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[This question paper contains 8 printed pages.]

30/11/17

Your Roll No.....

Sr. No. of Question Paper : 5610

H

Unique Paper Code : 217501

Name of the Paper : CHHT-511 : Inorganic Chemistry-IV

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

Semester : V

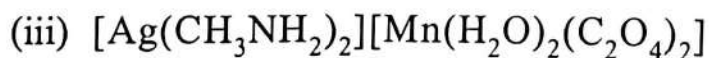
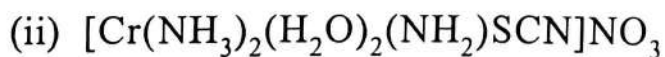
Duration : 3 Hours

Maximum Marks : 75

**Instructions for Candidates**

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

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



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(b) Write the formulae of the following complexes :

(i) Triammineaquadibromovanadium(III) Sulphate

(ii) Tris(ethylenediamine)chromium(III) tetrachloroferrate(III)

(iii) Sodium amminechlorobromonitrito-N-platinate(II)

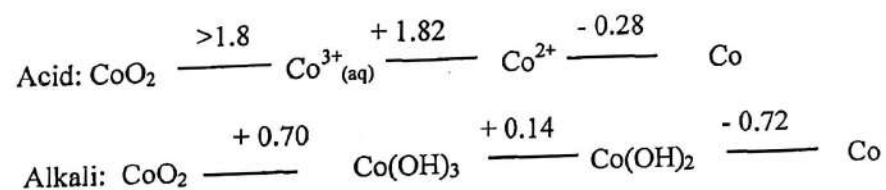
(c) A solution containing 2.665 g  $CrCl_3 \cdot 6H_2O$  was passed through a cation exchanger. The chloride ion so obtained gave 2.87 g of  $AgCl$  precipitate with  $AgNO_3$  solution. Determine the formula of the complex and give its structure on the basis of Werner's Coordination theory.

(d) The enthalpy of hydration of  $Cr^{2+}$  is  $-460 \text{ Kcal mol}^{-1}$ . In the absence of crystal field stabilization energy, the value for  $\Delta H$  would be  $-435 \text{ Kcal mol}^{-1}$ . Estimate the value of  $\Delta_0$  for  $[Cr(H_2O)_6]^{2+}$ . (6,3,3,3)

2. (a) When  $[Ni(NH_3)_4]^{2+}$  is treated with  $HCl$ , two compounds A & B having the formula  $Ni(NH_3)_2Cl_2$  are formed. A can be converted into B by boiling with dilute  $HCl$ . The

solution of A and B both react with oxalic acid to form a chelated and non-chelated complex, respectively. Deduce the structures of A and B.

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



(i) In which medium, acidic or alkaline, is  $Co(IV)$  more stable?

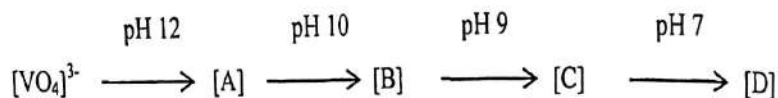
(ii) In which medium, acidic or alkaline, can  $Co^{2+}$  be more easily oxidized to  $Co^{3+}$ ?

(iii) Will  $Co^{3+}$  be able to oxidise water to oxygen? In which medium? Given  $E^0(H_2O/O_2) = -0.81 \text{ V}$

(c) A solution of  $[Ni(H_2O)_6]^{2+}$  is green, while a solution of  $[Ni(CN)_4]^{2-}$  is colourless. Suggest a explanation for this observation.

(d) Compare the ionic radii of divalent oxides of Ti, V, Cr and Mn in an octahedral environment. (3,6,3,3)

3. (a) Identify A, B, C and D



(b)  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  undergoes ligand substitution reaction, when treated with  $\text{NaNO}_2$ , to give 2 products A and B, depending on experimental conditions. A and B are isomeric pentaammine ions. Draw their structures and indicate the type of isomerism.

(c) Explain the following :

(i) Cobalt(II) is generally oxidized to cobalt(III) in presence of strong field ligands whereas the isoelectronic nickel(III) complexes are oxidizing agent.

(ii) Actinides have a greater tendency to form complexes than lanthanides.

(d) What type of spinel structure do you expect for  $\text{CoCr}_2\text{O}_4$ . Justify your answer. (4,3,4,4)

4. (a) What happens when;

(i)  $\text{H}_2\text{O}_2$  is added to a solution of chromate ion in an acidic medium, in presence of ether.

(ii) A suspension of hydrous oxide of iron, in concentrated sodium hydroxide, is subjected to chlorine oxidation.

(iii)  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is reduced with  $\text{Zn}/\text{H}^+$ , and the resulting solution is run into a fairly concentrated solution of sodium acetate in absence of air.

(iv)  $\text{Cl}_2$  (g) is passed over heated  $\text{TiO}_2$  in the presence of carbon.

(v)  $\text{MnO}_2$  is heated with excess of conc.  $\text{HCl}$ , and the gas so evolved is passed through  $\text{KI}$  solution.

(b) Calculate the magnetic moment of  $\text{Nd}^{3+}$  ion (Atomic Number of  $\text{Nd} = 60$ ,  $L = 6$ ).

(c) Draw the geometrical isomers of  $[\text{Rh}(\text{NH}_3)_3\text{Br}_3]$ . (10,3,2)

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

(i)  $[\text{Ni}(\text{CO})_4]$

(ii)  $[\text{MnBr}_4]^{2-}$

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



(b) When an aqueous solution of  $\text{Co}^{2+}$  ion is treated with KCN, a green colored compound, (A), is obtained. This compound dimerises to give purple colored compound (B). Compound, (B), on oxidation by air, gives a brown compound, (C), which on further oxidation with  $\text{Br}_2$ , gives compound, (D). When the solution of compound, (C) and D, are boiled together, a yellow coloured compound, (E), is formed. Identify A to E and also write down the reaction of  $\text{Co}^{2+}$  salt with KCN.

(c)  $[\text{NiSe}_4]^{2-}$  is square planar, whereas  $[\text{ZnSe}_4]^{2-}$  is tetrahedral. Explain. (6,6,3)

6. Explain giving reasons, which complex in each pair of the following will have :

(a) Greater stability :

(i)  $[\text{Ag}(\text{NH}_3)_2]^+$  and  $[\text{Ag}(\text{en})]^+$ ;

(ii)  $[\text{Co}(\text{en})_3]^{3+}$  and  $[\text{Co}(\text{dien})_2]^{3+}$

(dien = diethylenetriamine)

(b) Greater Lability :

(i)  $[\text{Ni}(\text{bipy})_3]^{2+}$  and  $[\text{Ni}(\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$ ;

(ii)  $[\text{Hg}(\text{CN})_4]^{2-}$  and  $[\text{Cr}(\text{CN})_6]^{3-}$

(c) All the Cr-F bond lengths in  $[\text{CrF}_6]^{3-}$  are equal but in  $[\text{CrF}_6]^{4-}$ , two Cr-F bonds are shorter than the remaining four. Explain giving diagram on the basis of CFT.

