Reg. No: ☐☐☐☐☐☐

St Aloysius College (Autonomous)
Mangaluru
Semester II - P.G. Examination - M.Sc. Chemistry
April - 2018

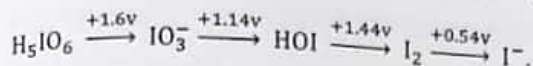# ADVANCED INORGANIC CHEMISTRY

Time: 3 Hours

Max.Marks:70

PART - A

1) Answer any FIVE sub divisions of the following   (5×2=10)

a) Calculate the skip potential for the conversion of periodic acid to iodine

$$H_5IO_6 \xrightarrow{+1.6v} IO_3^- \xrightarrow{+1.14v} HOI \xrightarrow{+1.44v} I_2 \xrightarrow{+0.54v} I^-.$$

b) Among $[CrO_4]^{-2}$ and $[MoO_4]^{2-}$ which is a good oxidising agent? Why?

c) Among $[Co(NO_2)_6]^{4-}$ ion and $[Co(NO_2)_6]^{3-}$ ion, which would absorb light of longer wavelength in the region.

d) Why octahedral complexes with three and eight d electrons on the central metal atom are stable. Under what condition a complex with seven d electrons on the central metal atom is stable?

e) In a series of complexes of the formula $[W(CO)_5 L]$, the C-O stretching frequency is maximum when L is PF_3.

f) Nickel forms pentacarbonyl, iron forms pentacarbonyl & chromium forms hexacarbonyl. Explain.

g) Differentiate between Orgel diagrams and Tanabe Sugano diagrams.

h) Calculate the number of microstates for d^3 system.

PART - B

Answer any FIVE of the following choosing at least one full question from each unit.

(12×5=60)

UNIT - I

2, a) Using the following Latimer diagram explain the disproportionation reaction of hydrogen peroxide $O_2 \xrightarrow{+0.68v} H_2O_2 \xrightarrow{+1.78v} H_2O$.   (4)

b) Explain the applications of Frost diagrams.   (4)

c) Explain the redox stability in water using Pourbaix diagram.   (4)

3, a) Using the following Latimer diagram construct the Frost diagram and comment of the oxidising nature of perchlorate.   (4)

$$ClO_4^- \xrightarrow{1.20} ClO_3^- \xrightarrow{1.18} ClO_2 \xrightarrow{1.19} HClO_2 \xrightarrow{1.70} HClO \xrightarrow{1.63} Cl_2 \xrightarrow{1.36} Cl^-$$

b) Although the number of electrons in the outer most transition element (1& 2) is same as in alkali metals and alkaline earth metals, yet transition metals are less reactive. Justify.   (4)

c) Explain the causes and consequences of Lanthanide contraction.   (4)

Contd.2

PH 581.2

UNIT - II

4. a) Account for the fact that for the same metal ion and for the same ligands, the d orbital splitting in a tetrahedral field is less than that in octahedral field. (4)

   b) Explain why Cu^{2+} does not form a regular octahedral complex where as Ni^{2+} does. (4)

   c) Explain with the help of molecular orbital theory, why Cl^- act as weak ligand where as CO act as a strong ligand in octahedral transition metal complexes. (4)

5. a) Explain the determination of composition and stability constants of complexes by Job's method. (4)

   b) Using CFT, prove that Mn_3O_4 is normal spinel & Fe_3O_4 is an inverse spinel. (4)

   c) Magnetic moment value of $[MnBr_4]^{2-}$ ion is 5.9 B.M. On the basis of VBT, predict the type of hybridisation and geometry of the ion. (4)

UNIT - III

6. a) What are Metal clusters? Explain Zintl ions and cheurel phases. (4)

   b) Explain classification and bonding in metal nitrosyls. (4)

   c) Illustrate the structural aspects of metal carbonyls using vibrational spectroscopy. (4)

7. a) Discuss the structures of $Ni(CO)_4$, $V(CO)_6$, $Cr(CO)_6$ & $Fe(CO)_5$. (4)

   b) Explain the preparation and properties of metal carbonyl halides. (4)

   c) What are pi-acceptor ligands? Give any 3 methods of preparation for metal carbonyl? (4)

UNIT - IV

8. a) State and explain spin selection and orbital selection rules. (4)

   b) In the spectra of $[V(H_2O)_6]^{+3}$ two peaks are obtained at $17300 cm^{-1}$ and $25600 cm^{-1}$, interpret the spectra, calculate the Racah parameter and wave number of missing transition. (4)

   c) Explain the mechanisms to overcome orbital selection rule in the electronic spectra of coordination compounds. (4)

