

**M. Sc (CHEMISTRY) – 2nd SEMESTER
INORGANIC CHEMISTRY-II, - 9040201
END TERM THEORY EXAMINATION**

Time: 03:00 Hrs

Max. Marks: 60

Instructions:

1. Write Roll No. on the Question Paper.
2. Candidate should ensure that they have been provided with correct question paper. Complaint(s) in this regard, if any, should be made within 15 minutes of the commencement of the exam. No complaint in this regard will be entertained thereafter.
3. Marks are indicated against each question.
4. Draw diagram wherever required.

PART – A (OBJECTIVE TYPE QUESTIONS OMR SHEETS)

- Q.1. Colour of a complex is satisfactorily explained by (30 × 1 = 30)
 a) Werner's theory c) Crystal field theory
 b) Valence Bond Theory d) Ligand field theory
- Q.2. The CFSE for a strong field d^7 octahedral complex is
 a) $-14Dq$ b) $-18Dq + 3P$ c) $-24Dq + 2P$ d) $-12Dq + 3P$
- Q.3. $[\text{CoF}_6]^{3-}$ complex ion is:
 a) Inner orbital and diamagnetic c) outer orbital and paramagnetic
 b) Outer orbital and diamagnetic d) inner orbital and paramagnetic
- Q.4. $[\text{NiCl}_4]^{2-}$ complex ion is:
 a) Tetrahedral and paramagnetic c) Square planar and diamagnetic
 b) Tetrahedral and diamagnetic d) Square planar and paramagnetic
- Q.5. C.F.T. describes the nature of M-L bonding as
 a) Purely covalent b) Purely ionic c) Purely coordinate d) All of the above
- Q.6. Which of the following will have the largest crystal field splitting?
 a) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ b) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ c) $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ d) $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$
- Q.7. In the visible spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, absorption takes place at $20,000\text{cm}^{-1}$ or 5000 Angstrom. The Δ_{oct} of the complex is:
 a) 200 kJ/mol b) 189 kJ/mol c) 220 kJ/mol d) 239 kJ/mol
- Q.8. For $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex ion the absorption spectrum is obtained for which of the following transitions:
 a) ${}^2T_{2g} \rightarrow {}^2E_g$ b) ${}^2T_2 \rightarrow {}^2E$ c) ${}^2E_g \rightarrow {}^2T_{2g}$ d) ${}^2E \rightarrow {}^2T_2$
- Q.9. Which of the following configurations in an octahedral complex shows tetragonal elongation?
 a) $t_{2g}^6 d_{x^2-y^2}^2 d_{z^2}^2$ c) $t_{2g}^6 d_{x^2-y^2}^2 d_{z^2}^1$
 b) $t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^1$ d) $t_{2g}^6 d_{x^2-y^2}^1 d_{z^2}^1$

- Q.10. Ground state term for d^2 configuration is:
 a) 3F b) 3P c) 1G d) 1S
- Q.11. The number of microstates for N ($1s^2 2s^2 2p^3$) are
 a) 15 b) 20 c) 21 d) 30
- Q.12. The Ground State term symbol for Cr ($3d^5 4s^1$) is:
 a) 3F_4 b) 3G_3 c) 7S_3 d) 3F_4
- Q.13. Tetrahedral complexes $[MnCl_4]^{2-}$ and $[MnBr_4]^{2-}$ are intensely colored because of
 a) Charge transfer transitions
 b) Laporte forbidden transitions
 c) Lack of centre of symmetry leads to mixing of p and d orbitals
 d) Jahn-Teller distortion
- Q.14. The Racah parameter, B' , may be calculated from the following equation:
 a) $B' = B(1 - 2hk)10^{-3} cm^{-1}$ c) $B' = B(2 - hk)10^{-3} cm^{-1}$
 b) $B' = B(1 - hk)10^{-6} cm^{-1}$ d) $B' = B(1 - hk)10^{-3} cm^{-1}$
- Q.15. For $[V(NH_3)_6]^{2+}$, the third band at $36,000 cm^{-1}$ can be assigned to:
 a) $^3T_{1g}(F) \rightarrow ^3A_{2g}(P)$ c) $^3T_{1g}(F) \rightarrow ^3T_{2g}(F)$
 b) $^3T_{1g}(F) \rightarrow ^3T_{1g}(P)$ d) $^3T_{2g}(F) \rightarrow ^3A_{2g}(P)$
- Q.16. Intensity of magnetization may be given as:
 a) Pole strength/Area c) Magnetic flux density
 b) Magnetic moment/Volume d) Volume susceptibility
- Q.17. Total magnetic induction (B) may be given as:
 a) $B = H + 4\pi I$ b) $B = H - 4\pi I$ c) $B = H/4\pi I$ d) $B = H \div 4\pi I$
- Q.18. The spin only magnetic moment for Ni^{2+} is:
 a) 3.87 B.M. b) 1.73 B.M. c) 2.84 B.M. d) 4.47 B.M.
- Q.19. Which of the following statements is true about Neel Temperature?
 a) Above this temperature, the substance shows simple paramagnetism
 b) Above this temperature, the substance follows Curie or Curie-Weiss law
 c) Both of the above statements are correct
 d) None of the above statements are correct
- Q.20. For $[Fe(phen)_2(NCS)_2]$,
 a) moments are aligned in parallel and antiparallel directions
 b) shows permanent magnetism even after the magnetic field is removed
 c) materials are weakly repelled by magnetic fields
 d) there are four unpaired electrons at high temperatures and the low spin dominates at low temperatures
- Q.21. Which of the following statements are correct about Diborane and Ethane?
 a) Both are dimers
 b) BH_3 is an electron deficient compound, while $-CH_3$ is a free radical
 c) Both are first members of their respective homologous series
 d) Both undergo reactions with Lewis bases