(d) Which of the following will have higher 10Dq and why?

(i)  $[\text{PtCl}_4]^{2-}$  or  $[\text{PdCl}_4]^{2-}$

(ii)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  or  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

(iii)  $[\text{Co}(\text{en})_3]^{3+}$  or  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  (3,3,3,6)

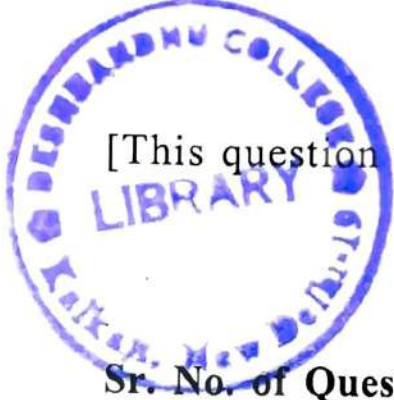
7. (a) Draw the molecular orbital diagram of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and explain its magnetic behavior.

(b) Write down the structure of a pure inorganic optically active compound.

(c) Despite having five unpaired electrons in  $\text{Mn}^{2+}$  in an octahedral environment its compounds are almost colorless. Explain.

(d) Explain why the chemical behavior of zirconium and hafnium is almost similar.

- (e)  $\text{Ni}^{2+}$  gives a low spin square planar complex with  $\text{CN}^-$  only whereas  $\text{Pt}^{2+}$ ,  $\text{Pd}^{2+}$  or  $\text{Au}^{3+}$  form low spin square planar complexes with  $\text{NH}_3$  and even with  $\text{Cl}^-$ . Explain. (4,3,3,3,2)



[This question paper contains 4 printed pages.]

2

05/12/17

Your Roll No.....

Sr. No. of Question Paper : 5611

H

Unique Paper Code : 217503

Name of the Paper : CHHT-512 : Organic Chemistry-IV

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

Semester : V

Duration : 3 Hours

Maximum Marks : 75

### Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all.
3. Q. No. 1 is compulsory and carries **15** marks.
4. **All** other questions are of **12** marks each.

1. Attempt any **five** :

(a) What are Omega-3-fatty acids? Give one example and draw its structure.

(b) Write the possible Zwitter ion structures of Lysine. Which is the most probable structure at its isoelectric point? Explain.

(c) D-Fructose is a reducing sugar. Explain.

P.T.O.

- (d) Draw all the theoretically possible tautomeric structures of the base Thymine and in which form it exist in nature.
- (e) Write the IUPAC name of the (+)-Maltose and draw its structure.
- (f) A heptapeptide A on reaction with 2,4-dinitrofluorobenzene followed by hydrolysis yields 2,4-dinitrophenylvaline. Partial hydrolysis of peptide A produce the following amino acids fragments :

- (i) Val-Leu                      (ii) Met-Phe  
 (iii) Leu-Gly-Met              (iv) Phe-Pro-Val

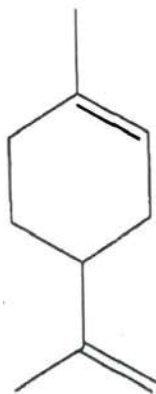
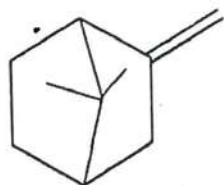
Complete hydrolysis of A produces two molecules of Valine. Deduce the structure of A. (5×3=15)

2. (a) What are the products formed when the hydrolysis of the following peptide is catalyzed by the enzyme  
 (1) Trypsin and (2) Chymotrypsin  
 Ala-Trp-Arg-Gly-Leu-Tyr-Met-Glu-Lys-Gly-Phe
- (b) Outline the entire sequence in the preparation of glycine using Gabriel's phthalimide synthesis.
- (c) Draw the structure formula of tripeptide glycylalanyl-phenylalanine and indicate the C-terminal and N-terminal amino acid. (3×4=12)

3. (a) How  $\text{HIO}_4$  (periodic acid) can be used to distinguish glucose and fructose. What products would you obtain from each and how many molar equivalents of  $\text{HIO}_4$  would be consumed in each case. Explain by giving reaction and write the structures of the product formed.
- (b) How can you distinguish between D-ribose and 2-deoxyribose by chemical test? Explain by giving the reactions. (6,6)
4. (a) Give the name and draw the structure of a nucleotide having adenine as a base found in DNA.
- (b) Outline a sequence of reaction by which D-(+)-fructose can be converted into 1,3,4,6- tetra-O-methyl-D-fructose. Draw all the configurational structures.
- (c) Show the steps in the synthesis of the dipeptide Ala.Gly using Merrifield's solid- phase automated method. (3×4=12)
5. (a) What is the significance of Iodine value? Calculate the iodine number of Triolein (Mol. Wt. = 884)
- (b) What is the difference between oxidative and hydrolytic rancidity? Explain.
- (c) Write down the open chain structure for the aldaric acid (glucaric acid) that would be obtained by the  $\text{HNO}_3$  oxidation of D-Glucose. Would you expect it to be optically active? (3×4=12)



6. (a) What is Isoprene rule? Indicate the Isoprene units in the following compound.



- (b) How will you prepare 6-methylhept-5-en-2-one from acetone? Give its conversion to citral.
- (c) How will you establish the existence of  $\alpha, \beta$ -unsaturated carbonyl group in citral? Discuss the mechanism of reaction. (3×4=12)
7. (a) Give the synthesis of the following drugs  
 (i) Ibuprofen (ii) Paracetamol
- (b) What is the main component of Turmeric? Give its structure and uses.
- (c) Define the following terms and give one example of each  
 (i) Antibiotics (ii) Antipyretics (3×4=12)
8. Write short notes on any **three** of the following :
- (a) Antacids
- (b) Difference between Starch and Cellulose
- (c) Synthesis of Vanaspati Ghee
- (d) Secondary structure of proteins (3×4=12)





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[This question paper contains 6 printed pages.]

Your Roll No.....  
7/12/17

Sr. No. of Question Paper : 5612

H

Unique Paper Code : 217505

Name of the Paper : CHHT-513 : Physical Chemistry

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

Semester : V

Duration : 3 Hours

Maximum Marks : 75

**Instructions for Candidates**

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. The Paper has **three** sections.
3. Section **A** is compulsory. Attempt at least **two** questions from each of sections **B** and **C**.
4. Attempt **six** questions in all.
5. 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>

P.T.O.