9. a) Write a note on quenching of orbital angular momentum. (4)

   b) Explain different types of change transfer spectra. (4)

   c) Explain Guoy's method for the determination of magnetic susceptibility. (4)

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St Aloysius College (Autonomous) Mangaluru
Semester II - P.G. Examination - M.Sc. Chemistry
April - 2018

# ADVANCED ORGANIC CHEMISTRY

Time: 3 Hours   Max.Marks:70

PART - A

1) **Answer any FIVE sub divisions of the following**   (5×2=10)

   a) Give reasons: Neopentyl halides are unreactive towards SN_2 reactions.

   b) What is ipso substitution? Give an example.

   c) Predict the major product formed when 2-bromobutane is treated with sodium methoxide in methanol. Justify your answer.

   d) What is Hofmann degradation reaction? Give an example.

   e) Briefly explain the reaction of Grignard reagents with carbonyl compounds.

   f) What is transesterification reaction? Give an example.

   g) Give reasons: Pyrrole is active but not pyridine, towards electrophilic substitution reactions.

   h) Give the systematic names of the following heterocyclic compounds.
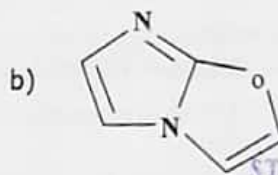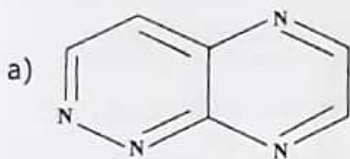
   a)   b)

PART - B

Answer any FIVE of the following choosing at least one full question from each unit.

(5x12=60)

UNIT - I

2. a) With suitable examples, explain the stereochemical aspects in nucleophilic substitution reactions.   (4).

   b) Explain any two factors influencing the rate of nucleophilic substitution reactions.   (4)

   c) Write the mechanism of i) Vilsmeyer-Haack reaction and ii) Mannich reaction.   (4)

3. a) What is neighbouring group participation and anchimeric assistance in substitution reactions? Explain with suitable examples.   (4)

   b) Describe the effect of nature of substituent on the direction of the electrophilic attack in aromatic systems.   (4)

   c) Explain the following reactions   (4)

      i) Von-Richer rearrangement   and ii) Smiles rearrangement

                                                    Contd...2

UNIT - II

4. a) Explain the following (4)

    i)   Coupling of alkynes through free radical intermediates.

    ii)   Arylation of aromatic compounds by diazonium salts.

  b) Explain the mechanism of E2 and E1cB eliminations. (4)

  c) Explain i) Chugaev reaction and ii) Cope elimination (4)

5. a) What are the important factors affecting the rate of free radical substitution reactions? Explain with suitable examples. (4)

  b) Explain with suitable examples, the Saytzeff and Hofmann rules governing the orientation during elimination reactions. (4)

  c) Explain i) Sandmeyer reaction and ii) Hunsdiecker reaction. (4)

UNIT - III

6. a) Explain any two mechanisms ester hydrolysis. (4)

  b) Describe the stereochemical aspects of addition of halogens to alkenes. (4)

  c) Explain the following (4)

    i) Hydroboration and ii) Michael addition

7. a) Explain the mechanism of esterification and transesterification reactions. (4)

  b) Explain, with suitable examples, the free radical additions to $C=O$ and $C=N$ systems. (4)

  c) Write short notes on the following (4)

    i) Reformatsky reaction and ii) witting reaction.

UNIT - IV

8. a) Give any two synthetic methods each for oxirane and aziridene. (4)

  b) Compare the general reactivity of indole and quinoline. (4)

  c) Explain the general reactions of pyrrole. (4)

9. a) Give a synthetic method each for thiophene and pyridine. (4)

  b) Compare the reactivity of pyrazole and imidazole towards electrophilic substitution reactions. (4)

  c) Arrange the following in the order of (4)

    i) their aromaticity and

    ii) their reactivity towards electrophilic substitution reactions. Justify your answer.

    Furan, pyrrole and thiophene.

