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St Aloysius College (Autonomous)

Mangaluru

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

May/June - 2023

ADVANCED INORGANIC CHEMISTRY

Time: 3 Hours

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Max. Marks: 70

PART - A

1. Answer any **FIVE** sub divisions of the following: (5x2=10)
- Give the significances of Frost diagrams.
 - Using the following Latimer diagram calculate the potential for the conversion of HNO_3 to HNO_2
$$\text{HNO}_3 \xrightarrow{0.803} \text{N}_2\text{O}_4 \xrightarrow{1.07} \text{HNO}_2$$
 - What is Nephelauxetic Series? Mention its significance.
 - The crystal field splitting and pairing energies of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ are 9200 and 20800 cm^{-1} respectively. Calculate the CFSE for the complex ion.
 - What are metal nitrosyl complexes?
 - Account for the fact that CO is a π -acceptor ligand.
 - Write a note on Racah parameter.
 - Deduce a microstate table for p^2 system.

PART - B

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

UNIT - I

- Explain how with the help of an Ellingham diagram, we can fix the criterion for the reduction of a metal oxide by carbon at a given temperature. (4)
 - Discuss lanthanide contraction and its application in the separation of lanthanides. (4)
 - Calculate the magnetic moment of Lanthanide ions having the ground state terms i) $^3\text{H}_4$ ii) $^5\text{I}_4$ (4)
- What are Pourbaix diagrams? To what use are they put? Explain giving an example. (4)
 - Compare the general characteristics of d and f block elements. (4)
 - Compare the spectral properties of lanthanides with that of d block elements. (4)

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UNIT - II

- 4.a) What are the important features of crystal field theory of coordination compounds? (4)
- b) Give the evidences for ligand field splitting based on ligation and lattice energies. (4)
- c) Describe the MO energy level diagram for octahedral complexes. (4)
- 5.a) Account for the fact that for the same metal ion and for the same ligands, d orbital splitting in a tetrahedral field is less than that in octahedral field. (4)
- b) Magnetic moment value of $[\text{MnBr}_4]^{2-}$ ion is 5.9 BM. Based on VBT predict the type of hybridisation and geometry of the ion. (4)
- c) Composition and stability constants can be determined using Bjerrum's pH metric method. Explain. (4)

UNIT - III

- 6.a) Explain how IR studies can be used in the structural elucidation of metal carbonyls. (4)
- b) Discuss the factors favouring M-M bond formation. (4)
- c) Compare the carbonyl stretching frequencies in the following pairs of compounds with reasoning. (4)
- i) $\text{Cr}(\text{CO})_6$ and $[\text{V}(\text{CO})_6]^-$ ii) $[\text{Cr}(\text{CO})_5(\text{PEt}_3)]$ and $[\text{Cr}(\text{CO})_5(\text{PPh}_3)]$
- 7.a) Explain the structure and bonding involved in metal carbonyl complexes. Suggest evidences for the back bonding in the complex. (4)
- b) Write a short note on dinitrogen complexes. (4)
- c) Briefly explain, how are abnormal ORD and CD diagrams used for the determination of absolute configuration of an optically active complex? (4)

UNIT - IV

- 8.a) Why are the electronic spectra of metal complexes exhibit weak absorption bands as compared to charge transfer transitions? Justify with reasoning. (4)
- b) Obtain the total number of microstates for divalent chromium and nickel ions. (4)
- c) Find out the spectroscopic ground terms for trivalent chromium and divalent nickel. (4)
- 9.a) The UV-Vis spectrum of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ exhibits three absorption bands at 17400, 24500 and 37500 cm^{-1} . Sketching an Orgel diagram, assign the bands to different transitions and calculate Dq, B', β . (4)
- (B of Cr^{3+} is 918 cm^{-1})
- b) Citing examples describe the different types of charge transfer transitions. (4)
- c) Explain quenching of orbital contribution to magnetic moment. (4)

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ADVANCED ORGANIC CHEMISTRY

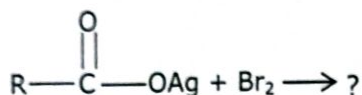
Time: 3 Hours

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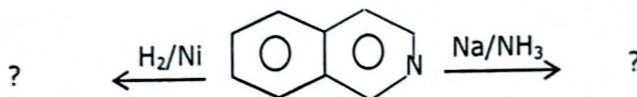
Max. Marks: 70

PART - A

1. Answer any **FIVE** sub divisions of the following: (5x2=10)
- Outline SEi mechanism.
 - What is Mannich reaction? Give an example.
 - What is Saytzeff and Hofmann orientation?
 - Predict the product and name the reaction.