## Section A

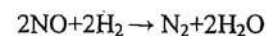
1. Attempt any five of the following :

- (i) Why does the equivalent conductance of a strong electrolyte decrease with increase in concentration of the solution?
- (ii) Why is phosphorescence a slow phenomenon?
- (iii) Why is adsorption an exothermic process?
- (iv) What is a Photo stationary State? Is it a true equilibrium state?
- (v) Explain Wien effect.
- (vi) Why does increase in temperature generally increases the rate of a reaction?
- (vii) What are the units of the Arrhenius frequency factor A? What is the physical significance of A (3×5)

## Section B

2. (i) Show that  $E_a = \frac{RT}{2} + E_0$  according to the collision theory of reaction rates. Here  $E_a$  is the activation energy and  $E_0$  is the minimum energy required for the reactants to undergo reaction.

- (ii) How does collision theory account for unimolecular reactions? Explain the mechanism by which unimolecular reactions occur.
- (iii) Following data have been obtained for the homogeneous gas reaction

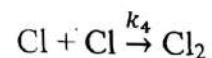
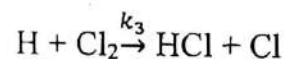
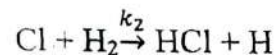
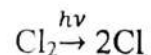


	$v_o/\text{Mol dm}^{-3} \text{sec}^{-1}$	$[\text{NO}]_o/\text{mol dm}^{-3}$	$[\text{H}_2]_o/\text{mol dm}^{-3}$
1.	$2.5 \times 10^{-5}$	$1.0 \times 10^{-2}$	$1.0 \times 10^{-3}$
2.	$22.5 \times 10^{-5}$	$3.0 \times 10^{-2}$	$1.0 \times 10^{-3}$
3.	$45.5 \times 10^{-5}$	$3.0 \times 10^{-2}$	$2.0 \times 10^{-3}$

Find the order with respect to NO and  $\text{H}_2$  and determine the rate constant. (4,4,4)

3. (i) Derive the Michaelis Menten equation for an enzyme catalyzed reaction.
- (ii) An enzyme catalyzed reaction has a Michaelis Menten constant of  $0.025 \text{ mol dm}^{-3}$  and a turnover number of  $2 \times 10^5 \text{ s}^{-1}$ . Calculate the initial rate and the maximum rate of this reaction if the total enzyme concentration is  $1.8 \times 10^{-8} \text{ mol dm}^{-3}$  and the initial concentration of substrate is  $4.5 \times 10^{-6} \text{ mol dm}^{-3}$ .
- (iii) What are promoters and inhibitors? Explain their action with suitable examples. (4,4,4)

4. (i) The mechanism for the photochemical reaction between  $H_2$  and  $Cl_2$  is as follows



Show that  $\frac{d[HCl]}{dt} = k [H_2] I_{abs}^{\frac{1}{2}}$

- (ii) In a gas phase first order reaction, the rate constants are found to be  $2.23 \times 10^{-5} \text{ min}^{-1}$  at 400 K and  $7.25 \times 10^{-4} \text{ min}^{-1}$  at 600 K. Calculate the activation energy of the reaction and the Arrhenius frequency factor.
- (iii) Write a short note on the absolute reaction rate theory. (4,4,4)
5. (i) Derive an expression for the Langmuir Adsorption Isotherm for a diatomic gas that undergoes dissociation into two atoms on adsorption.
- (ii) The volume of  $O_2$  gas (reduced to STP) adsorbed on the surface of 1 g sample of silica at  $0^\circ\text{C}$  was  $0.3 \text{ cm}^3$  at 150 torr and  $1.5 \text{ cm}^3$  at 760 torr. Calculate the

fraction of the surface covered at 760 torr. If the cross-sectional area of  $O_2$  molecule is  $0.15 \text{ nm}^2$ , calculate the surface area of 1 g of silica.

- (iii) Differentiate between physisorption and chemisorption. (4,4,4)

### Section C

6. (i) How can the composition of a complex be determined using Lambert Beer's Law?
- (ii) A solution of oxalic acid of concentration  $0.05 \text{ mol dm}^{-3}$  was irradiated by light of wavelength 254 nm. A  $10 \text{ cm}^3$  sample of the solution absorbed 90 J and the concentration was found to reduce to  $0.035 \text{ mol dm}^{-3}$ . What is the quantum yield of decomposition of oxalic acid?
- (iii) What is the Stark Einstein law? Under what conditions is it not valid? (4,4,4)
7. (i) Show that ionic mobility,  $\mu = \frac{\lambda}{F}$  where  $\lambda$  is the ionic conductance and F is Faraday.
- (ii) In a moving boundary experiment with 0.1 M HCl solution of specific conductance  $4.24 \text{ S m}^{-1}$ , 3 mA of



current are passed through a tube of  $0.3\text{cm}^2$  cross-sectional area. The boundary is seen to move by 3.08 cm in 1 hr. Calculate the mobility of hydrogen ion and the transport number of hydrogen ion.

(iii) Describe the titration curve of conductometric titration between a weak acid and a strong base. (4,4,4)

8. (i) Derive the Walden's equation.

(ii) The specific conductance of a saturated solution of  $\text{BaSO}_4$  at 298K is  $1.84 \times 10^{-3} \text{ S m}^{-3}$  and that of water is  $1.6 \times 10^{-4} \text{ S m}^{-1}$ . The ionic conductivities at infinite dilution of  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  are  $63.6 \times 10^{-4}$  and  $79.8 \times 10^{-4} \text{ Sm}^2\text{eq}^{-1}$  respectively. Calculate solubility and solubility product of  $\text{BaSO}_4$ .

(iii) The ionic conductivity of hydroxyl ion is very large. Describe the mechanism of conductance of hydroxyl ion in an aqueous solution. Will the same mechanism be followed if the solvent is changed? (4,4,4)



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Sf. No. of Q.P. : 6057

Roll No.....

Unique paper code: 2171501

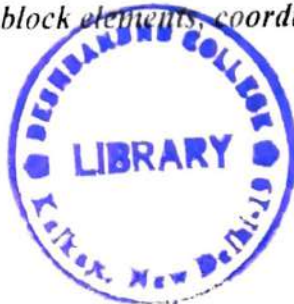
Name of the paper: *Theory Inorganic: d- block elements, coordination chemistry, lanthanides and actinides*

F-9

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

Semester: *Semester V, erstwhile FYUP*

Duration: 3 hr



Maximum Marks: 75

Instructions for Candidates

1. Write your Roll No. immediately on receipt of this question paper.
2. Attempt **five** questions in all.
3. All questions carry equal marks.

