

(10)

This question paper contains 7 printed pages]

Roll No.

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S. No. of Question Paper : 45

Unique Paper Code : 32171502

Name of the Paper : **Physical Chemistry-V : Quantum**

**Chemistry and Spectroscopy**

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

Semester : **V**

Duration : **3 Hours**

Maximum Marks : **75**

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

Answer *six* questions in all.

Question No. **1** is compulsory.

Attempt at least *two* questions from each section.

Attempt all parts of a question together.

Use of scientific calculators is allowed but they cannot be shared.

Logarithmic tables can be provided if required.

*Physical Constants :*

Planck's Constant	$6.626 \times 10^{-34} \text{ Js}$
Velocity of Light	$3 \times 10^8 \text{ ms}^{-1}$
Avogadro's Number	$6.023 \times 10^{23} \text{ mol}^{-1}$
Mass of Electron	$9.1 \times 10^{-31} \text{ kg}$
Nuclear Magneton	$5.05 \times 10^{-27} \text{ JT}^{-1}$
Bohr Magneton	$9.27 \times 10^{-24} \text{ JT}^{-1}$
Boltzmann Constant	$1.38 \times 10^{-23} \text{ JK}^{-1}$

P.T.O.

1. Attempt any five :

(a) What is the essential condition for a molecule to be microwave active ? Which of the following molecules will show a microwave rotational spectrum :  $H_2$ ,  $HCl$ ,  $CH_4$ ,  $SF_6$ .

(b) Determine whether or not the operators  $x^2 \frac{d^2}{dx^2}$  and  $\frac{d^2}{dx^2}$  commute. What is the significance of commutation ?

(c) If A and B are two atoms bonding along the z-axis, predict giving reasons which of the following orbitals can combine :

(i)  $2s(A)$  and  $2p_z(B)$

(ii)  $1s(A)$  and  $2s(B)$ .

(d) Explain briefly the appearance of hot bands in the infrared spectroscopy. Explain the effect of increase in temperature on the intensity of hot bands.

(e) The bond length decreases on removing an electron from  $O_2$  but increases on removing an electron from  $N_2$ . Explain.

(f) Explain the significance of Born-Oppenheimer approximation. Write the Hamiltonian operator for hydrogen atom using Born-Oppenheimer approximation.

(g) What is accidental degeneracy ? Explain with an example.

3×5

### Section A

2. (a) Find the expectation values of (i)  $x$  (ii)  $p_x$  (iii)  $p_x^2$  for a particle of mass  $m$ , in a one-dimensional box of length  $l$ , having the solution :

$$\Psi_n = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right).$$

Give the physical significance of each expression.

(b) Prove that the solutions with  $n = 1$  and  $n = 2$  for a particle in a box are orthogonal to each other.

(c) Determine the value of  $x$  at which the ground state wave function,  $\Psi$  for the harmonic oscillator exhibits a maxima.

Given :

$$\Psi = \left(\frac{a}{\pi}\right)^{\frac{1}{4}} \exp\left(\frac{-\alpha x^2}{2}\right). \quad 6,3,3$$

3. (a) Determine the energy of H atom using the trial wave function  $\Psi = e^{-ar}$  where  $a$  is an adjustable parameter and  $r$  is the distance of the electron from the nucleus.

Given :

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

(b) Discuss Bohr correspondence principle with respect to the behaviour of wave function of simple harmonic oscillator (SHO). Illustrate using its probability density plots.

(c) Sketch  $R(r)$  and  $4\pi r^2 R^2(r)$  Vs.  $r/a_0$  for  $3p$  orbital for hydrogen atom. Calculate the number of radial nodes in this orbital. 6,3,3

4 (a) Molecular orbital theory gives equal weightage to covalent and ionic structure whereas valence bond theory ignores ionic character. Explain using the trial wave function of  $H_2$  molecule.

(b) Benzene may be taken as a two-dimensional box of edge length 0.4 nm consisting of six  $\pi$  electrons. Calculate the energy required for the promotion of an electron from the ground to the first excited state of benzene.