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St Aloysius College (Autonomous)
Mangaluru
Semester II– P.G. Examination – M. Sc. Chemistry
April – 2018

ADVANCED PHYSICAL CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

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

   a) What is Balmer series? Where does it occur in the H-Spectrum?

   b) What is Kronecker delta?

   c) Why are approximation methods needed?

   d) What are antisymmetric waves?

   e) Define dihedral angle with an example.

   f) Determine the bond angle between the sp hybrid orbitals.

   g) What do you mean by Stirling's approximation?

   h) What are molar partition functions?

PART – B

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

UNIT- I

2. a) Describe Bohr's theory of H-atom.

   b) Describe the quantum mechanics of a simple harmonic oscillator.

   (6+6)

3. a) Explain Compton effect. What is its significance?

   b) Derive Schrodinger's equation for a particle in one dimensional box.

   c) Write briefly on Orbital diagrams.

   (4+4+4)

UNIT - II

4. a) Discuss the perturbation method.

   b) Give an account of non-crossing rule and correlation diagrams.

   (6+6)

5. a) Explain the rules for the formulation of Slater orbitals.

   b) Write briefly on the SCF method for many electron systems.

   (6+6)

UNIT – III

6. a) Explain the theory of directed valence.

   b) State the set of approximations introduced by Huckle, for linear conjugated systems.

   c)   How are the electron density and bond orders calculated in HMO theory?

(4+4+4)

7.   a)   Explain the application of HMO theory to benzene.

     b)   Explain the application of HMO theory to butadiene.

(6+6)

UNIT – IV

8.   a)   Describe the Fermi-Dirac statistics.

     b)   Briefly explain the Debye theory of heat capacities of the solids

(5+7)

9.   a)   How is the equilibrium constant calculated in terms of partition functions? Explain.

     b)   Deduce the Sackur-Tetrode equation.

(5+7)

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St Aloysius College (Autonomous)
Mangaluru
Semester II– P.G. Examination – M. Sc. Chemistry
April – 2018

MOLECULAR SYMMETRY AND MOLECULAR SPECTROSCOPY

Time: 3 Hours

Max. Marks: 70

PART - A

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

a) Distinguish between vertical and dihedral planes.

b) "Symmetry elements constitute a group." Justify with suitable example.

c) List the elements present in the C_{2v} and C_{3v} point groups and give an example for each.

d) What is zero point energy? Give its significance.

e) Give the significance of stark effect in microwave spectroscopy.

f) What is broadening of spectral lines?

g) Define Stoke's and Antistoke's lines.

h) What are combination bands?

i) Write two advantages of Raman spectroscopy over IR spectroscopy.

PART – B

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

UNIT- I

2. a) Define symmetry operation. Explain improper rotation with an example.

b) Derive matrix representation for Cn(z) axis of rotation in anti clockwise direction.

c) Deduce the character table for C_{2v} point group.

(4+6+4)

3. a) Briefly discuss the determination of symmetry species for translations and rotations.

b) Briefly explain the Mulliken symbols for IR.

c) Show that an H_2O molecule is an abelian group.

(5+4+5)

UNIT - II

4. a) Explain the following terms:

i) Stark effect   ii) Morse potential energy diagram.

b) Write a note on effect of isotopic substitution on rotational energy levels of diatomic molecules.

   c)   Give the classification of molecules based on moment of inertia.

                                                                 (5+5+4)

5.   a)   Briefly explain how bond length of a diatomic molecule can be determined by rotation spectra.

   b)   Deduce the expression for vibrational energy levels for an harmonic oscillator.

   c)   Discuss the vibrational spectra of CO_2.

                                                                (4+5+5)

UNIT – III

6.   a)   Write a note on:

       i) Sampling techniques employed in IR spectroscopy.

       ii) Mutual exclusion principle.

   b)   Briefly explain the principle and applications of Laser Raman Spectroscopy.

   c)   Discuss the selection rules for Raman Spectroscopy and IR spectroscopy.

                                                                (6+4+4)

7.   a)   Discuss the classical theory of Raman spectroscopy.

   b)   Write a note on rotational Raman spectra.

   c)   Which of the following will show rotational spectra and why?

       i) HCl   ii) CO_2 iii) H_2 iv) CH_4 v) CH_3Cl and   vi) CO

                                                                (5+4+5)

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Reg. No.