1. Give brief reasons for **any 5** of the following:

- a. The absorption spectra of lanthanides is sharp and not influenced by ligands.
- b. The geometry of a four coordinate Ni (II) complex depends on the ligand. Explain using VBT.
- c. High spin octahedral complexes of Mn(II) are faintly colored while low spin complexes are more strongly coloured.
- d. The magnetic moment of compound  $MCl_2$  is 5.92 BM where M is a 3d metal of transition series. Identify the metal M.
- e. Why do transition metals display variable oxidation states? Illustrate with specific examples.
- f. Potassium permanganate and potassium dichromate are intensely coloured despite the fact that Mn(VII) and Cr(VI) have  $d^0$  configuration?

(5X3)

2 (a). Write the formulae of the following:

- i. Zinc tetrafluorobromate (III)
- ii. Tetrakis(phosphoroustrifluoride)palladium (O)
- iii. Potassiumcarbonylpentacyanoferrate(II)
- iv. Tetrakis(ethylamine)copper(II) tetrahydroxocuprate(II)

2 (b). Give the IUPAC names of the following:

- a.  $Cs_2[OsCl_5N]$
- b.  $[FeI_2(H_2O)_4]_2 [FeCl_4]$
- c.  $[CuCl_2(CH_3NH_2)_2]$

2 (c) Why transition metals are less reactive then group I and group II metals?

(8+6+1)

3 Give brief reasons for **any 3** of the following:

- a. All octahedral complexes of Cr(III) are of the inner orbital type.

- b. What is the difference between a bidentate and an ambidentate ligand? Give an example of each type.
- c. Using VBT predict the hybridisation, geometry and magnetic properties of the following:
- (i)  $[\text{Pt}(\text{CN})_4]^{2-}$  (ii)  $\text{Zn}[\text{NiCl}_4]$
- d. Which will have a greater crystal field splitting and why?
- (i)  $[\text{CoF}_6]^{3-}$  or  $[\text{Co}(\text{en})_3]^{3+}$
- (ii)  $[\text{Ni}(\text{CN})_4]^{2-}$  or  $[\text{Pt}(\text{CN})_4]^{2-}$

(3X5)

4 Write short notes (any 3)

- (i) Separation of lanthanides by ion exchange method
- (ii) Geometrical isomerism in coordination number 4
- (iii) Inner and outer orbital complexes
- (iv) Lanthanide contraction and its consequences
- (v) Strong field and weak field ligands

(3X5)

- 5 (a) Draw the molecular orbital energy level diagram for a sigma bonded octahedral complex. Explain using MOT that  $10 Dq$  value in  $[\text{Co}(\text{CN})_6]^{3-}$  ion is increased as a result of pi bonding.

(b) What are 'allowed' and 'forbidden' transitions? Solution of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  ion is green but  $[\text{Fe}(\text{CN})_6]^{4-}$  is yellow in colour. Explain and characterize the origin of the transitions in these species.

(c) Lanthanide ions do not form complexes with amines in aqueous solutions. Give reason.

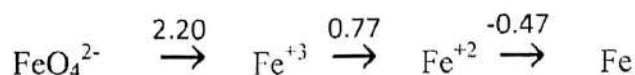
(6+6+3)

6 Answer the following:

- a) What is Jahn Teller distortion? Explain with an example.
- b) Write the possible isomers of  $[\text{Cu}(\text{en})_2(\text{NCS})_2]\text{Br}$ .
- c) Calculate the CFSE in terms of  $\Delta_o$  of a  $d^6$  metal ion placed in an octahedral arrangement with strong field ligand.
- d) Give the electronic configuration of  $\text{Sm}^{3+}$  (at. No 62) and  $\text{Er}^{3+}$  (at. No 68).
- e) Low spin tetrahedral complexes are not known. Why?

(5X3)

7 (a) Given below is the Latimer diagram for Fe in acidic media:



Answer the following question:

- i. Why is  $\text{FeO}_4^{2-}$  a strong oxidizing agent?
- ii. Mention the state which undergo as disproportionation and justify your answers.
- iii. Calculate  $E^\circ$  value of  $\text{FeO}_4^{2-}/\text{Fe}^{+2}$ .

(b) Predict the isomerism in the following:

- i.  $[\text{CoCl}(\text{NH}_3)_5]\text{SO}_4$  and  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Cl}$
- ii.  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

(c) Which is stronger base  $\text{La}(\text{OH})_2$  or  $\text{Lu}(\text{OH})_3$  ?

(6+6+3)





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The question paper contains 3 printed pages

Roll No: .....

S. No. of Question Paper: 6058

Unique Paper Code: 2171502

Name of the Paper: **Organic: Carbohydrates, Spectroscopy and Dyes**

F-9

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

Semester : V

Duration : **3 Hours**

Maximum Marks: **75**

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

*Attempt any six questions. All questions carry equal marks.*

- Q. 1 (a) Explain why in the synthesis of Azo dye temperature is kept low (0-5 °C), a suitable pH is required and diazonium is coupled with a compound having highly activating group.
- (b) Give two examples each of chromophores and auxochromes. Explain briefly how the presence of chromophore gives rise to the potentiality of color.
- (c) Describe the method for the synthesis of Indigo. How is it fixed to the fabric?
- (d) What are mordant dyes? Give the synthesis of any mordant dye.

3+2+3.5+4

- Q. 2 (a) How do anomers and epimers differ. Give suitable example.
- (b) How is the ring size of glucose determined with by oxidation with HIO<sub>4</sub>? Illustrate.
- (c) Explain why fructose is a reducing sugar. Name the rearrangement involved in the process.
- (d) Explain the mechanism of mutarotation.

2+2.5+4+4

Q. 3 (a) Draw the structure of a compound which has the molecular formula C<sub>3</sub>H<sub>6</sub>Cl<sub>2</sub> such that its NMR spectrum shows only one peak.

- (b) Why absorption bands are observed in UV spectroscopy instead of sharp peaks. Differentiate between cis-cinnamic acid and trans-cinnamic acid by UV.



(c) How will you distinguish between the following pair of compounds with the help of IR spectroscopy: (i) propanol and propanal (ii) ethanol and diethylether

(d) Draw the NMR spectrum of pure and impure ethyl alcohol.

3+3+3+3.5

Q. 4 (a) Differentiate between ethyl acetate and methyl propionate by NMR.

(b) A compound with molecular formula  $C_5H_{12}O$  shows the following absorption in NMR:

$\delta$  0.9 (t,3H), 1.2 (s, 6H), 1.5 (q,2H) and 1.64 (broad s, 1H)  
propose the structure and assign all the peaks.

(c) Explain the importance of fingerprint region in IR spectroscopy. How can the IR spectroscopy be used to differentiate between inter and intramolecular hydrogen bonding.

(d) What is TMS? Why it is added to a sample before taking its NMR spectra?

3.5+3+3+3

Q.5 (a) Convert **any three** of the following:

(i) Glucose to fructose.

