching frequencies : 1750, 1735 and 1717 cm^{-1}

(e) What do you understand about IR active compounds? Which of the following compounds are IR active?

N_2, HCl, CH_3-Cl, O_2, Cl_2, CH_2=CH_2, CH_3CHO, CH_3-CH=CH-CH_3, CH_3-CH=CH_2

(2.5,3,2,3,2)

7. (a) What are active methylene compounds? Give two examples.

(b) Write the name of reaction, chemical reaction and its mechanism, which is used for the synthesis of ethyl acetoacetate from ethyl acetate and sodium ethoxide followed by acidification.

(c) Draw the keto-enol forms of acetyl acetone and ethyl acetoacetate. The percentage of enol form in acetyl acetone is greater than ethyl acetoacetate. Why?

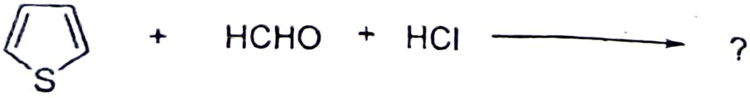
(d) How will you prepare pentane-2,4-dione from ethyl acetoacetate?

(2,4.5,4,2)

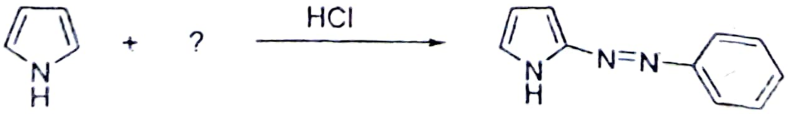
8. (a) Complete the following reactions :

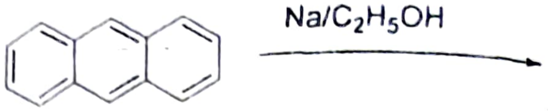
(i)

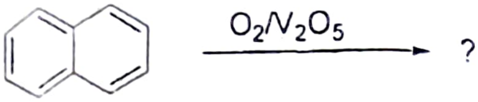
(ii)



(iii)



(iv) 

(v) 

(b) How do you synthesize anthracene using Haworth synthesis?

(c) Anthracene undergoes addition and electrophilic substitution reaction preferentially at C-9 and C-10 position. Explain

(d) Pyrrole is weak acid in nature. Explain.

(5,3,2.5,2)