St Aloysius College (Autonomous)
Mangaluru
Semester I – P.G. Examination – M.Sc. Physics
November – 2017

MATHEMATICAL PHYSICS - I

Time: 3 Hours   Max. Marks: 70

PART - A

Answer all questions choosing one from each unit.   (15x4=60)

UNIT -I

1. a) Evaluate $\int_c \vec{F} \cdot \vec{dr}$ where $\vec{F} = x^2\hat{\imath} + xy\hat{\jmath}$ and c is the boundary of the square in the plane $z = 0$ and bounded by lines $x = 0$, $y = 0$, $x = a$ & $y = a$.   (5)

   b) Find gradient of ϕ and divergence of $\vec{A}$ in orthogonal curvilinear coordinates.   (10)

OR

2. a) State Gauss's divergence theorem and verify the same for $\vec{A} = x^2\hat{\imath} + y^2\hat{\jmath} + z^2\hat{k}$ over the unit cube $0 \le x,y,z \le 1$ (10)

   b) Find the square of the element of arc length in spherical polar coordinates.   (5)

UNIT -II

3. a) State Cayley-Hamilton theorem. Verify the theorem for the following matrix.
$$A = \begin{bmatrix} 2 & -1 & 1 \\ -1 & 2 & -1 \\ 1 & -1 & 2 \end{bmatrix}$$

(7)

   b) Write a note on algebra of tensors.   (8)

OR

4. a) Explain orthogonal matrices, hermitian and unitary matrices with examples.   (6)

   b) Explain with examples the transformation properties of contravarient and covariant tensors.   (5)

   c) Explain symmetric and antisymmetric tensors.   (4)

UNIT -III

5. a) Mention the classification of linear second order partial differential equations into various types, giving an example for each.   (6)

   b) By the use of separation of variables method solve the one dimensional heat equation $k \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t}$ satisfying the boundary condition $T(0,t) = T(L,t) = 0$, L being the length of the rod.   (9)

OR

6. a) Obtain the solution of Laplace's equation in general cylindrical coordinates.   (8)

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Mangaluru
Semester II – P.G. Examination – M.Sc. Chemistry
April- 2019
ADVANCED INORGANIC CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

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

a) Metal sulphides cannot be directly reduced with carbon. Give reason with the help of Ellingham diagram.

b) Actinides have a greater tendency to form complexes than Lanthanides. Justify.

c) Account for the statement that in the crystal of CuF_2, all Cu-F bond distance are not equal.

d) Which of the two, $[CoCl_4]^{2-}$ and $[CoI_4]^{2-}$ is expected to have higher Δ_t and why?

e) Substitution reactions of polynuclear metal carbonyls with tertiary phosphines often induce the formation of bridging carbonyls. Justify.

f) What is cotton effect?

g) Give an account for ligand-to-metal charge transfer bonds.

h) The complexes $[Mn(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$ have magnetic moments of nearly 5.92BM. justify based on electronic structure of these complexes.

PART - B

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

UNIT – I

2.a) Convert Latimer diagram into reduction half-cell reactions (4)

$$ClO_4^- \xrightarrow{+0.37} ClO_3^- \xrightarrow{+0.30} ClO_2^- \xrightarrow{+0.68} ClO^- \xrightarrow{+0.42} Cl_2 \xrightarrow{+1.36} Cl^-$$

b) Depict using a diagram the condition of potential and pH under which water is thermodynamically stable towards oxidation or reduction. (4)

c) Give a comparative study of properties of 3d and 4d series elements. (4)

3.a) Describe the methods involved in reduction of oxide ores. (4)

b) Explain the significances of frost diagrams. (4)

c) Elaborate on the spectral and magnetic properties of actinides elements compared to lanthanides. (4)

UNIT – II

4.a) Explain why Cr^{2+} does not form a regular octahedral complex with a weak field ligand whereas Mn^{2+} forms a regular octahedral complex with ligand? (4)

Contd...2

PH 581.2

b) The nephelauxetic effect for ammonia is less than that for CN^-. Explain. (4)

c) Sketch the $\sigma\, MO$ diagram for a square ML_4 complex. (D_{4h} symmetry). (4)

5.a) Rationalize the following observations.

    i. $[Fe(H_2O)_6]^{3+}$ is stronger oxidizing agent than $[Fe(CN)_6]^{3-}$

    ii. $[Fe(H_2O)_6]^{3+}$ is weaker oxidizing agent than $[Fe(O-phen)_3]^{3+}$ (4)

b) Calculate the spin-only magnetic moment for a d^7 ion in octahedral and tetrahedral ligand fields. (4)

c) How is composition and stability constant of complexes determined using Rossotti and Rossotti method? (4)