(ii) Arabinose to glucose.

(iii) Mannose to arabinose.

(iv) Glucose to mannose.

(b) How was the stereochemistry of the naturally occurring (+) glucose established? 7.5 + 5

Q.6 (a) Which is more stable isomer of D-Glucose ( $\alpha$  or  $\beta$ )?

(b) The IR spectra of ethylacetoacetate show strong IR absorption at  $3050\text{ cm}^{-1}$ ,  $1748\text{ cm}^{-1}$ ,  $1724\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$ . Explain the peaks.

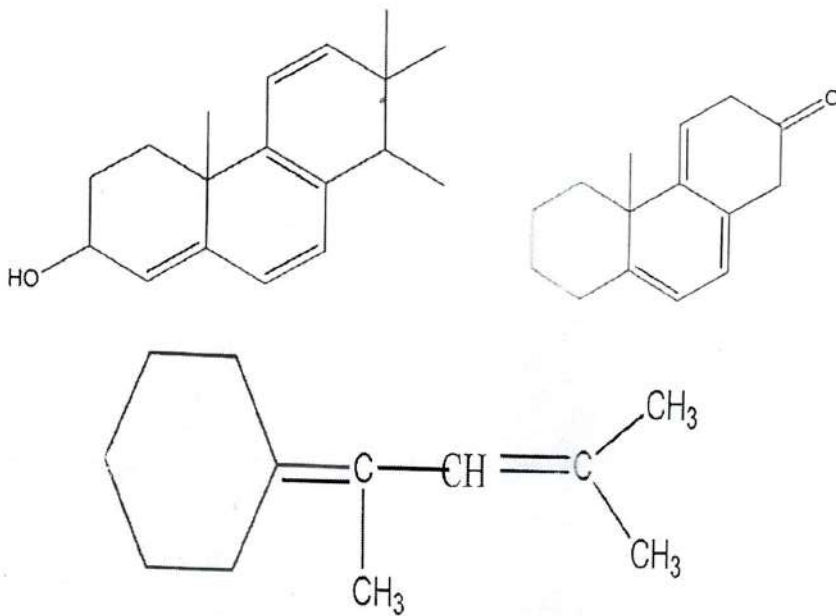
(c) What is invert sugar and why it is so named.

(d) Using structure explain why lactose behave as a reducing sugar while sucrose behave as non reducing? 3 + 3.5+2+4

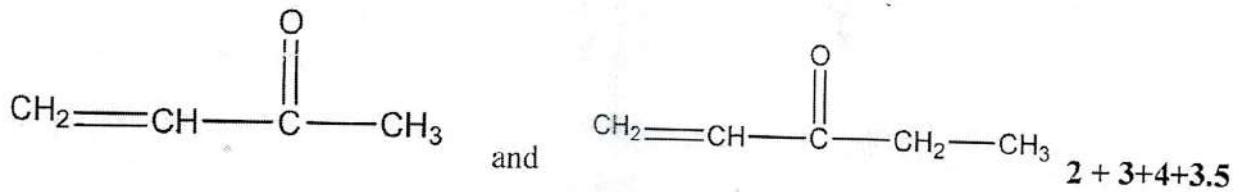
Q.7 (a) Explain why methyl orange is yellow in basic solution but red in acidic solution.

(b) What are phthalein dyes? How do they differ from triphenyl methane dye?

(c) Calculate  $\lambda_{\text{max}}$  for the following compounds:



(d) Giving reason to indicate whether you would use UV spectroscopy or IR spectroscopy for distinguishing between:



Q.8. Write short notes on **any four** of the following:

- (i) Witt's theory of colour and constitution.
- (ii) Structure of starch and cellulose.
- (iii) Xanthine dyes.
- (iv) Shielding and deshielding of protons in NMR spectroscopy.
- (v) Factors influencing chemical shift and coupling constant.

(6)



Sl. No. of Q.P.: 6059

13/12/17

F-9

Unique Paper Code : 2171503

Name of the Paper : Paper 13, Physical Chemistry: Phase Equilibrium and Binary

Solutions

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

Semester : V

Duration: 3 Hours

Max. Marks: 75

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

Attempt five questions in all. Question no. 1 is compulsory.

Attempt at least one question from each section.

Use of scientific calculator is allowed.

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

1. Attempt any five:

3 x 5

- a) Explain the moving of glaciers in the light of phase diagram of water.
- b) Eutectic point is invariable. Explain briefly.
- c) If one component behaves ideally other component also behave ideally in a binary liquid solution. Why?
- d) Tie lines in binodal curve are not parallel either to composition axis or to themselves. Explain.
- e) Calculate the Miller indices of the crystal plane which cuts through the crystal axis at: (6a, 3b, 3c), (2a, -3b, -3c).
- f) Both NaCl and KCl belong to FCC type of lattice but they show different intensity pattern. Explain why?

Section A

2. a) Define Gibbs Phase Rule. Derive the Phase rule for a reactive system.

4

b) The vapor pressure of decane is 10 torr at 55.7 °C and 400 torr at 150 °C. Calculate  $\Delta H_{\text{vap,m}}$  and  $\Delta S_{\text{vap,m}}$  at 100 °C, and the normal boiling point.

5

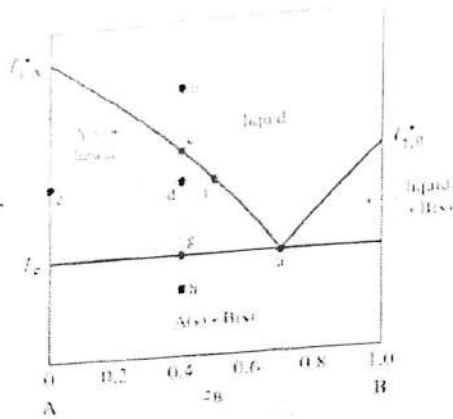
c) What is enantiotropy? Draw a well labelled phase diagram to explain this phenomenon for Sulphur.

6

3. a) What is a Tie line? State Lever rule and derive lever rule for the tie line ef in the diagram given below.

4





b) Describe water - acetic acid - chloroform phase diagram. 5

c) Construct the phase diagram for zinc and magnesium system using the following data.

Melting point of Mg:  $655^{\circ}\text{C}$

Melting point of Zn:  $500^{\circ}\text{C}$

A solid compound  $\text{MgZn}_2$  is formed which melts at  $540^{\circ}\text{C}$ .