(c) Normalize the given wave function :

$$\Phi_m = \exp(i m \phi)$$

What is the significance of quantum number  $m$  with respect to hydrogen atom ? 6,3,3

5 (a) A rigid rotator consists of two particles of mass  $m_1$  and  $m_2$  joined by a rigid rod of length,  $r$ . Based on classical considerations, show that the total energy of a rigid rotator is  $L^2 / 2I$ , where  $L$  is the angular momentum and  $I$  is the moment of inertia. How does this result differ from quantum mechanical result ?

(b) Define Hermitian operator. Show that  $\frac{d^2}{dx^2}$  is a Hermitian operator.

(c) Under what conditions, the wave function  $\Psi$  is said to be an acceptable wave function ? What is the physical significance of  $\Psi^2$  ? 6,3,3

### Section B

6. (a) Given that the nuclear spin quantum number of  $^{12}C_6$  is zero and that of  $^1H_1$  is half :

(i) Calculate the nuclear angular momentum of these nuclei.

(ii) How many different energy states do these nuclei have in a magnetic field ?

(iii) Calculate the magnetic moment of  $^1H_1$ . Given :  $g = 5.585$ .



- (b) What are the characteristics of TMS which makes it useful as a reference in PMR spectrum ?
- (c) Based on free electron model, calculate the wave number for the longest wavelength transition in pentadienyl radical. Given : C - C is 154 pm; C=C is 135 pm.

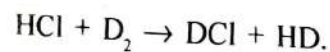
6,3,3

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

$\bar{\nu}$ ( $\text{cm}^{-1}$ )	Infra-red	Raman
519	Active	Active (polarized)
1151	Active	Active (polarized)
1361	Active	Active (depolarized)

Giving proper explanation arrive at the geometry of the molecule. Assign the wave numbers to specific vibrations.

- (b) The vibrational wave number of the following molecules in their  $v = 0$  states are : HCl :  $2885 \text{ cm}^{-1}$ ; DCI :  $1990 \text{ cm}^{-1}$ ;  $D_2$  :  $2990 \text{ cm}^{-1}$  and HD :  $3627 \text{ cm}^{-1}$ . Using the concept of zero point energy calculate the energy change in  $\text{kJ mol}^{-1}$  of the reaction :



45

- (c) Stokes and anti-Stokes lines in pure rotational Raman spectrum have similar intensities while Stokes lines are more intense than anti-Stokes lines in vibrational Raman spectrum. Explain. 6,3,3
8. (a) The low resolution NMR spectrum of  $C_5H_{10}O_2$  exhibits three absorptions at  $\delta$  values of 3.2, 2.1 and 1.2 with relative intensities 1 : 3 : 6 respectively. Predict the structure of the molecule giving reasons. Draw and explain the NMR spectrum expected under high resolution.
- (b) Discuss the concept of natural line width of spectral line. It is quiet significant in case of ESR compared to that of electronic transition, explain.
- (c) Sketch the ESR spectra of *p*-benzoquinone in low resolution and high resolution. 6,3,3
9. Write short notes on any *three* of the following :
- (a) Larmor precession
- (b) Effect of isotopic substitution on rotational spectrum.
- (c) Variation theorem
- (d) Spin-spin coupling 4×3

7

1,800

(11)



30/12/18

[This question paper contains - printed pages]

Your Roll No.....

Sr. No. of Question Paper : 1593  
Unique Paper Code : 217501  
Name of the Course : B.Sc. (H) CHEMISTRY  
Name of the Paper : CHHT-511: Inorganic Chemistry - IV  
Semester : V  
Duration: 3 Hours

Maximum Marks : 75

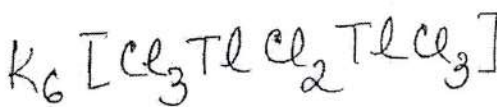
I

Instructions for Candidates

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

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

- (i)  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{3+}$
- (ii)  $[\text{Rh}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{NCS}(\text{NH}_2)]\text{NO}_3$
- (iii)  $[\text{Ni}(\text{acac})\{\text{P}(\text{C}_6\text{H}_5)_3\}_4]\text{NO}_3$
- (iv)  $\{(\text{CH}_3)_4\text{N}\}_2[\text{MoBr}_5\text{N}]$
- (v)  $[(\text{Cl}_3\text{TiCl}_2\text{TiCl}_3)(\text{PO}_4)_2]$
- (vi)  $[\text{Fe}(\text{en})_3][\text{Ni}(\text{CN})_5]$