UNIT - III

6.a) Illustrate the preparation and structural aspects of metal carbonyl halides. (4)

b) Apply the concept of the vibrational spectra for analyzing metal carbonyls. (4)

c) Discuss in detail, the evidences in favour of back bonding in metal carbonyls. (4)

7.a) Discuss the structure of $CO_2(CO)_8H, Fe_2(CO)_9$ and account for its stability. (4)

b) Why dinitrogen was proved to be impossible to form complex until 1965? Write the preparation of dinitrogen complex. (4)

c) Suggest the rules determining skeletal bonding in

    i) $[Ru_5N(CO)_{14}]^-$ ii) $Os_5C(CO)_{15}$ (4)

UNIT - IV

8.a) The uv-visible spectra of $[Ni(H_2O)_6]^{+2}$ shows peaks at $8499cm^{-1}$, $14222cm^{-1}$ and $26022cm^{-1}$. Interpret the spectra and comment on nature of metal ligand bond. (B for free Ni^{+2} is $1040cm^{-1}$) (4)

b) Predict the μ_s values for i) $K_2[Mn(H_2O)_6](SO_4)_2$ and ii) $K_4[Mn(CN)_6]$ (4)

c) Justify i) d^n and d^{10-n} systems have same term symbol.

    ii) $[Fe(H_2O)_6]^{2+}$ is paramagnetic whereas $[Fe(CN)_6]^{4-}$ is diamagnetic (4)

9.a) Explain Tanabe-Sugano diagram for the d^6 system. (4)

b) Discuss diamagnetic and paramagnetic behaviours of metal complexes. (4)

c) Explain quenching of magnetic moment. (4)

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PH 582.2

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April- 2019
ADVANCED ORGANIC CHEMISTRY

Time: 3 Hours

Max. Marks: 70

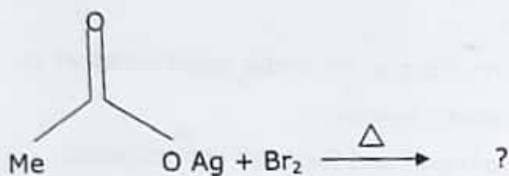### PART - A

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

a) Outline SE1 mechanism.

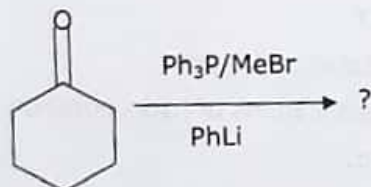b) Predict the product(s) in the following and name the reaction.

$$\xrightarrow[\text{H}_2\text{O}]{\text{DMF/POCl}_3} \ ?$$

c) Complete the following reaction. Give its mechanism.

$$\text{Me} \qquad \text{O Ag} + \text{Br}_2 \xrightarrow{\triangle} \ ?$$

d) What is the effect of solvent on free radical substitution reactions?

e) Explain the term "trans esterification" with an example.

f) Predict the product(s) in the following.

$$\xrightarrow[\text{PhLi}]{\text{Ph}_3\text{P/MeBr}} \ ?$$

g) Write the product of the following reaction with mechanism.

$$\xrightarrow[\text{100}^\circ\text{C}]{\text{NaNH}_2} \ ?$$
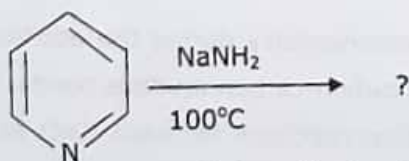
h) Give any one method of synthesis of Pyrazole.

PART - B

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

UNIT – I

2.a) Give an account of neighbouring group participation in nucleophilic   (4)
substitution reaction.

b) Describe the mechanisms of   (4)

    i)   Mannich reaction

    ii)   Sommelet-Houser rearrangement.