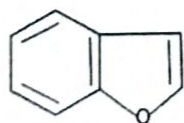


- e) Formulate the product(s) in the following:

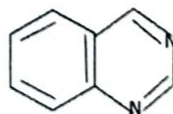


- f) Write the product formed when HBr is added to propylene in the absence and presence of peroxide.
- g) Name the following heterocyclic compounds.

1)



2)



- h) What is Oxirane? Justify its reactivity.

PART - B

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

UNIT - I

- Discuss the mechanism and stereochemistry of S_{N}^1 reaction. (4)
- Write briefly an electrophilic substitution reaction accompanied by double bond shifts. (4)
- Outline the mechanism of Von-Richter rearrangement. (4)

- 3.a) Write a note on neighbouring group participation in nucleophilic substitution reaction. (4)
- b) Describe S_NAr and Aryne mechanisms proposed for aromatic nucleophilic substitution reactions. (4)
- c) Explain any two factors influencing the role of nucleophilic substitution reactions. (4)

UNIT - II

- 4.a) Explain E₁ mechanism with an example. Comment on the orientation during elimination reactions. (4)
- b) Give a brief account of mechanism of pyrolysis of esters of carboxylic acid. (4)
- c) Write a short note on
i) Auto-oxidation ii) Sandmeyer reaction (4)
- 5.a) Discuss the effects of substrate structures, attacking base, leaving group and solvent on reactivity in elimination reactions. (4)
- b) Discuss E₁C_b reaction with mechanism. (4)
- c) Give an account of Hofmann degradation. (4)

UNIT - III

- 6.a) What is an Aldol condensation? Illustrate with an example. (4)
- b) How the stereochemistry/stereoselectivity of addition of halogens to carbon-carbon multiple bond. (4)
- c) Illustrate the Perkin reaction mechanism with an example. (4)
- 7.a) What is the advantage of Reformatsky reaction over Grignard reagents, write the mechanism of Reformatsky reaction. (4)
- b) Explain the mechanism of transesterification reaction. (4)
- c) Briefly explain the mechanism of A_{AC}2 mechanism. (4)

UNIT - IV

- 8.a) Outline the mechanism of Fischer-Indole synthesis. (4)
- b) Explain synthesis of Aziridine with suitable example. (4)
- c) How pyrroles reacts with chloroform in the presence of a base. Give the mechanism. (4)
- 9.a) How quinolone and isoquinoline behave towards the electrophilic and nucleophilic substitution reaction. (4)
- b) Illustrate the Hantzsch synthesis of Pyridine. (4)
- c) Give any one mechanism for the synthesis of furan. (4)

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ADVANCED PHYSICAL CHEMISTRY

Time: 3 Hours

PART – A

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1. Answer any **FIVE** sub-divisions of the following: (2x5=10)
- Find the de Broglie wavelength of an electron travelling at $1/10^{\text{th}}$ the speed of light. ($m_e = 9.1 \times 10^{-31}$ kg, $h = 6.626 \times 10^{-34}$ Js)
 - Normalize the wave function $\Psi(x) = A \sin \frac{n\pi x}{L}; 0 < x < L$
 - For which systems, perturbation theory can be applied? Give an example.
 - The energy functional from a trial wave function is $E(z) = z^2 - 3z$. Determine the variationally optimized or minimized energy.
 - Write the general secular equations for linear conjugated system.
 - Account for 1, 4- addition in Diels-Alder reaction from free valence index.
 - Calculate the translational partition function for benzene in a volume of 1 m^3 at 25°C .
 - What is partition function? Give its significance.

PART – B

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

UNIT- I

- Obtain the expression for energy levels and wavefunctions for a particle in One-dimensional box and give their graphical representation. (5)
 - Set up Schrodinger wave equation for the hydrogen atom. Carryout the transformation of co-ordinates. Separate the equation into the translational part and the electronic part. (7)
- Explain the concept of degeneracy using a particle in Three-dimensional Box problem. (4)
 - Write postulates of quantum mechanics and mention the rules for setting up quantum mechanical operators. (4)
 - Set up operators for linear momentum and angular momentum. (4)

UNIT- II

- Obtain the energy of the ground state of the helium atom employing variation method. (6)
 - Setup secular equations and secular determinant for homonuclear diatomic molecule. (6)
- State and explain Born Oppenheimer approximation. (4)
 - Outline the salient features of the Hartree-Fock self-consistent field (SCF) theory for solving the Schrodinger wave equation for a many electron atom. (5)

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c) Draw correlation diagram for hetero diatomic molecule.