- Q.22. Which of the following is a *nido*-Borane with one vertex missing?
 a) $B_6H_6^{2-}$ b) B_5H_{11} c) B_2H_6 d) B_5H_9
- Q.23. Carboranes are prepared from boranes with the following reagent:
 a) Acetylene b) Lithium Aluminum Hydride
 c) Borax d) KOH/MeOH
- Q.24. Which of the following is a *closo* six vertex polyhedron?
 a) $Os_5(CO)_{16}$ b) $Os_5C(CO)_{15}$ c) $Fe_2(CO)_9$ d) $Rh_6(CO)_{16}$
- Q.25. The order of CO bond strengths in the following metal hexacarbonyls is likely to be:
 a) $V(CO)_6^- < Cr(CO)_6 < Mn(CO)_6^+$
 b) $Cr(CO)_6 < Mn(CO)_6^+ < V(CO)_6^-$
 c) $Mn(CO)_6^+ < Cr(CO)_6 < V(CO)_6^-$
 d) $V(CO)_6^- < Mn(CO)_6^+ < Cr(CO)_6$
- Q.26. Which of the following is the correct bonding mode of CO in $Rh_6(CO)_6$?
 a) Free CO^+ b) μ^2 c) μ^3 d) Terminal M-CO
- Q.27. The correct bond orders for NO^+ , NO and NO^- are:
 a) 2; 2.5; 3 b) 3; 2.5; 2 c) 3; 2; 2.5 d) 2.5; 3; 2
- Q.28. The bond length of $[Ru(NH_3)_5(N_2)]^{2+}$ shows Ru-N is shorter than that of Ru-NH₃. This is due to
 a) Bridging three-centre 2 electron bonds
 b) Side on bridging bonding mode
 c) Back bonding between filled *d*-orbital and empty π^* antibonding MO of N₂
 d) End-on-bridging bonding mode
- Q.29. The end-on-terminal bonding mode in Oxygen complexes is _____ due to _____
 a) Bent; presence of lone pairs
 b) Linear; presence of double bond
 c) Bridging; presence of vacant sites
 d) Bridging; electron deficiency
- Q.30. The cone angles of PH_3 ; $P(OCH_3)_3$; $P(C_6H_5)_3$ in degrees are:
 a) 87; 107; 145 b) 145; 107; 87 c) 107; 87; 145 d) 87; 145; 107

PART – B (DESCRIPTIVE TYPE)

Q.1. Answer any FIVE questions.

(5×2 = 10)

- a) Draw a neatly labeled M.O. diagram for low spin $[Co(NH_3)_6]^{3+}$ ion.
- b) Write a short note on Nephelauxetic effect.
- c) The ground state terms for p^2 configuration are 3P , 1D and 1S . Using Hund's rules, arrange these terms in the order of increasing energy. Also explain Russel-Saunders coupling for triplet terms.
- d) Explain Faraday's method to measure magnetic susceptibility.
- e) Give any four bonding modes of Metal-Oxygen complexes.
- f) Explain the relationship between HB and HC; H_2C^- and H_2N with clear diagrams.

Q.2. Answer any THREE questions.

(3×4 = 12)

- a) Derive the geometry of $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$. Also explain whether they are paramagnetic or diamagnetic and why.
- b) Explain orbital contribution regarding magnetic moment of the substance under different conditions of J states.
- c) Describe structure and Total Electron Count (TEC) of B_6H_{10} and B_5H_9 .
- d) Discuss back bonding with diagrams for Carbonyl, Dinitrogen, Dioxygen and Tertiary Phosphine metal complexes.
- e) With the help of Wade's rules, calculate the no. of skeletal electron pairs and predict the structure for $\text{Rh}_6(\text{CO})_{16}$ and $\text{Os}_5\text{C}(\text{CO})_{15}$.

Q.3. Answer any ONE question.

(8×1 = 8)

- a) Give the classification of Metal Carbonyls based on
 - i) Ligands
 - ii) Number of Metal Atoms and structure of Metal CarbonylsExplain the various ways IR Spectroscopy can be used as a tool to study structure and bonding in metal carbonyls.
- b)
 - i) Give the various factors that affect the magnitude of Δ_{Oct} .
 - ii) The magnetic moment of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is 5.92 B.M. and that of $[\text{Fe}(\text{CN})_6]^{3-}$ is 1.73 B.M. Explain on the basis of C.F. Theory.
 - iii) Why do tetrahedral complexes give much more intense *d-d* spectra than octahedral complexes?
 - iv) Explain why in tetrahedral complexes, the *g* subscript has been dropped from orbital notation.

M. Sc. (CHEMISTRY) - 2nd SEMESTER (Re-Appeal)
INORGANIC CHEMISTRY-II, 09040201
END TERM THEORY EXAMINATION

TIME: 03:00 Hrs.

Max. Marks: 80

Instructions:-

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3. Attempt **five** questions in all. **Q. No.1** is compulsory. Attempt four other questions, selecting one question from each unit. All questions carry equal marks.

Q1.

(8×2 = 16)

- a) Distinguish between double salts and coordination compounds.
- b) Briefly explain spin state cross over phenomenon.
- c) Why NO^+ is considered to be three electron donor and NO^- is one electron donor?
- d) Arrange the following in accordance with decreasing Carbonyl stretching frequency ($\nu_{\text{C-O}}$) in cm^{-1} , $\text{Ni}(\text{CO})_4$, $[\text{Co}(\text{CO})_4]^-$ and $[\text{Fe}(\text{CO})_4]^{2-}$.
- e) What are closo- and nido-carboranes?
- f) How do you differentiate between terminal and bent nitrosyl group in metal nitrosyl complexes?
- g) Derive term symbols for p^4 and p^6 configuration.
- h) Write a short note on nephelauxetic series.

UNIT -I

Q.2.