(b) Write the formulae of the following complexes:

- (i) Triammineaquadichlorochromium(III) Phosphate
- (ii) Cesium hexafluorophosphate(V)
- (iii) Hexaamminenickel(II) hexachlorocobaltate(III)

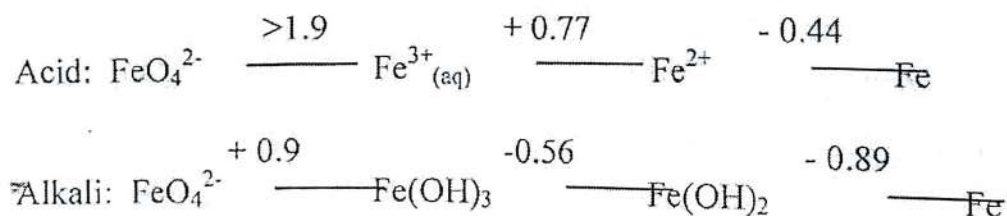
(c) A solution containing 2.674 g of  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  was passed through a cation exchanger. The chloride ion solution thus obtained, gave 4.305 g of  $\text{AgCl}$  precipitate with  $\text{AgNO}_3$  solution. Determine the correct formula of the complex and give its structure on the basis of Werner's theory.

(d) Calculate in  $\text{KJ mol}^{-1}$  the crystal field stabilization energy (CFSE) attained by  $\text{Fe}^{2+}$  in an octahedral oxide ion environment. Given  $\Delta_0$  for  $\text{Fe}^{2+}$  in an oxide environment is  $124 \text{ KJ mol}^{-1}$ . What will be the CFSE in a tetrahedral environment of oxide ion. ?

(6,3,3,3)

2. (a) A complex compound with molecular formula  $\text{MCl}_2(\text{NH}_3)_4$  forms two type of colored crystals, viz., red(A) and blue (B). 1 mole of A reacts with 1 mole of  $\text{Ag}_2\text{C}_2\text{O}_4$  to give 2 moles of a white precipitate; B, does not react with  $\text{Ag}_2\text{C}_2\text{O}_4$ . Draw the structure of complexes.

(b) Given below are the Latimer diagrams for iron in acid and alkaline media:



(i) In which medium, acidic or alkaline, is the oxidation of Iron(II) to Iron(III) thermodynamically easier?

(ii) Is iron (VI) more stable in acid or alkaline solution?

(iii) Will acidic ferrous oxidize  $\text{H}_2\text{O}_2$  to oxygen, in acid solution?

Given  $E^0(\text{H}_2\text{O}/\text{O}_2) = -0.70 \text{ V}$



(c) Both  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  appear colorless in dilute solutions. Suggest a suitable explanation for this observation.

(d) Compare the ionic radii of divalent Fe, Co, Ni and Cu in an octahedral environment.

(4,6,3,2)

3.(a) Find out the magnetic moment of  $\text{Pr}^{3+}$  (Atomic Number of Pr = 59, L=5).

(b) Draw the geometrical isomers of  $[\text{Ir}(\text{Py})_3\text{Br}_3]$  and  $[\text{Pt}(\text{NH}_3)\text{PyClBr}]$

(c) When pentaamminecarbonatocobalt(III) complex is treated with  $\text{NaNO}_2$  and dil. HCl, an unstable red colored compound, (A), is formed. If this compound is heated or conc. HCl is added, a yellow colored stable compound, (B), is formed. Both the compounds are isomers. Name the type of isomerism and also write the structures of both the compounds.

(d) On acidifying the solution of ammonium metavanadate, compound A, is obtained. When compound A, is treated with  $\text{SO}_2$ , a deep blue solution, (B), is obtained. Shaking the solution (A) with zinc amalgam, results in a violet solution (C). Mixing solutions (B) and C, in equal amounts, a green solution (D) is obtained. Identify A, B, C and D and write down the reaction of acidification of ammonium metavanadate.