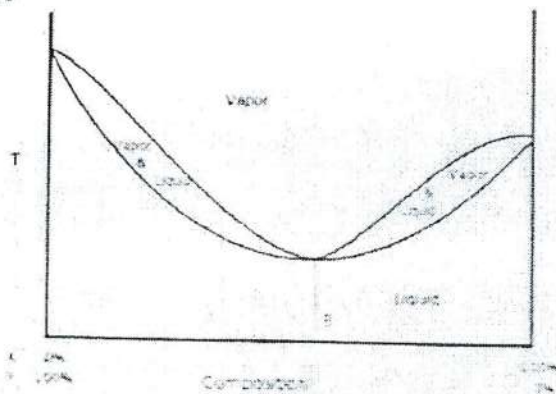
One eutectic point at  $350^{\circ}\text{C}$  with 20 mole percent of Zn and second at  $430^{\circ}\text{C}$  with 92 mole percent of Zn.

Draw a cooling curve for an isopleth at 40 mole percent of Zn. 6

### Section B

4. a) Derive Gibbs-Duhem-Margules equation and state any one application of this equation. 5

b) What is an azeotrope? Discuss the fractional distillation of a liquid pair X and Y at compositions along point A and B.



c) Derive the relation between vapor pressure of solution (P) and composition of vapor phase ( $y_A$ ) in an ideal binary solution. Draw a plot of pressure P vs.  $y_A$  and  $1/P$  vs  $y_A$ . 5

5. a) A mixture of an organic liquid A and water boils at  $90^{\circ}\text{C}$  when the barometer reads 734 mm Hg. The distillate contains 27 mass per cent of water and 73 mass percent of liquid A. Calculate (i) the vapor pressure of A at  $90^{\circ}\text{C}$ , (ii) the molar



- mass of A. 4
- b) Show that multi step solvent extraction is more efficient than single step extraction. 5
- c) Explain the effect of change of Pressure and addition of impurities on Critical Solution Temperature (CST). 6

### Section C

6. a) Calculate the interplanar spacing between the (221) planes of a cubic lattice of length 4,5 Å. 4
- b) State Bragg's Law. Derive Bragg's equation for the reflection of X-rays from the faces of a crystal. 5
- c) Describe the powder diffraction method to determine crystal structure. Explain how this method can be used to analyze the structure of a cubic system. 6
7. Write short notes on any **THREE** of the following: 5,5,5
- a) Nernst Distribution law & its applications
- b) Konowaloff's Law
- c) Rotating crystal method
- d) Miller Indices and Weiss Indices of a crystal plane



[This question paper contains 3 printed pages.]

Sr. No of Question Paper : 6060

Your Roll No.....

Unique Paper Code : 2171504

Name of the Paper : XIV (Section A: Inorganic Chemistry and  
Section B: Organic Chemistry)

P-9

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

Semester : V

Duration : 3 Hours

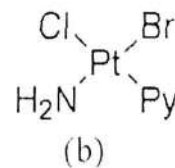
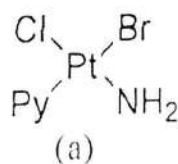
Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of the question paper)  
This paper has two sections. Attempt any three questions from each section.

### Section A

Attempt any three questions. All questions carry equal marks.

1. (a) What is trans-effect. What product is obtained when  $[\text{PtCl}_4]^{2-}$  is treated with:  
(i)  $\text{NH}_3$  followed by  $\text{R}_3\text{P}$   
(ii)  $\text{R}_3\text{P}$  followed by  $\text{NH}_3$   
(b) Metal-halogen bonds are labile than metal-nitrogen bond. Use this information and trans effect to derive the synthesis for the following geometric isomers from  $[\text{PtCl}_6]^{2-}$



- (c) Compare and contrast between homogeneous and heterogeneous catalysis.  
(d) Give the expression for the correlation of  $\Delta G$  with  $\log_{10} \beta$ . Discuss the comparative stability of chelate and non-chelated complexes. Give one example of each. (3.3.3.3.5)
2. (a) Predict the geometries of the complexes which result from the following reactions:



- (b) The successive stability constants for the species formed in aqueous solutions when ethylenediamine reacts with Ni(II) are as follows:

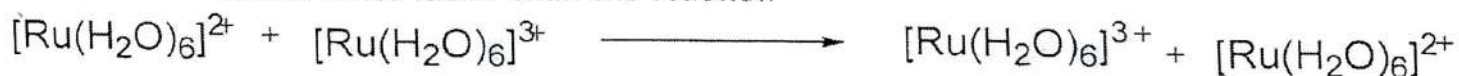
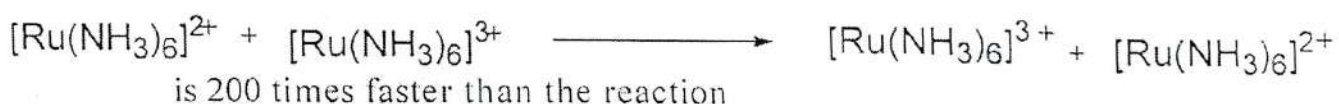
$$\log K_1 = 7.5, \log K_2 = 6.4, \log K_3 = 4.4. \text{ Calculate the value of } \beta_3$$

- (c) Nickel complexes are observed to undergo substitution much faster than platinum complexes. Offer an explanation. (5.4.5.3)

3. (a) The hydrolysis of chelated carbonato complex of cobalt (III) is much faster in acid than in neutral solution. Explain.
- (b) Anhydrous  $\text{CrCl}_3$  dissolves more rapidly in a dilute solution of  $\text{CrCl}_2$  than in pure water. Explain.
- (c) Discuss the mechanism of any two of the following:
- Wilkinson Catalysis
  - Hydroformylation
  - Wacker Process
  - Fisher Tropsch reaction
- (2.5,2.8)

4. (a) Explain the term thermodynamic and kinetic stability. Are the terms interrelated?
- (b) Water exchange by dissociation becomes increasingly important in both  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ . Explain.
- (c) The hydroxide ion is stronger base than ammonia yet it react much slowly than square planar complexes. Explain. (5.4,3.5)

5. (a) Explain the term lability and inertness giving example on the basis of CFT.
- (b) The outer sphere electron exchange reaction:



Account for this difference by giving an evaluation of the relative importance of the factors contributing to the energies of activation.

- (c) What is dissociative mechanism in substitution reaction? Give the energy diagram for the transition species where an intermediate is isolated. (4.5.3.5)

### Section B

Attempt any **three** questions. All questions carry equal marks.

1. (a) Write two medicinal uses each of curcumin and vitamin C.
- (b) Outline the steps involved in Hofmann's exhaustive methylation by taking quinoline as an example.