- a) Discuss the orbital, spectral and geometry consequences of Jahn-Teller distortion. **(6)**
- b) With the help of MO diagrams, explain how π -donor and π -acceptor ligands affect crystal field stabilization energy (CFSE)? **(6)**
- c) Show the charge transfer MLCT transitions in ML_6 octahedral complex. **(4)**

OR

Q.3.

- a) Draw and explain MO energy level diagram for square planar complexes. **(8)**
- b) The electronic absorption band for $[\text{Ni}(\text{en})_3]^{2+}$ occur at higher frequencies corresponding to the band for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. **(4)**
- c) MnO_4^- is intensely colored. **(4)**

UNIT II

Q.4.

- a) What are Orgel diagrams? Draw and discuss a combined Orgel energy level diagram for $d^1(\text{O}_h)$ and $d^9(\text{O}_h)$. **(8)**
- b) Draw and explain the T.S. diagram for d^3 complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$. **(8)**

OR

Q.5.

- a) State and explain Laporte and spin selection rules. (4)
- b) Why do tetrahedral complexes of an element give much more intense $d-d$ spectra than its octahedral complexes? (4)
- c) Give the combined Orgel diagram for d^1 , d^4 , d^6 , d^9 octahedral complexes. (8)

UNIT -III

Q.6.

- a) How can we calculate the magnetic moment of the compound from its molar susceptibility? Calculate the magnetic moment in B.M. for Mn^{2+} and Cr^{3+} ion from spin-only formula. (6)
- b) Describe Gouy's method for determination of magnetic susceptibility. (4)
- c) Write short notes on: (6)
 - i. Temperature independent paramagnetism
 - ii. Diamagnetic correction
 - iii. Curie Point

OR

Q.7.

- a) Explain the structure and bonding of i) B_6H_{10} and ii) B_9H_{15} . (4)
- b) Give the preparation of *ortho*, *meta*, *para*-carboranes and draw the structure of 1,2-dicarbido-closo-dodecarborane. (8)
- c) Explain the relationship between (4)
 - i) $Fe(CO)_3$ and $Co(CO)_3$
 - ii) HB and HC

UNIT IV

Q.8.

- a) Draw and discuss the structure of the following metal carbonyls: (6)
 - i) $Co_2(CO)_8$
 - ii) $Rh_6(CO)_{16}$
- b) How can we differentiate between terminal and bridging carbonyl groups in metal carbonyls? (4)
- c) Describe the methods of preparation and uses of dinitrogen complexes. (6)

OR

Q.9.

- a) Explain the important reactions of transition metal carbonyls. (4)
- b) Discuss the bonding in metal nitrosyls in detail. (8)
- c) What are the various types of tertiary phosphine complexes? Give their methods of preparation and reaction. (4)

Roll No. _____

M.Sc. Chemistry-2nd Sem
Physical Chemistry -II (09040202)
END TERM THEORY EXAMINATION

Time: 3:00 Hrs

Max. Marks: 60

Instructions:

1. Write Roll No. on the Question Paper.
2. Candidate should ensure that they have been provided with correct question paper. Complaint(s) in this regard, if any, should be made within 15 minutes of the commencement of the exam. No complaint in this regard will be entertained thereafter.
3. Parts of a question should be attempted in sequential order. Marks are indicated against each question.
4. Draw diagram wherever required.

PART –A (OBJECTIVE TYPE QUESTIONS OMR SHEETS)

- Q. 1. For a particle in a 3-D box, the potential energy is
- a) Zero within the box and infinite outside the box
 - b) Zero within the box and finite outside the box
 - c) Infinite within the box and zero outside the box
 - d) Zero within the box and zero outside the box
- Q. 2. The degeneracy of a particle of mass 'm' in a 3-D box of width 'a' having energy $12h^2/8ma^2$ is
- a) Zero
 - b) Infinite
 - c) One
 - d) Six
- Q. 3. Zero point energy of a simple harmonic oscillator is
- a) Zero
 - b) $h\nu/2$
 - c) $h\nu$
 - d) $h\nu/4$
- Q. 4. The energy of a diatomic molecule rotating about an axis perpendicular to the internuclear axis and passing through the center of gravity of the molecule is
- a) $E = (J+1)h^2/8\pi^2$
 - b) $E = J(J+2)h^2/8\pi^2$
 - c) $E = J(J+1)h^2/8\pi^2$
 - d) $E = J(J+1)h^2/8\pi^2 I$
- Q. 5. The values $n = 2, l = 1$ and $m = 0, \pm 1$ corresponds to
- a) 2p orbital
 - b) 2s orbital
 - c) 2d orbital
 - d) 1s orbital
- Q. 6. Total number of radial node for 3s orbital is
- a) Three
 - b) One
 - c) Two
 - d) Zero
- Q. 7. For an orbital $l = 2$ then this orbital will be
- a) p-orbital and $m = 0, \pm 1, \pm 2$
 - b) d-orbital and $m = 0, \pm 1, \pm 2$
 - c) f-orbital and $m = 0, \pm 1, \pm 2$
 - d) d-orbital and $m = 0, \pm 2$
- Q. 8. The correct mathematical expression for the first law of thermodynamics is
- a) $dE = dq + dw$
 - b) $dE = dq + dS$
 - c) $dE = dH + dw$
 - d) $dE = dG + dV$