(3,4,3,5)

4. (a) What happens when:

(i) Ammonium dichromate is heated.

(ii) A 30% solution of hydrogen peroxide is added to an alkaline solution of potassium Chromate.

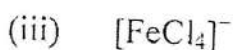
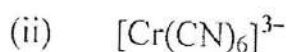
(iii)  $\text{SO}_2$  is passed through alkaline  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution.

(iv) Titanium tetrachloride reacts with ethanol in the presence of ammonia.

- (v) An aqueous solution of a Mn(II) salt is oxidized by powerful oxidizing agent like sodium bismuthate in presence of dilute nitric acid.
- (b) Explain why, the absorption band of cerium (III) ion is broad, while that of other lanthanide ions is sharp.
- (c) What type of spinel structure do you expect for  $\text{NiFe}_2\text{O}_4$ .

(10,2,3)

5 (a) Using VBT, predict the geometry and magnetic moment of the following species:



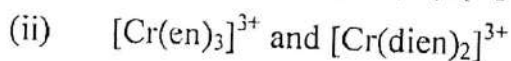
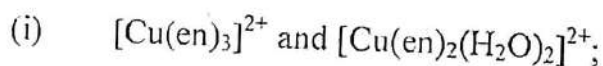
(b) When a pink aqueous solution of Co(II) salt is treated with aqueous ammonia, a blue precipitate, (A), is formed, which dissolves forming a yellow brown solution, (B), with an excess of the reagent. On standing in air, this solution turns red, (C). Compound (C) can also be prepared by passing air in an aqueous solution of Co(II) in presence of  $\text{NH}_4\text{Cl}$  and activated charcoal. If activated charcoal is omitted, than brown coloured compound (D) is formed. If compound (D) is oxidized by  $\text{S}_2\text{O}_8^{2-}$ , green coloured compound (E) is formed. Identify A to E and write the reaction involved in the preparation of compound, C, by passing air in Co(II) in the presence of  $\text{NH}_4\text{Cl}$  and activated charcoal.

(c) Copper shows +1 and +2 oxidation states whereas gold shows +1 and +3 oxidation states. Why?

(6,6,3)

6 Explain which complex in each pair of the following will have:

(a) Greater stability:



(dien = diethylenetriamine).

(b) Greater liability :



- (i)  $[\text{Fe}(\text{bipy})_3]^{2+}$  and  $[\text{Fe}(\text{bypy})_2(\text{H}_2\text{O})_2]^{2+}$ ;  
 (ii)  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Co}(\text{CN})_6]^{3-}$
- (c) Chromium(II) fluoride and manganese(II) fluoride, both have a central metal ion surrounded by six fluoride ligands. All the Mn-F bond lengths are all equal whereas two Cr-F bonds are shorter than the remaining four. Explain giving diagram on the basis of CFT.
- (d) Which will have higher  $10Dq$  value and why?
- (i)  $[\text{Ni}(\text{CN})_4]^{2-}$  or  $[\text{NiCl}_4]^{2-}$   
 (ii)  $[\text{Rh}(\text{NH}_3)_6]^{3+}$  or  $[\text{Ir}(\text{NH}_3)_6]^{3+}$   
 (iii)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  or  $[\text{Cr}(\text{en})_3]^{3+}$

(3,3,3,6)

- 7 (a) Draw the molecular orbital diagram of  $[\text{Co}(\text{CN})_6]^{3-}$  and explain its magnetic behavior.  
 (b) Write down the structure of chiral complex  $[\text{Co}\{(\text{OH})_2\text{Co}(\text{NH}_3)_4\}_3]^{6+}$ .  
 (c) Although  $\text{Fe}^{3+}$  has five unpaired electrons but  $[\text{FeF}_6]^{3-}$  is colorless. Explain.  
 (d) Although lanthanides are almost identical in (+3) oxidation state, they are effectively separated by ion-exchange method. Explain.  
 (e) The density of the elements of 5d- transition series is almost twice as compared to the elements of 4d transition series. Explain?