- (c) Give the synthesis of (-) Chloramphenicol. For what purpose it is used. Give its side effects. (3,4,5.5)
2. (a) How would you establish the presence of  $-NCH_3$  group in an alkaloid? Explain.  
(b) Give synthesis, uses and side effects of paracetamol. What type of drug is it?  
(c) What are "Ziegler-Natta" catalysts? How do these help in polymerization of propene? (3,4,5.5)
3. (a) Give biosynthesis of geranyl pyrophosphate from isopentenyl pyrophosphate.  
(b) Give the structure of Ibuprofen. Write steps for its synthesis.  
(c) What do you understand by isotactic, syndiotactic and atactic polymers? Explain with the help of suitable example. (3,4,5.5)
4. (a) Write short note on any two of the following  
(i) Vulcanization  
(ii) Biodegradable Polymers  
(iii) Medicinal importance of Antacid (Ranitidine)  
(b) What is a plasticizer? Explain your answer by giving the example of two plasticizers commonly used. Give their structure.  
(c) Give structure, synthesis and therapeutic uses of chloroquine. (4,4,4.5)



This question paper contains 4+1 printed pages]

8

30/11/17

Roll No.

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S. No. of Question Paper : 6486

Unique Paper Code : 32171501

Name of the Paper : Organic Chemistry-IV

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

Semester : V

Duration : 3 Hours

Maximum Marks : 75

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

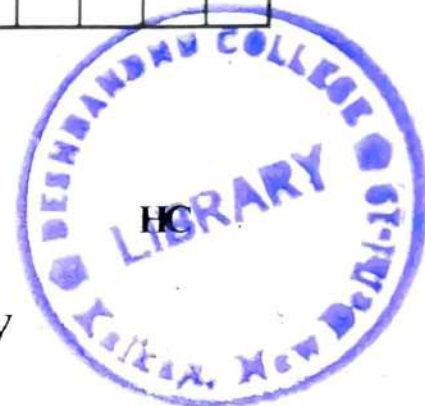
Question No. 1 is compulsory.

Attempt *six* questions in all.

1. Answer any *five* of the following :

- (a) What products are obtained when Gly-Phe-Ala-Lys-Val-Tyr-Arg-Glu-Ser is treated with (i) Trypsin, (ii) Chymotrypsin ?
- (b) Explain the stereospecificity of an enzyme on the basis of the Lock and Key Model.
- (c) What are essential fatty acids ? Give *two* examples along with their structures.

P.T.O.



- (d) Give synthesis, uses and side effects of paracetamol.
- (e) Differentiate between Nucleoside and Nucleotide. Give the structure of deoxycytidine.
- (f) Write the structure of  $\text{NAD}^+$ . Giving an example, explain its role in biochemical reactions catalyzed by enzymes.
- (g) Give the structure of an amino acid which :
- gives yellow colour with ninhydrin
  - has sulphur in the side chain
  - has  $-\text{OH}$  group in the side chain
- 5×3
2. (a) How will you prepare Gly-Val-Asp by Solid Phase Peptide synthesis ?
- (b) What is denaturation of proteins ? Give *two* examples. At which pH does denaturation occur most readily ?
- (c) Discuss the effect of concentration of the substrate on the rate of an enzyme catalyzed reaction. 6,3,3
3. (a) A heptapeptide, X, on hydrolysis with 6N-HCl showed the presence of the following amino acid residues :
- 1 Asp, 1 Val, 1 Lys, 2 Gly, 1 Ala, 1 Tyr

On treatment with anhydrous hydrazine at  $100^\circ\text{C}$ , X gave Gly and a mixture of amino acid hydrazides. Treatment with FDNB followed by hydrolysis gave the di-DNP derivative of Lys. Enzymatic hydrolysis of X yielded the following simpler peptides :

(Gly, Val); (Val, Lys); (Gly, Tyr); (Gly, Ala, Val); (Tyr, Asp, Gly)

Give the complete sequence of amino acids in the heptapeptide and explain the reactions involved.

- (b) Determine the isoelectric point of Lysine, given :  
 $\text{pK}_a(\text{COOH}) = 2.2$ ,  $\text{pK}_a(^+\text{NH}_3) = 9.0$ ,  $\text{pK}_a(\text{side chain}) = 10.5$

Give the structure of Zwitterion of Lysine.

- (c) Explain the following terms (any *two*) :

(i) Allosteric enzymes

(ii) Zymogen

(iii) Holoenzyme 6,2,4

4. (a) Draw the structures of glyceryl tristearate and glyceryl trioleate. Explain which has a higher melting point. Calculate the iodine value of glyceryl trioleate.

- (b) Explain the term rancidity of oils and fats. How many types of rancidity occur in oils and fats ? Discuss.
- (c) Give synthesis and therapeutic uses of chloroquine.

4,4,4

5. (a) Write the schematic representation of Krebs cycle. Mention the names of intermediates, enzymes and coenzymes involved in the process.

- (b) Which drug is used in the treatment of typhoid ? Give its structure, chemical name and synthesis from *p*-nitroacetophenone ?

6,6

6. (a) What is the full form of ATP ? Give its structure. What is its role in biological reactions ?

- (b) Give the structure and chemical name of Ibuprofen. Write steps for its synthesis.

- (c) Who won the 1962 Nobel Prize in Physiology or Medicine for the discovery of the molecular structure of DNA ? Draw the segment of RNA molecule with the bases guanine, uracil, adenine and cytosine, indicating 5' and 3' ends.

4,4,4

7. (a) Write all the possible tautomeric forms of base thymine. Out of these, which form is present in DNA ? Give the Fisher and Roeder synthesis of thymine.

- (b) Write steps for the preparation of Valine by Gabriel's phthalimide synthesis.

- (c) Give the steps involved in the conversion of glucose to glyceraldehyde-3-phosphate, during glycolysis.

6,3,3

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

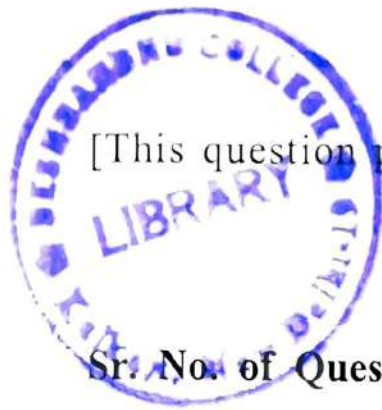
- (i) Structure and therapeutic uses of curcumin

- (ii) Secondary and tertiary structure of proteins

- (iii) Mechanism of action of trypsin

- (iv) Watson and Crick model of DNA

4,4,4



9

[This question paper contains 8 printed pages.]

512117

Your Roll No.....

Sr. No. of Question Paper : 6487

HC

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

**Instructions for Candidates**

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Answer **six** questions in all.
3. Question No. **1** is compulsory.
4. Attempt at least **two** questions from each section.
5. Attempt all parts of a question together.
6. Use of scientific calculators is allowed but they cannot be shared.
7. Logarithmic tables can be provided if required.

**Physical Constants**

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

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

P.T.O.