- Q. 19.** The correct expression of Stokes-Einstein equation is
 a) $D = RT/f$ b) $D = KT/f$ c) $D = KT$ d) $D = K/f$
- Q. 20.** The equation $f = 6\pi\eta r v$ is known as
 a) Stoke law b) Hook law c) Walden law d) Nernst law
- Q. 21.** "It is impossible to convert heat into work without compensation" the statement is true for
 a) 1st law of thermodynamics b) 2nd law of thermodynamics
 c) 3rd law of thermodynamics d) Nernst heat theorem
- Q. 22.** The normalized wave function for P_y orbital is
 a) $(3/4\pi)^{1/2}(y/z)$ b) $(3/8\pi)^{1/2}(x/y)$
 c) $(3/4\pi)^{1/2}(y/r)$ d) $(3/4\pi)^{1/2}(y/x)$
- Q. 23.** The penetrating power of 3s, 3p and 3d electrons follow the order
 a) $3s > 3p > 3d$ b) $3s > 3p < 3d$ c) $3s < 3p > 3d$ d) $3s < 3p < 3d$
- Q. 24.** The time-dependent form of Schrodinger equation is
 a) $H\psi_{total} = V_{total} + E_{total}\psi_{total}$ b) $H\psi_{total} = V\psi_{total} + E_{total}\psi_{total}$
 c) $E\psi_{total} = V_{total}\psi_{total}$ d) $H\psi_{total} = E_{total}\psi_{total}$
- Q. 25.** For an irreversible process
 a) $\Delta S_{sys} + \Delta S_{surr} = 0$ b) $\Delta S_{sys} + \Delta S_{surr} < 0$
 c) $\Delta S_{sys} + \Delta S_{surr} \geq 0$ d) $\Delta S_{sys} + \Delta S_{surr} \leq 0$
- Q. 26.** Nuclear explosion is an example of
 a) Stationary chain reaction b) Non-stationary chain reaction
 c) Equilibrium reaction d) Propagation reaction
- Q. 27.** The correct expression of Michaelis-Menton equation is
 a) $r = V_{max}[S] / (K_m + [S])$ b) $r = V_{max}[S][E]_0 / (K_m + [S])$
 c) $r = V_{max}[S] / K_2[S][E]_0$ d) $r = K_2[S][E]_0 / (K_m + [S])$
- Q. 28.** For d-orbitals
 a) $l = 2$ and $m = 0, \pm 1, \pm 2$ b) $l = 2$ and $m = 0, \pm 2$
 c) $l = 1$ and $m = 0, \pm 1$ d) $l = 0$ and $m = 0, \pm 1, \pm 2$
- Q. 29.** If no force acts on a rigid rotator then the potential energy of the rigid rotator can be set as
 a) Unity b) Zero c) Infinite d) fraction
- Q. 30.** The energy level of a particle of mass 'm' in a 3-D box of width 'a' is triply degenerate, the energy of the particle in that level is
 a) $12h^2/6ma^2$ b) $9h^2/4ma^2$ c) $3h^2/8ma^2$ d) $9h^2/8ma^2$

PART - B (DESCRIPTIVE TYPE)

Attempt any SIX questions

(6 x 5 = 30)

- Q.1. Discuss the solution of Schrodinger wave equation for a particle in a 3-D cubic box with edges of length a assuming that the potential is zero inside the box and infinite outside the box. What is meant by degeneracy of energy levels?
- Q.2. Explain the determination of shape of p-orbitals. Why the s-orbitals are symmetrically spherical in shape?
- Q.3. Derive the expression for the entropy change accompanying variation of (i) temperature and volume (ii) temperature and pressure.
- Q.4. What is phase rule? Draw and explain the phase diagram of a mixture of two component system having eutectic point.
- Q.5. What are the stationary and non-stationary chain reactions? Derive the overall rate expression for thermal decomposition of acetaldehyde.
- Q.6. Using steady state approximation for [ES], derive the Michaelis-Menten equation for an enzyme catalyzed reaction. Discuss the various cases.
- Q.7. What is ionic drift velocity? Derive the Stokes-Einstein equation for the diffusion coefficient.
- Q.8. Explain the Onsager phenomenological equation.

*****ETE*****

M. Sc. CHEMISTRY-2ND SEMESTER (RE.)
PHYSICAL CHEMISTRY-II - 0904202
END TERM THEORY EXAMINATION

Time: 3:00 Hrs

Max. Marks: 80

Instructions:

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3. Attempt 5 Questions in all. Q. No. 1 is compulsory. Students are required to attempt other **FOUR** questions selecting one from each unit. Marks are indicated against each question.
4. Draw diagram wherever required.

- Q.1.** Answer the following Questions. (2x8=16)
- a) What are the congruent and in-congruent points of a phase diagram?
 - b) The zero point energy of a simple harmonic oscillator can not be zero. Explain.
 - c) Explain the radial distribution function.
 - d) 2s atomic orbital is spherical. Why?
 - e) Explain Nearest heat theorem.
 - f) What is the physical significance of fugacity?
 - g) Explain the Walden's rule.
 - h) Write the Schrodinger wave equation for a particle in a 3-D cubic box and for the hydrogen atom.

UNIT-I

- Q.2.** Explain the concept of degeneracy among energy levels for a particle in 3-D box. (16)
- Q.3.** Set up the Schrodinger wave equation for a simple harmonic oscillator and solve it by polynomial method. (16)

UNIT-II

- Q.4.** What is phase rule? Explain the each term involve in phase rule equation with suitable examples. Discuss the phase diagram of system having eutectic point. (16)
- Q.5.** Explain the concept of fugacity. How the fugacity of a gas can be determined? (16)

UNIT-III

- Q.6.** Define branching and non-branching chain reactions. Derive the overall rate expression for the reaction between hydrogen and bromine. (16)
- Q.7.** Using steady state approximation for [ES], derive the Michaelis-Menten equation and explain the various cases with the help of a suitable diagram. (16)

UNIT-IV

- Q.8.** What is ionic mobility? Derive Stokes-Einstein equation. (16)
- Q.9.** What is Onsager phenomenological equation, explain in detail. (16)

M. Sc (CHEMISTRY) – 2nd SEMESTER
ORGANIC CHEMISTRY-II - 9040203
END TERM THEORY EXAMINATION

Time: 03:00 Hrs

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PART – A (OBJECTIVE TYPE QUESTIONS OMR SHEETS)