(4,3,3,3,2)

Sr-NO. 07 Q.P. : 1595

(12)

107

7/12/18

Unique Paper Code: 217505  
Name of the Paper : CHHT-513 : *Physical Chemistry - IV*  
Name of the Course : B.Sc. (H) Chemistry  
Semester : V  
Duration : 3 hours  
Maximum Marks : 75 Marks



I

### Instructions for Candidates

The Paper has three sections. Section A is compulsory. Attempt at least two questions from each of sections B and C. Attempt six questions in all. Graph paper may be used wherever required. Use of scientific calculator is allowed.

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

Velocity of Light -  $3 \times 10^8$  ms<sup>-1</sup>

Avogadro's Number  $6.023 \times 10^{23}$  mol<sup>-1</sup>

### Section A

Q.1 Answer any five

- Explain the unusually high mobility of H<sup>+</sup> and OH<sup>-</sup> ions.
- What is meant by an inhibition step in a chain reaction mechanism?
- Discuss the change in molar conductivity with dilution of weak electrolytic solutions.
- Write three basic postulates of Collision theory of reaction rates.
- Explain the use of wetting agents.
- Write three main differences between photochemical reaction and thermo-chemical reactions.
- Describe briefly the three explosion limits of a non-stationary chain reactions.

3x5

### Section B

Q.2

- a) In a Hittorf's experiment HCl solution was electrolyzed between Ag/AgCl electrodes. The solution contained 400 μg HCl per gram of water. In this solution 2mA current was passed for 150min. After electrolysis the solution in the cathodic compartment contained 0.025g HCl in 50g of solution. Calculate the transport number of H<sup>+</sup> and Cl<sup>-</sup> ions.

4

- Q.3
- (a) Describe the following application of conductance measurements,  
 i. Determination of ionic product of water. 2+2  
 ii. Determination of solubility product.  
 (b) How the conductance and equivalent conductance of the given solution is determined experimentally. Describe the electric circuit of the instrument and the apparatus used. Explain all the principle involved of the instrument and apparatus. 4

Q.3

- (i) What must be the concentration of HCl and NaCl in a solution if the transference number of  $H^+$  is 0.5. Given the limiting molar conductivities of  $Na^+$ ,  $H^+$  and  $Cl^-$  are 50.1, 349.8 and  $76.35 S cm^2 mol^{-1}$  respectively.  
 (ii) Define mobility of an ion in a solution. 2+2
- (b) (i) The conductivity of a saturated solution of  $CaF_2$  at  $18^\circ C$  is  $4.2 \times 10^{-5} S cm^{-1}$ . The molar conductivity of water used here is  $2.0 \times 10^{-6} S cm^{-1}$ . The limiting molar conductivities of  $Ca^{2+}$  and  $F^-$  are 104.0 and  $48.0 S cm^2 mol^{-1}$  respectively. Calculate the solubility and solubility product of  $CaF_2$ . 4  
 (ii) Define mobility of an ion in a solution. 2+2
- (c) Explain the principle involved in the conductometric titration of strong acid and strong base and the weak acid and strong base. 4

Q.4

- (a) (i) Calculate the ionic product of water if the molar conductivities of  $H^+$ ,  $OH^-$  and water is given as 349.8, 198.5 and  $5.54 \times 10^{-8} S cm^2 mol^{-1}$ .  
 (ii) At  $18^\circ C$ ,  $\Lambda_m^\circ$  for  $NaNO_3$  is  $105.2 S cm^2 mol^{-1}$  and  $\lambda_m^\circ$  for  $NO_3^-$  ion is  $61.7 S cm^2 mol^{-1}$ . Calculate the transport number of  $Na^+$  in this solution. 2+2
- (b) Write short note on (i) Photosensitisation, (ii) Chemical Actinometry. 2+2
- (c) Describe the relevance of parameters "A" and "B" qualitatively of Debye-Huckel-Onsagar equation. Explain under what external conditions the conductance approaches the limiting values. 4

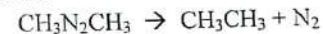
### Section C

Q.5

- (a) (i) What is the change in half life period of second order reaction if the initial concentration changes from 0.025 M to 0.001 M.