(3)

UNIT- III

6. a) Find out π -electron energies for allyl radical, allyl cation and allyl anion. (6)

b) Set up and solve HMO determinants for 1, 3-butadiene system. Explain the calculation of the delocalization energy for butadiene system. (6)

7. a) Calculate electron density, bond order and free valence for ethylene system. (4)

b) Calculate bond angle in SP^3 hybridization of carbon atom. (4)

c) Discuss extended Huckel molecular orbital theory. (4)

UNIT- IV

8. a) Derive an expression for the molecular translational partition function of an ideal gas. (4)

b) Derive Sackur-Tetrode equation. (4)

c) Deduce the expression of third law of thermodynamics in terms of partition function. (4)

9. a) Define classically microcanonical ensemble, the canonical ensemble and the grand canonical ensemble, illustrating them with suitable diagrams. (6)

b) Deduce expression of equilibrium constant in terms of partition function. (6)

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MOLECULAR SYMMETRY AND MOLECULAR SPECTROSCOPY

Time: 3 Hours

Max. Marks: 70

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PART - A

1. Answer any **SEVEN** sub-divisions of the following: (7x2=14)
- Explain the following with diagrams:
 - Principle Axis of Rotation (C_n)
 - Plane of Symmetry (σ)
 - What is meant by Point Groups? Illustrate with examples.
 - What is meant by symmetry operations?
 - Define the following terms:
 - Wavelength
 - Frequency
 - Wavenumber
 - Velocity
 - What is the moment of inertia of a diatomic molecule whose internuclear distance is 150 pm and the reduced mass is 1.5×10^{-27} kg.
 - Give the different modes of vibrations of CO_2 molecule. How are its IR and Raman spectrums different?
 - What are the essential conditions for the molecules to absorb microwave radiation? Discuss any two applications of microwave spectroscopy.
 - What is Raman spectra?
 - What type of potential energy curve is obtained for a simple harmonic oscillator and why?

PART - B

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

UNIT - I

- Explain Great Orthogonality Theorem (G.O.T.) (3)
 - Prove that H_2O molecule is Abelian whereas NH_3 molecule is non-Abelian group. (3)
 - Construct the character table for the C_{3v} point group. (4)
 - Give examples of molecules with symmetry elements:
 - C_4 (n =even)
 - S_3 (n =odd)
 (4)
- Write the conditions (Group rules) for the symmetry elements to form a symmetry point group. (3)
 - Explain Class with example. (3)
 - Derive the matrix representation for $C_n(z)$ rotation axis in anticlockwise direction. (4)
 - Explain reducible representation of a group by taking water molecule as an example. (4)

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UNIT - II

4. a) Explain different types of molecular energies. (3)
- b) The pure rotational (microwave) spectrum of gaseous HCl consists of a series of equally spaced lines separated by 20.80 cm^{-1} . Calculate the internuclear distance of the molecule. The atomic masses are: $\text{H}=1.673 \times 10^{-27} \text{ kg}$; $^{35}\text{Cl}=58.06 \times 10^{-27} \text{ kg}$. ($h=6.626 \times 10^{-34} \text{ Js}$) (3)
- c) Show that the energy difference between the adjacent lines in a rotation spectrum of a diatomic molecule is constant for a rigid rotator model. (4)
- d) Derive an expression for vibrational energy of a diatomic molecule taking it as a simple harmonic oscillator. Sketch the vibrational energy levels of such a molecule. (4)
5. a) Why a diatomic molecule should be considered as anharmonic oscillator? Write Morse equation for the energy of anharmonic oscillator. (3)
- b) Explain the Stark effect in Microwave spectroscopy. (3)
- c) Derive an expression for the rotational energy of a diatomic molecule taking it as a rigid rotator. Draw the rotational energy level diagram for such a molecule. (4)
- d) Derive an expression for vibrational energy of a diatomic molecule taking it as a simple harmonic oscillator. Sketch the vibrational energy levels of such a molecule. (4)

UNIT - III

6. a) How do you explain Rayleigh's line, Stokes line and anti-Stokes lines in Raman Spectra? (3)
- b) Draw the experimental set-up of Raman spectrophotometer and explain how its functioning? (3)
- c) Explain the following: (4)
- i) Mutual exclusion rule for CO_2 and H_2O molecule in the Raman spectrum
 - ii) Anti-Stokes lines less intense than the Stokes lines in the Raman spectrum.
- d) With neat diagram explain detail instrumentation involved in FTIR spectroscopy. (4)
7. a) Explain the experimental setup of a double beam dispersive IR spectrometer and its advantages. (3)
- b) What are P, Q and R branches of rotation-vibration spectrum? (3)
- c) Explain the following in Raman Shift (4)
- i) Effect of vibration
 - ii) Effect of rotation
- d) Write short notes on the following (4)
- i) Resonance Raman spectroscopy
 - ii) Advantage and disadvantages of Raman spectroscopy