- Q.1. Which of them act as Phase Transfer Catalysts? (1)
 a) Quarternary Ammonium salts b) Crown ethers
 c) Both a & b d) None of them
- Q.2. Which one of them can act as an ambident nucleophile. (1)
 a) Br b) Cl c) CN⁻ d) OCH₃⁻
- Q.3. Rate law expression for S_N2 reaction is: (1)
 a) rate = k[substrate] b) k[substrate][nucleophile]
 c) both a & b d) None
- Q.4. Which of the following is concerted process (1)
 a) S_N1 b) S_N2 c) Both S_N1 & S_N2 d) None
- Q.5. Reaction of alkyl Halides in S_N2 reactions follows the order:- (1)
 a) R-Br > R-Cl > R-F > R-I b) R-F > R-Cl > R-Br > R-I
 c) R-I > R-Cl > R-Br > R-F d) R-I > R-Br > R-Cl > R-F
- Q.6. Treatment of 2- Bromopropanoic acid with dil. alkali results in a substitution product with complete retention of configuration due to:- (1)
 a) NGP by pair of electrons on carboxylate anion
 b) Due to S_N1 reaction
 c) Due to S_N2 reaction
 d) None of the above
- Q.7. Carbocations in which positive charge is delocalized by resonance involving an unshared pair of electrons or a double bond in the allylic position are referred as non-classical carbocations. This statements is:- (1)
 a) True
 b) False
 c) May be True or False depending on conditions
 d) None of them
- Q.8. S_N2 reactin proceeds with:- (1)
 a) Complete retention of configuration b) Inversion of configuration
 c) Racemization d) None

- Q.9. Which of the following is hydride donor reagent:- (1)
 a) LiAlH_4 b) NaBH_4 c) Both a & b d) None
- Q.10. LiAlH_4 reduces esters the (1)
 a) Aldehydes b) Ketones c) Alcohols d) None
- Q.11. Benzoin condensation is a dimerization of two aromatic aldehydes under the catalytic influence of (1)
 a) K^+ b) CN^+ c) KCN d) $\text{C}_2\text{H}_5\text{OH}/\text{HOH}$
- Q.12. Cinnamic Acid can be synthesized by (1)
 a) Perkin condensation b) Aldol condensation
 c) Knoevenagel condensation d) Both (i) & (iii)
- Q.13. Metal hydride reduction of nitriles leads to the formation of (1)
 a) Amides b) Amines c) Oximes d) Alcohols
- Q.14. Benzaldehyde cannot act as reactant in (1)
 a) Perkin condensation b) Knoevenagel condensation
 c) Aldol condensation d) Benzoin condensation
- Q.15. Which of the following reactions can be used for the formation of C-C-N bond in organic synthesis (1)
 a) Aldol condensation b) Mannich reaction c) Micheal addition d) Wittig reaction
- Q.16. Reaction intermediate of *E1* reaction is (1)
 a) carbocation b) carbanion c) carbene d) cyclic transition state
- Q.17. Which among the following undergoes nitration most easily (1)
 a) Benzene b) Acetanilide c) Acetophenone d) Chlorobenzene
- Q.18. Which of the following ylides will be most stable and least reactive for nucleophilic addition reaction with aldehydes or ketones? (1)
 a) $\text{C}_6\text{H}_5\text{P}^+\text{CH}_2^-$ b) $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}^-\text{CH}_3$
 c) $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}^-\text{CH}_2\text{CH}_3$ d) $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}^-\text{COOC}_2\text{H}_5$
- Q.19. Stobbe condensation is given by (1)
 a) $\text{CH}_2(\text{COOC}_2\text{H}_5)_2$ b) $(\text{CH}_2)_2(\text{CH}_2\text{COOC}_2\text{H}_5)_2$
 c) $(\text{CH}_2\text{COOC}_2\text{H}_5)_2$ d) $(\text{COOC}_2\text{H}_5)_2$
- Q.20. Consider the following statements : (1)
 i) In *E2* reaction of acyclic compounds both leaving groups should be anti-periplanar
 ii) In *E2* reaction of cyclohexane derivative both leaving groups should be present in axial positions
 iii) In *E1* reaction product formation takes place by Hofmann rule
 iv) In *E1* reaction product formation takes place by Saytzeff rule
 of these statements
 a) 1,2 & 3 are correct b) 1,2 & 4 are correct
 c) 1,2,3 & 4 are correct d) 1&2 are correct

- Q.21. In the given reaction :
 $\text{CH}_3\text{CHCH}_3\text{CHOHCH}_3 \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{Alkenes}$
 Number of alkenes formed will be: (1)
- a) one b) two c) three d) four
- Q.22. In which compound electrophilic addition takes place according to Anti-markovnikov rule? (1)
- a) $\text{CH}_2=\text{CH}-\text{NO}_2$ b) $\text{CH}_2=\text{CH}-\text{CHO}$ c) $\text{CH}_2=\text{CH}-\text{CN}$ d) $\text{CH}_3-\text{CH}=\text{CH}_2$
- Q.23. In the given reaction
 $\text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow{\text{Hg}(\text{OAc})_2/\text{HOH}} [\text{X}]$
 [X] will be (1)
- a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ b) $\text{CH}_3\underset{\text{OH}}{\text{CH}}\text{CH}_3$ c) $\text{CH}_3\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{HgOAc}$ d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{HgOAc}$
- Q.24. Which amongst the following will be most reactive in SEI reaction? (L= leaving group) (1)
- a) CH_3L b) ClCH_2L c) Cl_2CHL d) CCl_3L
- Q.25. In the following ions, which will be a better leaving group in aliphatic electrophilic substitutions? (1)
- a) t-Bu^+ b) I^- c) D^+ d) MeO^-
- Q.26. Which of the following is an electrofuge : (1)
- a) Cl^- b) H^-
 b) OH^- d) D^+
- Q.27. Vilsmeier-Haack reaction includes (1)
- a) Nitration of active aromatic compounds
 b) Acylation of active aromatic compounds
 c) Formylation of active aromatic compounds
 d) Sulphonation of active aromatic compounds
- Q.28. Which of the following is not a *meta*-directing group: (1)
- a) CN b) NO_2 c) CHO d) OH
- Q.29. Smiles rearrangement are : (1)
- a) Intermolecular electrophilic substitutions
 b) Intermolecular nucleophilic substitutions
 c) Intramolecular electrophilic substitutions
 d) Intramolecular nucleophilic substitutions
- Q.30. What is the electrophile in electrophilic substitution of acetyl chloride (CH_3COCl) and AlCl_3 reacting with benzene ? (1)
- a) Cl^+ b) AlCl_3 c) $\text{CH}_3\text{C}=\text{O}^+$ d) CO^+