Contd...2

PH 582.2

c) Discuss briefly the mechanism and stereochemistry of SN^1 reaction. (4)

3.a) Discuss briefly the factors influencing the rates of nucleophilic substitution reactions. (4)

b) Write briefly on electrophilic substitution reactions accompanied by double bond shifts. (4)

c) Write notes on the following:
   i) Arenium ion mechanism (4)
   ii) Von-Richter rearrangement

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UNIT – II

4.a) Describe the mechanism of free radical substitution reactions. (4)

b) Discuss briefly E1 and E2cB mechanisms. (4)

c) Write a brief account of mechanism of pyrolysis of esters of carboxylic acids. (4)

5.a) Discuss the reactivity for the aliphatic and aromatic substances at a bridge head, in free radical reactions. (4)

b) Give a comparative account of Hofmann and Saytzeff eliminations. (4)

c) Explain the following reactions.
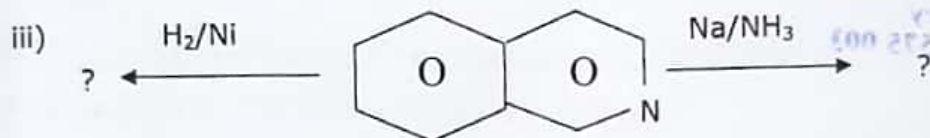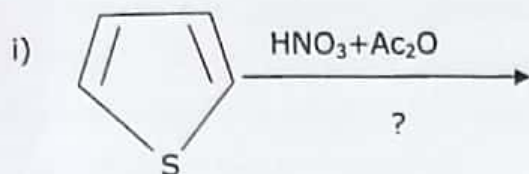   i) Auto-oxidation   ii) Ullmann reaction (4)

UNIT - III

6.a) Outline BAc^2 and AAc1 mechanisms of Ester hydrolysis. (4)

b) Discuss the mechanism and synthetic applications of hydroboration. (4)

c) Explain the mechanisms of the following.
   i) Michael addition   ii) Knoevenagel condensation (4)

7.a) Write briefly on orientation and stereochemistry during the addition of halogens and hydrogen halides to carbon-carbon multiple bonds. (4)

b) Describe any two electrophilic addition reactions for each C=O and C=N systems. (4)

c) Write short notes on the following:
   i) Addition of oxygen across double bonds.
   ii) Reformatsky reaction (4)

UNIT - IV

8.a) Compare and contrast the reactivity and reactions of Furan and Pyrrole. (4)

b) Outline the mechanism of Skrup's Quinoline synthesis. (4)

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c) Give any two synthetic methods each for thiranes and azirenes. (4)

9.a) Describe Fischer-Indole synthesis with mechanism. (4)

 b) Formulate any two methods of synthesis of thiazole. (4)

 c) Predict the product(s) in the following.

i)

$HNO_3 + Ac_2O$

?

ii) Imidazole $\quad \xrightarrow{Br_2/CHCl_3}$?

iii)

$\xleftarrow{H_2/Ni}$?

$\xrightarrow{Na/NH_3}$? (4)

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PH 583.2

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Semester II – P.G. Examination – M.Sc. Chemistry
April- 2019
ADVANCED PHYSICAL CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

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

a) Mention the condition for orthogonality.

b) An electron is confined in a one-dimensional box of length 10A°. Calculate its ground state energy in eV.

c) Write the expression of Slater type orbitals.

d) State and explain non-crossing rule.

e) Give the significance of Coulomb integral and resonance integral in HMO theory.

f) Determine the delocalization energy for 1, 3-butadiene.

g) What is micro canonical ensemble? Illustrate.

h) Calculate the rotational partition function for the O-H radical at 27°C, given that the bond length (0-H) is 0.971A°.

PART - B

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

UNIT – I

2.a) Deduce the operators for linear momentum and angular momentum.   (4)

b) State and explain the postulates of quantum mechanics.   (4)

c) A particle of mass $2x10^{-26}$g is in one dimensional box of length 4nm. Find the frequency and wavelength of the photon emitted when the particle goes from n=3 to n=2 level.   (4)

3.a) Set up Schrodinger wave equation for the hydrogen atom. Carryout the transformation of co-ordinates. Separate the equation into translational and electronic part.   (6)

b) Discuss briefly the application of Schrodinger wave equation to a particle in the ring.   (6)

UNIT – II

4.a) Outline the application of first order perturbation theory to Helium atom.   (5)

b) Deduce secular equation and formulate Secular determinants.   (3)

c) Explain the valence bond treatment of hydrogen molecule.   (4)

Contd...2

5.a) State the variation principle and obtain the energy of the ground state of the hydrogen atom employing variation method.   (5)

b) Discuss Born-Oppenheimer approximation.   (4)

c) Draw correlation diagram for homo diatomic molecule.   (3)

UNIT – III

6.a) Set up and solve HMO determinants for allyl system. Calculate bond order, charge density and free valence for allyl radical system.   (7)

b) Explain briefly extended Huckel molecular orbital theory.   (5)