- (ii) Find the activation energy if the rate of reaction increase by a factor of 1.41, when the temperature increase from 293 K to 300K. 2+2
- (b) The integrated rate law of a second order reaction  $3A \rightarrow B$  is of the form  $[A] = [A]_0 / (1 + kT [A]_0)$ . (Symbols have their usual meanings)  
 Deduce the integrated rate equation for the change in concentration of B, [B] with time. 4

- (c) The decomposition of Azomethane



took place at 600 K. The variation in partial pressure of azomethane is given below. Confirm that this reaction is first order reaction and find out rate constant and half life period for the decomposition.

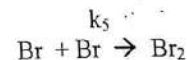
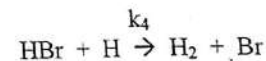
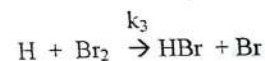
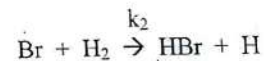
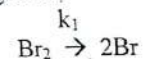
t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

Q.6

- (a) For the photochemical reaction of  $H_2$  and  $Br_2$



the following reaction mechanism is suggested.



Using steady state approximation deduce the following rate law

$$\frac{d[HBr]}{dt} = \frac{2k_3(k_1/k_5)^{1/2}[H_2][Br_2]^{1/2}}{1 + (k_4/k_3)\{[HBr]/[Br_2]\}}$$



- b) Explain Lindemann time lag theory of collision theory of reaction rates. On this basis explain why a second order reaction follows first order kinetics when we lower the pressure in gaseous state. 4
- c) Explain briefly the general acid base catalysis and specific acid base catalysis. 4

Q. 7

- a)
- Discuss the characteristics of enzymatic reactions.
  - Explain the temperature coefficient of reaction rates. 2+2
- b)  $\text{NO}_2$  gas is adsorbed on silica to the extent of  $0.85 \text{ cm}^3 \text{ g}^{-1}$  at 500 kPa and 190 K but at 250 K the same extent of adsorption was achieved when pressure was 3.5 MPa. What is the molar enthalpy of adsorption? 4
- c) Describe the Moving boundary method for determination of transport number. 4

Q.8

- a) Derive Gibbs Adsorption Equation. 4
- b) (i) Explain the difference between Fluorescence and Phosphorescence. 2
- (ii) Comment on free energy change of the photochemical reaction giving reasons. 2
- c) i) The bond energy in a molecule is  $142.95 \text{ kJ mol}^{-1}$ . What is the longest wavelength of the E.M radiation capable to dissociate it. 1
- (ii) 10 ml of solution of 0.0495 M oxalic acid and 0.01 M uranyle sulphate was irradiated with E.M. radiation of  $2540 \text{ \AA}$ . After the solution absorbed 88 J of radiation energy the concentration of oxalic acid was reduced to 0.0383 M. Calculate the quantum yield of photochemical decomposition of oxalic acid. 3

13

P-5



4/12/18

[This question paper contains 2 printed pages.]

Sr. No of Question Paper : 1874

Year Roll No.....

Unique Paper Code : 2171502

Name of the Paper : Organic Chemistry [Carbohydrates, Spectroscopy, & Dyes]

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

Semester : V

Duration : 3 Hours

Maximum Marks : 75

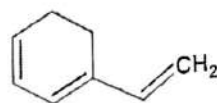
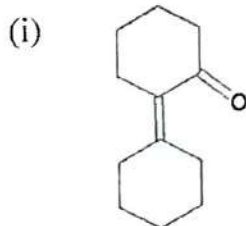
(Write your Roll No. on the top immediately on receipt of the question paper)  
Question No. 1 is compulsory. Attempt six questions in all.