PART – B (DESCRIPTIVE TYPE)

Short Answer Type Questions (Attempt any five questions):-

- Q.1. Write a short note on ambident nucleophiles. (2)
- Q.2. What is *ipso* attack? Explain giving suitable examples. (2)
- Q.3. What is anchimeric assistance. (2)
- Q.4. Write a short note on diazonium coupling. (2)
- Q.5. Discuss synthetic application & mechanism of Smiles rearrangement. (2)
- Q.6. Explain why *E2* reaction is more common than *E1* & *E1cB* reactions. (2)
- Q.7. What are pyrolytic eliminations? (2)

Attempt any three questions:

- Q.8. Discuss the orientation in elimination reactions with particular reference to Saytzeff & Hoffmann rules. (4)
- Q.9. What are Wittig reagents. How do they react with aldehydes and ketones. (4)
- Q.10. Predict the effect of substrate structure on reactivity in aliphatic nucleophilic substitution reactions. (4)
- Q.11. Write the mechanism of Hydroboration with suitable example. Discuss stereochemical aspects of Hydroboration also. (4)
- Q.12. Explain why aniline is more reactive than acetanilide in electrophilic substitutions? (4)

Attempt any one question:

- Q.13. What is Neighbouring group participation. Describe in detail NGP by σ and π bonds. (8)
- Q.14. Discuss the mechanism of following reactions with suitable examples : (4+4)
- (i) Perkin Condensation
- (ii) Mannich Reaction

M. Sc. CHEMISTRY 2nd SEMESTER (RE)
Organic Chemistry – II , 9040203
END TERM THEORY EXAMINATION

Time: 03:00 Hrs

Max. Marks: 80

Instructions:

1. Write Roll No. on the Question Paper.
2. Candidate should ensure that they have been provided with correct question paper. Complaint(s) in this regard, if any, should be made within 15 minutes of the commencement of the exam. No complaint in this regard will be entertained thereafter.
3. Attempt 5 Questions in all. Q. No. 1 is compulsory. Students are required to attempt other **FOUR** questions selecting one from each unit. Marks are indicated against each question.
4. Draw diagram wherever required.

Q.1. Answer the following Questions.**(2x8=16)**

- a) Write a short note on ambident nucleophiles?
- b) What is *ipso* attack?
- c) What is Gatterman-Koch reaction?
- d) Write a short note on non-classical carbocations?
- e) Which is the most common elimination reaction among E2, E1, E1cb and why?
- f) Explain Markovnikov's rule using suitable example?
- g) What is Mannich reaction? Write one equation of the reaction.
- h) What is Hofmann rule? Explain giving suitable example.

UNIT-I

- Q.2. (i) Write a detailed note on mechanism and stereochemistry of S_N1 reaction using suitable example. (8)**
- (ii) What is anchimeric assistance? How do you distinguish phenonium ion from non-classical carbocations? Discuss giving appropriate examples. (8)**

OR**Q.3. Write a detailed note on the effect of following on reactivity in substitution reactions:**

- | | |
|--------------------------------------|------------------------------|
| (i) Structure of alkyl group | (ii) Nature of solvent |
| (iii) Nature of nucleophilic reagent | (iv) Nature of leaving group |
- (16)**

UNIT-II

- Q.4. (i) Explain why Cl is deactivating still *-o, p* directing but NO_2 is deactivating but *meta* directing. (8)**
- (ii) Write a detailed note on ArS_N2 reaction giving evidences in favor of mechanism? (8)**

OR**Q.5. Write notes on:**

- (i) Von-Richter rearrangement
- (ii) Vilsmeier reaction
- (iii) Diazonium coupling

(6+6+4=16)

UNIT-III

- Q.6. (i) Acid catalysed dehydration of neopentyl alcohol yields 2-methyl-2-butene as the major product. Outline the mechanism showing all steps in its formation.
(ii) Give evidence to prove that E2 reactions are predominantly *anti*-eliminations and there is correlation between conformation and reactivity?
(iii) Write a detailed note on Pyrolytic *syn* elimination?

(5+6+5=16)

OR

- Q.7. (i) When 3,3-dimethyl-1-butene is treated with HBr, a rearrangement takes place. Which alkyl bromide would you expect from the reaction and why?
(ii) What will be major product of reaction of 2-methyl-2-butene with each of the following reagents?

- (a) HBr
(b) Hg(OAc)₂, H₂O followed by NaBH₄
(c) HBr + Peroxide
(d) BH₃/THF, followed by H₂O₂/hydroxide ion

- (iii) A hydrocarbon which has a molecular formula C₆H₁₂, was subjected to ozonolysis giving equimolar amounts of ethyl methyl ketone (CH₃CH₂COCH₃) and acetaldehyde (CH₃CHO). Assign structure to it giving suitable explanation.