7.a) Discuss the application of HMO theory to cyclic system and obtain the expression for energies of π state.   (5)

b) Explain the theory of directed valence.   (4)

c) Deduce the expression of electron charge density on the basis of HMO method.   (3)

UNIT - IV

8.a) Describe Debye theory of heat capacities of the solids.   (4)

b) Deduce the expression of entropy in terms of partition function.   (4)

c) Derive Maxwell-Boltzmann distribution law.   (4)

9.a) Define i) Ensemble   ii) Boson   iii) Phase space   iv) microstate   (4)

b) Obtain the expression of vibrational partition function.   (4)

c) Deduce Sackur-Tetrode equation.   (4)

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Reg. No. : ☐☐☐☐☐☐☐

St Aloysius College (Autonomous)
Mangaluru
Semester II – P.G. Examination – M.Sc. Chemistry
April- 2019
MOLECULAR SYMMETRY AND MOLECULAR SPECTROSCOPY

Time: 3 Hours   Max. Marks: 70

PART - A

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

   a) Explain the following with diagrams:

      i)   Principle axis of rotation (C_n)   ii) Plane of symmetry (σ)

   b) Define the following with example:

      i)   Abelian and non-Abelian groups   ii)   Subgroup

   c) How can we study the following properties of a substance on the basis of group theory?

      i) Optical activity of molecule   ii) Polar and non-polar nature of molecule

   d) Calculate the energy associated with a radiation having wavelength 4000 A^0.   Give answer in kcal mole^{-1} and also in kilo Joules mole^{-1}.

   e) The fundamental vibration frequency of HCl is 2890 cm^{-1}, calculate the force constant of this molecule. The atomic masses are $^1H=1.673 \times 10^{-27}$ kg; $^{35}Cl=58.06 \times 10^{-27}$ kg.

   f) How many fundamental vibration frequencies would you expect to observe in the infrared absorption spectrum of H_2O?

   g) Sketch the fundamental modes of vibration of CO_2 and predict which modes will be infrared active and which will be Raman-active.

   h) Write four characteristic properties of Raman lines.

   i) List out the advantages of Laser Raman Spectroscopy.

PART - B

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

UNIT – I

2.a) Depict the molecular point group of $POCl_3$ and ethene. Explain in detail.   (4)

   b) Using Great Orthogonality Theorem (G.O.T) derive the character table for C_{2v} point group.   (6)

   c) Derive the matrix representation for rational axis Cn in anticlockwise direction.   (4)

PS 584.2

3.a) Write a brief note on applications of group theory to molecular vibrations and chemical bonding. (4)

b) Using G.O.T. construct the character table for the NH_3 molecule? (6)

c) Define class. Show that in C_{3v} point group C_3^1 & C_3^2 are in mutual conjugation. (4)

UNIT – II

4.a) Define and explain each of the following with neat diagram:
i) absorption ii) emission iii) transmission iv) fluorescence
v) refraction vi) dispersion vii) scattering viii) reflection (4)

b) Show that on the rigid rotator (rotor) model the energy difference between the adjacent lines in a rotation spectrum of a diatomic molecule is constant (6)

c) Explain i) Fundamental vibrations ii) Overtone iii) hot bands. Mention why an overtone is a week signal. (4)

5.a)   i) Derive an equation for wavenumber of a diatomic molecule in terms of force constant and reduced mass using the concept of simple Harmonic oscillator.

ii) Discuss the factors which determine the width, broadening and intensity of spectral lines. (4)

b) Explain the following.
i)   Determination of bond lengths
ii)   Isotope effect on rotation spectra
iii)   Microwave spectrometer (6)

c) Explain the following.
i) Zero point energy
ii) Morse potential energy diagram (4)

UNIT - III

6.a) Explain the instrumentation of IR spectrophotometer and differentiate between dispersive IR and Fourier Transform IR. (4)

b) Explain the classical and Quantum theory of Raman Effect. (6)

c) Describe systematically the origin of P, Q and R branches in vibrational-rotational spectra of polyatomic molecules. (4)

7.a) Explain – i) Instrumentation of Raman spectrometer.
ii) Mutual exclusion principle. (4)

b) Explain and derive the equation for pure rotational raman spectra and vibrational-rotational raman spectra and also draw the diagram for both the case. (6)

c) i) Differentiate between Raman spectroscopy and IR spectroscopy. (4)
ii) Explain Resonance Raman spectroscopy.

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