1. Answer any five of the following:

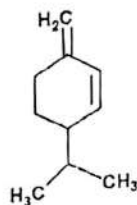
- (a) Differentiate between auxochrome and chromophore by taking suitable examples.
- (b) Why TMS (Tetramethylsilane) is chosen as reference compound in NMR spectroscopy?
- (c) What are the characteristic feature of a dye?
- (d) Convert D-Glucose into D-Fructose.
- (e) How many types of chemically equivalent protons are there in  $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ . Give reason.
- (f) Explain the mechanism of mutarotation.
- (g) Indicate the conditions under which the following changes take place? [3x5]  
Leuco base  $\rightleftharpoons$  Color base  $\rightleftharpoons$  Dye

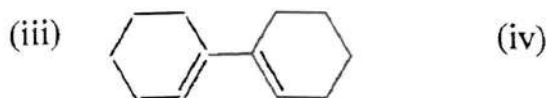
2. (a) Explain the uses of I.R. spectroscopy in the differentiation of compounds having inter- and intramolecular hydrogen bonding.
- (b) 1-Butene shows  $\text{C}=\text{C}$  stretching at  $1650 \text{ cm}^{-1}$  in its IR spectrum whereas 1,3-Butadiene shows  $\text{C}=\text{C}$  stretching at  $1610 \text{ cm}^{-1}$ . Explain giving reason.
- (c) Nitrobenzene absorbs strongly at  $1525$  and  $1350 \text{ cm}^{-1}$ . Assign these peaks to the corresponding vibrational frequencies. [4,4,4]

3. (a) Calculate the  $\lambda_{\text{max}}$  value for the following compounds giving details (Any three)



1





Values for calculation:

Heteroannular diene = 214 nm

Acyclic/Six membered cyclic  $\alpha,\beta$ -unsaturated ketone = 215 nm

Homoannular diene = 253 nm

Alkyl substituent or ring residue = 5 nm

Exocyclic double bond = 5 nm

Extended conjugation = 30 nm

- (b) Identify the geometric isomers of stilbene ( $C_6H_5-CH=CH-C_6H_5$ ) from their  $\lambda_{max}$  values of 294 nm and 274 nm, giving reasons for the assignment?
- (c) Compare the PMR spectrum of ordinary (impure) ethanol and pure ethanol. Give reason for the difference? [6,3,3]

4. An organic compound A with molecular formula  $C_6H_{12}O$  showed the following data:

UV ( $\lambda_{max}$ ) = 288 nm,  $\epsilon = 24$

IR very strong band at  $1715\text{ cm}^{-1}$

NMR :  $\delta$  2.0 (3H, singlet), 1.0 (9H, singlet).

(i) Calculate double bond equivalence.

(ii) Explain

(1) UV transition

(2) IR absorption band

(3) NMR peaks along with splitting pattern.

Give the structure of the compound.

[12]

5. (a) Give one synthesis of Indigo from anthranilic acid or aniline.
- (b) Explain the yellow green fluorescence produced by fluorescein dye.
- (c) Write down the possible structures of Phenolphthalein in:
- (i) Acidic medium
- (ii) Alkaline medium
- (iii) Strongly alkaline medium
- Explain in which medium will Phenolphthalein be pink in color and why? [4,4,4]
6. (a) Explain Amadori rearrangement for the formation of fructosazone from D-Fructose.
- (b) What are reducing and non-reducing sugars? Explain with the help of suitable structures and give one example for each category.
- (c) What is epimerisation? Suggest a method for the conversion of D-glucose to D-mannose. [4,4,4]
7. (a) Calculate the approximate wave number of the fundamental absorption peak due to the stretching vibration of the O-H group.
- Force constant for O-H group =  $7.7 \times 10^5$  dyne/cm



Reduced mass =  $9.41 \times 1.67 \times 10^{-24}$  g.

- (b) C=O stretching in IR of acetone comes at  $1720 \text{ cm}^{-1}$  while C=O stretching in acetamide ( $\text{CH}_3\text{CONH}_2$ ) comes at  $1680 \text{ cm}^{-1}$ . Give reason.
- (c) Explain why the absorption bands in UV spectrum are generally broad when compared to the absorption bands in IR spectrum? [4,4,4]

8. Write short notes on the following (any **three**):

- (a) Mordant Dyes  
(b) Anisotropic effects in alkenes  
(c) Phthalein dyes  
(d) Biological importance of carbohydrates

[4,4,4]