(4+8+4=16)

UNIT-IV

- Q.8. (i) Write mechanism of the following reactions using suitable example:

(5+5=10)

- a) Knoevenagel reaction
b) Benzoin condensation

- (ii) What are Wittig reagents? Give mechanism of their reaction with carbonyl compounds? (6)

OR

- Q.9. (i) Discuss the mechanism of reactions involving transfer of hydride ion from a donor molecule to carbonyl carbon.
(ii) Comment on the mechanism of acidic and basic hydrolysis of esters?
(iii) Write the mechanism of addition of Grignard's reagent on carbonyl compounds. Write the products obtained from aldehydes and ketones giving suitable examples.

(4+8+4 = 16)

*****ETE MAY JUNE 2018*****

**M. SC. (CHEMISTRY) - 2ND SEMESTER
GENERAL SPECTROSCOPY - 9040207
END TERM THEORY EXAMINATION**

Time: 03:00 Hrs

Max. Marks: 60

Instructions:

1. Write Roll No. on the Question Paper.
2. Candidate should ensure that they have been provided with correct question paper. Complaint(s) in this regard, if any, should be made within 15 minutes of the commencement of the exam. No complaint in this regard will be entertained thereafter.
3. Marks are indicated against each question.
4. Draw diagram wherever required.

PART – A (OBJECTIVE TYPE QUESTIONS OMR SHEETS)

- Q.1.** The different type of energies associated with a molecule are (1)
a) Electronic energy b) Vibrational energy
c) Rotational energy d) All of the mentioned
- Q.2.** The correct order of different types of energies is (1)
a) $E_{el} \gg E_{vib} \gg E_{rot} \gg E_{tr}$ b) $E_{el} \gg E_{rot} \gg E_{vib} \gg E_{tr}$
c) $E_{el} \gg E_{vib} \gg E_{tr} \gg E_{rot}$ d) $E_{tr} \gg E_{vib} \gg E_{rot} \gg E_{el}$
- Q.3.** The region of electromagnetic spectrum for nuclear magnetic resonance is (1)
a) Microwave b) Radio frequency c) Infrared d) UV-rays
- Q.4.** Which of the following is an application of molecular spectroscopy (1)
a) Structural investigation
b) Basic of understanding color
c) Study of energetically excited reaction products
d) All of the mentioned
- Q.5.** Which of the following statement is correct (1)
a) Ultraviolet radiation has a longer wavelength than infrared radiation
b) Microwave radiation possesses more energy than infrared radiation
c) Infrared radiation has a shorter wavelength than visible light
d) Infrared radiation has a lower wavelength than visible light
- Q.6.** Which of the following wavelength ranges as associated with UV-spectroscopy (1)
a) 0.8-500 μm b) 400-100 nm c) 380-750 nm d) 380-750 μm
- Q.7.** The force constant for CO and CS are 1902 and 849 Nm^{-1} respectively. Which statement is incorrect? (1)
a) The wave number associated with the stretching of CO is higher than that of CS
b) Less energy is required to dissociate CS than CO
c) Stretching the bond in CO requires less energy than the stretching the bond in CS
d) The trend in the bond energies for the CO and CS follows the trend in force constant
- Q.8.** Which of the following transitions between rotational energy levels is not allowed? (1)
a) $J = 1$ to $J = 0$ b) $J = 3$ to $J = 1$ c) $J = 2$ to $J = 1$ d) $J = 3$ to $J = 2$

- Q.9. For which of the following molecules could a pure rotational spectrum not be observed in the gas phase (1)
 a) CO b) HCl c) N₂ d) NO
- Q.10. For a proton in a molecule, if σ is positive then (1)
 a) $B_{\text{observed}} = 0$ b) $B_{\text{observed}} < B_{\text{applied}}$ c) $B_{\text{observed}} > B_{\text{applied}}$ d) $B_{\text{applied}} = 0$
- Q.11. The chemical shift value in NMR spectrum is represented by (1)
 a) σ b) μ c) δ d) ϕ
- Q.12. Which of the following is the commonly used internal standard in NMR spectroscopy (1)
 a) TMS b) AIBN c) BINAP d) CH₃CN
- Q.13. The rotational energy of a diatomic molecule is (1)
 a) $E = J(J+1)h^2/8\pi^2I$ b) $E = (J+1)h^2/8\pi^2I$
 c) $E = J(J+1)Ih^2/8\pi^2$ d) $E = J(J+1)h^2$
- Q.14. In the expression of rotational energy of a diatomic molecule the "constant B" is (1)
 a) Vibrational quantum number b) Rotational quantum number
 c) Rotational constant d) Vibrational constant
- Q.15. In the rotational spectrum of molecule the spacing between any two nearest absorption signals is equal to (1)
 a) 3B b) B c) 6B d) 2B
- Q.16. A homonuclear diatomic molecule shows no change the dipole moment during the symmetrical stretching vibration, the molecule is (1)
 a) Raman active b) Infrared active c) Infrared inactive d) Rigid rotator
- Q.17. In the vibrational spectrum of anharmonic oscillator the transition from $v'' = 0$ to $v' = 1$ is known as (1)
 a) Fundamental absorption b) Hot band
 c) First overtone d) Second overtone
- Q.18. The selection rule for a rigid rotator is (1)
 a) $\Delta J = 0$ b) $\Delta J = \pm 1$ c) $\Delta V = \pm 1$ d) $\Delta J = \pm 2$
- Q.19. $\Delta J = \pm 1$ and $\Delta V = \pm 1, \pm 2$ etc is the selection rule for (1)
 a) NMR spectra b) IR spectra
 c) Vibrational spectra d) Vibrational-Rotational spectra
- Q.20. A diatomic molecule will be microwave active if it has (1)
 a) Permanent dipole moment b) Zero dipole moment
 c) Negative dipole moment d) Dipole moment < 0
- Q.21. The transition between states will be allowed if (1)
 a) $\Delta S = -1$ b) $\Delta S = \pm 1$ c) $\Delta S = 0$ d) $\Delta S = +1$
- Q.22. According to Laporte's selection rule (1)
 a) d-d transition is allowed b) p-d transition is allowed
 c) s-d transition is allowed d) f-f transition is allowed
- Q.23. Ground state term for low spin d^5 configuration will be (1)
 a) ²S b) ⁴I c) ²F d) ²I