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	$1.38 \times 10^{-23} \text{ JK}^{-1}$

1. Attempt any **five** :

- (a) Zero point energies are a manifestation of the uncertainty principle. On the basis of this statement explain why zero point energy of simple harmonic oscillator can't be zero whereas that of rigid rotator can be zero.
- (b) If  $\psi_1$  &  $\psi_2$  are eigenfunctions of linear operator  $\hat{A}$  with the same eigen value  $a$ , then show that any linear combination of  $\psi_1$  &  $\psi_2$  will also be an eigenfunction of  $\hat{A}$  having the same eigen value.
- (c) Explain the difference between internal conversion and inter-system crossing in electronic spectra.
- (d) What is the essential condition for a molecule to show ESR spectrum. Which of the following will show ESR spectra :  $\text{H}^-$ ,  $\text{CO}_2^-$ ,  $\text{CH}_3^+$ ,  $\text{NO}_2$ ,  $\text{C}_5\text{H}_5^-$ ,  $\text{Na}^+$ .

- (e) A particle of mass  $m$ , is confined to a two-dimensional region having dimensions,  $0 \leq x \leq a$  and  $0 \leq y \leq b$ . The potential energy inside the box is zero and is infinity at the boundaries of the box. Write the expression for the operator, wave function,  $\psi_{n_x, n_y}(x, y)$  and energy,  $E_{n_x, n_y}$  for the system.
- (f) What is the effect on the microwave spectrum of  $\text{C}^{16}\text{O}$  if  $^{16}\text{O}$  is substituted by  $^{18}\text{O}$ ?
- (g) Determine whether the following wave-functions are acceptable or not as state functions over the indicated interval :

(i)  $\exp(-x) \quad 0 \leq x \leq \infty$

(ii)  $\exp(-x) \quad -\infty \leq x \leq \infty \quad (3 \times 5)$

### Section A

2. (a) State the variation theorem. Let the particle in a box be represented by the function  $\Psi = x^2(1-x)^2$ . Applying the variation theorem to the function calculate the ground state energy ( $V = 0$  for  $0 \leq x \leq 1$  and  $V = \infty$  elsewhere) and the percentage error. Given the actual  $E_0 = \frac{h^2}{8ml^2}$ , does this function satisfy the variation theorem?

- (b) What are orthonormal functions? Show that the set of functions :

$$\Phi_m = \frac{1}{\sqrt{2\pi}} \exp(im\phi) \text{ for } 0 \leq \phi \leq 2\pi \text{ are orthonormal.}$$

- (c) A particle of mass  $10^{-6}$  kg is rolling on the smooth floor of a  $1 \times 10^{-4}$  m wide box with a speed of  $3.3313 \times 10^{-3}$  m s $^{-1}$ . Applying the problem of particle in a one dimensional box, calculate the quantum number corresponding to the translational energy of the ball. Will you consider the energy to be quantized in a practical sense? (6,3,3)
3. (a) A particle of mass  $m$ , attached to a flexible spring is undergoing simple harmonic oscillations.

- (i) Give the expression for energy based on quantum mechanical treatment.
- (ii) Find the expression for  $\Delta E$ .
- (iii) Plot the wave-function and probability density curves for  $v = 0, 1$  and  $2$ .

What is the position at which the particle spends the maximum time in the ground state? Compare this observation with the classical mechanic behaviour.

- (b) Arrange the following species in the increasing order of bond length :  $O_2, O_2^+, O_2^-, O_2^{2-}$ .

(c) Evaluate  $[\hat{L}_x, \hat{L}_y]$ . (6,3,3)

4. (a) Write the LCAO-MO trial wave function of  $H_2^+$  using Molecular Orbital approach. Derive the expressions for molecular orbital wave functions corresponding to the bonding and anti-bonding energy levels of  $H_2^+$ .
- (b) Sketch the bonding and antibonding molecular orbitals of  $H_2^+$ .
- (c) For a particle of mass  $m$ , in a cube of edge length  $l$ , the energy of a quantum level is found to be

$$E = 14 \left( \frac{h^2}{8ml^2} \right)$$

Calculate the quantum numbers and find the degeneracy corresponding to this level. (6,3,3)

5. (a) Evaluate the expectation value of radius at which the electron in the ground state of Hydrogen atom ( $Z=1$ ) is found. Given the wave function for this state is

$$\Psi_{1,0,0} = \frac{1}{\sqrt{\pi}} \left( \frac{z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{z}{a_0}} \text{ where } a_0 \text{ is the Bohr radius and}$$

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

- (b) Normalize the wave-function  $x(a-x)$  over the range  $0 \leq x \leq a$ .
- (c) Sketch  $R(r)$  and  $4\pi r^2 R^2(r)$  vs  $r/a_0$  for 3s orbital for hydrogen atom. Calculate the number of radial nodes in this orbital. (6,3,3)

### Section B

6. (a) Sketch and explain the low resolution and high resolution PMR spectra of pure ethanol. How is the spectra modified in the presence of traces of alkali? How is the high resolution NMR spectra of impure  $\text{CH}_3\text{CH}_2\text{OH}$  different from that of  $\text{CH}_3\text{CH}_2\text{OD}$ ?
- (b) The first UV peak of butadiene observed at 210 nm, corresponds to a transition from  $n=2$  to  $n=3$ . Based on free electron model, calculate the length of the box to which this transition corresponds?
- (c) Predict and draw the intensity distribution in the hyperfine lines of the ESR spectrum of the radical  $\cdot\text{CH}_3$  ( $I = \frac{1}{2}$ ). (6,3,3)

7. (a) The fundamental vibration band of  $\text{HCl}^{35}$  is centred at  $2886 \text{ cm}^{-1}$  and the first overtone at  $5679 \text{ cm}^{-1}$ . Calculate the force constant, anharmonicity constant and zero point energy of the molecule.
- (b) What do you understand by Larmor precession? How does the precessional frequency vary with the applied field strength?
- (c) Explain the difference between dissociation and pre-dissociation. (6,3,3)
8. (a) Show that separation between P & R branches of vibration rotation spectra of a hetero-nuclear diatomic molecules is given by:
- $$\sqrt{\frac{8 kTB}{hc}}$$
- (b) The spacing between the successive lines of Raman rotational spectrum of  $\text{O}_2$  molecule is  $8B$  while for  $\text{H}_2$  molecule it is  $4B$ . Explain.
- (c) Spectral analysis shows that a molecule has a fundamental vibrational frequency equal to  $2960 \text{ cm}^{-1}$ . Predict the position of the stokes and antistokes lines for this vibrational mode, if the Raman spectrometer is using Hg light of wave length  $435.8 \text{ nm}$ . (6,3,3)

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

(a) Factors affecting the intensity of transition

(b) Frank-Condon principle

(c) Rule of mutual exclusion

(d) Configuration interaction

(4×3)