PH 541.2 Reg. No. :

St Aloysius College (Autonomous), Mangaluru

Semester II – P.G. Examination – M.Sc. Analytical Chemistry

May - 2024

ADVANCED INORGANIC CHEMISTRY

Time: 3 Hours **Max. Marks: 70**

PART - A

1. **Answer any FIVE questions of the following:** **(5x2=10)**

a) What is electrolytic reduction. Give an example.

b) Define metallurgy and distinguish between pyrometallurgy and hydrometallurgy, highlighting their respective applications in metal extraction.

c) Discuss the comparative nephelauxetic effect caused by the ligands F^- & I^-

d) What are coordination compounds? How do they differ from double salts?

e) What are pi-acceptor ligands. Give examples.

f) How does IR spectra differentiate between terminal CO and bridging CO.

g) What is quenching of orbital angular momentum?

h) Calculate the number of microstates in d^4 system

PART - B

Answer any FIVE of the following choosing at least one full question from each unit: **(5x12=60)**

UNIT – I

2.a) Explain any two methods for the separation of lanthanides. **(4)**

b) Compare 3d, 4d and 5d series elements with respect to 'tendency to form complexes' and 'atomic size'. **(4)**

c) Give a comparative study of properties of lanthanides & actinides. **(4)**

3.a) Write a comparative note on spectral and magnetic properties of actinides with d-block elements. **(4)**

b) Explain the significance of Frost diagrams. **(4)**

c) Outline the importance of Pourbaix diagram to explain stability of water. **(4)**

UNIT – II

4.a) The complex ion $[Co(NH_3)_6]^{3+}$ is octahedral and diamagnetic, the complex ion $[CoF_6]^{3-}$ is also octahedral but paramagnetic. How does VBT account for this observation? Explain. **(4)**

b) Classify and explain the types of ligands based on the number of donor atoms present in them. **(4)**

c) Discuss the stepwise determination of stability constants of complexes by Bjerrum's pH-metric method. **(4)**

Contd...2

5.a) Explain the splitting of d-orbitals in tetrahedral crystal field. (4)

b) How does the ligation energy provide evidence for the ligand field splitting? (4)

c) Explain the possible geometries of Coordination Number from 2 to 5? Give an example for each. (4)

UNIT - III

6.a) Write a note on stereochemical non-rigidity of metal complexes. (4)

b) Discuss the chemistry of metal dinitrogen complexes. (4)

c) Explain any two methods each for the preparation of metal carbonylates and metal carbonyl halides. (4)

7.a) Explain the reactions of metal carbonyls. (4)

b) Write a note on Cotton effect in metal complexes. (4)

c) With an example, explain the structure and bonding of metal nitrosyls. (4)

UNIT - IV

8.a) Explain the variation of magnetic susceptibility against temperature in para-, ferro- & antiferromagnetcic substances. (4)

b) Write the microstate table for p^2 system. (4)

c) Differentiate between Orgel diagram &Tanabe-Sugano diagram and draw Tanabe- Sugano diagram for d^2 metal ion dissolved in aqueous solution in an octahedral environment. (4)

9.a) Explain the spectra of $[Co(H_2O)_6]^{3+}$ (4)

b) Explain the charge transfer spectra. (4)

c) Describe Gouy's method of determination of magnetic moment. (4)

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Time: 3 Hours **Max. Marks: 70**

PART - A

1. **Answer any FIVE questions of the following:** **(5x2=10)**

a) What are ipso attack? Explain

b) Illustrate SNi reaction with a suitable example

c) Describe E1CB reaction

d) What are selective radicals? Give example

e) Give an example for Michael addition.

f) With suitable mechanism explain the product formed on the addition of HBr to Cyclopropene ring?

g) Explain the mechanism for the synthesis of Aziridene.

h) Thiophene oxide is formed when thiophene undergoes oxidation. Outline the mechanism

PART - B

Answer any FIVE of the following choosing at least one full question from each unit: **(5x12=60)**

UNIT – I

2.a) Explain the mechanism of SEi with example **(4)**

b) Discuss Sommelet-Houser rearrangement **(4)**

c) Explain reaction and reactivity in monosubstituted benzene **(4)**

3.a) Discuss Von-Richter rearrangement **(4)**

b) Discuss the mechanism and stereochemistry of SN2 reaction **(4)**

c) Explain anchemeric assistance in nucleophilic substitution reaction **(4)**

UNIT – II

4.a) Illustrate direction of elimination in unsymmetrical alkyl halides **(4)**

b) Describe auto oxidation reaction **(4)**

c) Give an account of Hofmann exhaustive methylation **(4)**

5.a) Explain the mechanism of pyrolysis of xanthate ester **(4)**

b) Write a note on

i) Hunsdiecker reaction

ii) Sandmeyer reaction **(4)**

c) Explain the factors affect the reactivity of elimination reaction **(4)**

Contd...2

UNIT - III

6.a) Explain the addition of grignard reagent to acid chlorides (4)

b) Explain A_{AC}^2 mechanism of ester hydrolysis (4)

c) Explain Reformatsky reaction mechanism (4)

7.a) Give an account of addition of boron hydride to carbon carbon multiple bonds (4)

b) Discuss the mechanism of Knoevenagel condensation (4)

c) Write a note on trans esterification reaction (4)

UNIT - IV

8.a) Explain the mechanism for acetylation of furan (4)

b) Depict the resonance in thiazole and indicate the position suitable for electrophilic substitution reaction (4)

c) Prove that syn addition to cis and trans isomer gives erythro and threo products respectively (4)

9.a) Describe the mechanism of addition of halogen to carbon-carbon double bond (4)

b) Explain Hanztsch mechanism (4)

c) Explain the mechanism involved in the oxidation of indole (4)

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ADVANCED PHYSICAL CHEMISTRY

Time: 3 Hours **Max. Marks: 70**

PART - A

1. **Answer any FIVE questions of the following:** **(5x2=10)**

a) Does the uncertainty in position increase or decrease with increasing quantum number in a harmonic oscillator?

b) State the second postulate of quantum mechanics.

c) Why are helium and hydrogen atoms often used as examples in applying the variation method?

d) Why is oxygen paramagnetic according to molecular orbital theory?

e) What is meant by hybridization of carbon atom?

f) What is meant by partial bond order in a conjugated system?

g) How does M-B statistics differ from F-D statistics?

h) Give the postulates of M-B distribution

PART - B

Answer any FIVE of the following choosing at least one full question from each unit: **(5x12=60)**

UNIT – I

2.a) Discuss the boundary conditions applied to the Schrödinger equation for a particle in a 1D box. **(4)**

b) Discuss the application of S.W.E for a simple harmonic oscillator. **(4)**

c) Write a note on matrices. **(4)**

3.a) Derive and discuss the commutation relations between the components of angular momentum (L_x, L_y, L_z) in quantum mechanics. **(4)**

b) What is a Hermition operator? Explain its properties. **(4)**

c) Write a note on S.W.E for a rigid rotor. **(4)**

UNIT – II

4.a) Describe the role and importance of potential energy surfaces in understanding reaction mechanisms within the Born-Oppenheimer approximation. **(4)**

b) Write a note on Russell-Saunders coupling with examples **(4)**

c) Discuss the importance of Slater's rules in estimating effective nuclear charges in many-electron atoms. **(4)**

Contd...2

5.a) Explain the molecular orbital methods in predicting the properties of the hydrogen molecule. (4)

b) Illustrate with an example how bonding and antibonding orbitals are formed in a homonuclear diatomic molecule using the LCAO approach. (4)

c) Explain how correlation diagrams can be used to understand the electronic transitions in a molecule, particularly in spectroscopy. (4)

UNIT - III

6.a) Give a comparson of Simple and Extended Huckel theory. (4)

b) Calculate the bond angle for sp^2 hybridised carbon atom. (4)

c) Explain geometry of molecules based on theory of directed valence (4)

7.a) Calculate the bond angle for a sp^3 Hybridred carbon atom (4)

b) Explain why the Experimental bond angle in H_2O and NH_3 differs from calculated Theoritically. (4)

c) Define Huckel Molecular Orbital (HMO) theory and explain how it is applied to analyze the electronic structure of a four-carbon atom system. (4)

UNIT - IV

8.a) Derive extended M-B distribution law. (4)

b) Derive an expression for entropy(Sackur-Tetrode) of a monoatomic gas. (4)

c) Derive an expression for Debye heat capacity of solids. (4)

9.a) Derive an Expression for Equilibrium constant in terms of partition Function. (4)

b) What is meant by total partition function? Give the equation for total partition function. (4)

c) Derive the partition function for vibrational motion of a molecule. (4)

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MOLECULAR SYMMETRY AND MOLECULAR SPECTROSCOPY

Time: 3 Hours **Max. Marks: 70**

PART - A

1. **Answer any SEVEN questions of the following:** **(7x2=14)**

a) Define symmetry operation. Mention any two symmetry operations.

b) What is group multiplication table? Represent the group multiplication table for C_{2v} point group.

c) Give the energy expression for the rotational energy levels of a diatomic rigid rotator

d) Explain Doppler broadening

e) Mention the components of a raman spectrometer.

f) Why is Raman spectroscopy advantagous over IR spectroscopy

g) What are reducible representations (RR)? Write the RR of H2O molecule based on arrow basis.

h) Define Refraction of light

i) State the Mutual exclusion principle.

PART – B

Answer any FOUR of the following choosing at least one full question from each unit: **(4x14=56)**

UNIT- I

2. a) What is a point group? Illustrate how H_2O molecule satisfies the mathematical rules for the formation of point group. **(4)**

b) What are commuting symmetry operations? Prove that the symmetry operations of C_{2v} point group are commuting. **(5)**

c) Set up the character table for NF_3 molecule based on "The great Orthogonality theorem". **(5)**

3. a) Find out the symmetry of vibrational modes in H_2O molecule. **(4)**

b) Obtain the matrix for rotation operation (C_2^z) in anti-clockwise direction. **(5)**

c) Define the term class. Give the number of classes in C_{2v}, C_{3v}, D_{3h} and D_{2h} point group. **(5)**

UNIT- II

4. a) The fundamental and the first overtone transitions of $^{14}N^{16}O$ are centered at 1876.06cm^{-1} and 3724.20cm^{-1}. Evaluate the equilibrium vibrational frequency, the anharmonicity constant, zero point energy and the force constant of the molecule. Given the reduced mass of $^{14}N^{16}O$ = 12.397 **(4)**

b) Describe the different modes of molecular vibrations. **(5)**

c) Obtain an expression for the natural vibrational frequency **(5)**

Contd...2

5. a) Write a comparative note on the rotational energy levels, selection rules and the rotational spectra of a diatomic molecule treated as a rigid and a non rigid rotator. (4)

b) Give a detailed account of the regions of the electromagnetic spectrum. Assign the regions to the types of energy transitions in molecules. (5)

c) Explain the influence of the isotopic substitution on the rotational spectra of triatomic molecule. (5)

UNIT- III

6. a) Write a note on the polarizibility ellipsoid (4)

b) Outline the various components of the IR spectrometer. (5)

c) Explain the classical theory of Raman spectroscopy (5)

7. a) Discuss the selection rules for Raman spectroscopy and IR spectroscopy (4)

b) Explain the effect of rotation on Raman shift (5)

c) Explain the quantum theory of Raman spectroscopy (5)

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