- Q.24. 6S is a ground state term for the complex having (1)
 a) d^2 configuration b) d^7 configuration c) d^5 configuration d) d^4 configuration
- Q.25. For an octahedral Co^{2+} complex the spin allowed d-d transition will be (1)
 a) ${}^4T_{1g}(F)$ to ${}^4T_{2g}(F)$ b) ${}^2T_{1g}(F)$ to ${}^4T_{1g}(F)$
 c) ${}^4T_{2g}(F)$ to ${}^4T_2(F)$ d) ${}^4T_{1g}(F)$ to ${}^4T_{2g}(P)$
- Q.26. Out of the following which relationship is correct (1)
 a) $J_{cis} > J_{trans}$ b) $J_{cis} < J_{trans}$ c) $J_{cis} = 0$ d) $J_{trans} = 0$
- Q.27. The number of nmr signals in the 1H NMR spectrum of acetone will be (1)
 a) 7 b) 5 c) 2 d) 1
- Q.28. Among the following which can not be used as solvent for the record of 1H NMR spectrum of a compound (1)
 a) $CDCl_3$ b) DMSO c) CH_3CN d) CD_3CN
- Q.29. Total nmr signals in the 1H NMR spectrum of CH_3CHBr_2 will be (1)
 a) 6 b) 4 c) 2 d) 8
- Q.30. The ground state term for $[Ni(H_2O)_6]^{2+}$ complex is (1)
 a) 2F b) 3F c) 4F d) 0F

PART – B (DESCRIPTIVE TYPE)

Short answer type questions (attempt any 5)

(5x3= 15)

- Q.1. What are the Hund's rules for the determination of ground state term of a complex?
- Q.2. What is the selection rule for the rotational transitions of a diatomic rigid rotator? Mention the essential condition for a molecule to be microwave active.
- Q.3. What are the shielding and deshielding effects in the proton nmr spectra?
- Q.4. What is the Laporte selection rule for the electronic transitions?
- Q.5. Write a short note on double resonance technique.
- Q.6. Explain, what do you understand by fundamental absorption, overtone transition and hot-bands?
- Q.7. An aromatic compound (Molecular mass = 135) gives the following signals in its PMR spectrum (i) a singlet for 3H at δ 2.09; (ii) a distorted singlet for 1H at δ 3.09; (iii) a multiplet for 3H at δ 7.27; (iv) a multiplet for 2H at δ 7.75. Predict the structure of the compound.

Long answer type questions (attempt any 3)

(3x5 = 15)

- Q.1. Draw and explain the Orgel diagram of $[V(H_2O)_6]^{3+}$.
- Q.2. Derive the energy expression in terms of wave number for a diatomic rigid rotator. Write down the energy difference expression for the two nearest rotational energy levels.
- Q.3. A compound having molecular formula $C_9H_{11}Br$ showed the following signals in the PMR data. (i) a multiplet for 2H at δ 2.25; (ii) a triplet for 2H at δ 2.75; (iii) a triplet for 2H at δ 3.38; (iv) a singlet for 5H at δ 7.22. Assign the structure of the compound giving reasons.
- Q.4. Discuss the Frank-Condon principle with the help of systematic electronic spectra.
- Q.5. Draw a typical vibrational-rotation spectrum of a diatomic molecule with proper labeling of its P, Q and R branches.

M. Sc (Chemistry) 2nd Semester (RE)
General Spectroscopy - 9040207
END TERM THEORY EXAMINATION

Time: 03:00 Hrs

Max. Marks: 80

Instructions:

1. Write Roll No. on the Question Paper.
2. Candidate should ensure that they have been provided with correct question paper. Complaint(s) in this regard, if any, should be made within 15 minutes of the commencement of the exam. No complaint in this regard will be entertained thereafter.
3. Attempt 5 Questions in all. Q. No. 1 is compulsory. Students are required to attempt other FOUR questions selecting one from each unit. Marks are indicated against each question.
4. Draw diagram wherever required.

- Q.1.** Answer the following Questions. (2×8 = 16)
- a) Explain electromagnetic radiation with the help of a diagram.
 - b) Explain the impact of polar solvents on
 - i) $n \rightarrow \pi^*$
 - ii) $\pi \rightarrow \pi^*$
 - c) Name the types of bending vibrations.
 - d) Which of the following diatomic molecules do not absorb in the infrared region?
HCl, ClBr, N₂, H₂, O₂
 - e) Calculate the chemical shift in ppm (δ) for a proton that has resonance 126 Hz downfield from TMS on spectrophotometer that operates at 60 MHz.
 - f) Why is TMS used as a reference standard in NMR spectroscopy?
 - g) Write a short note on spectrochemical series.
 - h) Write Mulliken notations for S, P, D and F energy terms in an octahedral field.

UNIT-I

- Q.2.** Discuss the spectrum of a non rigid rotor. What is the effect of isotopic substitution on rotational spectra of linear molecules? (12 + 4 = 16)

OR

- Q.3.** What is Frank Condon Principle? Explain the intensity of a vibrational electronic band and dissociation energy. (7 + 5 + 4 = 16)

UNIT-II

- Q.4.** (a) The complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ shows a single absorption band at $20,300\text{cm}^{-1}$. Calculate Δ (crystal field energy).
 (b) What will be the term symbol for ground state configuration of d^3 .
 (c) Draw Orgel diagram for d^2 configuration in octahedral complexes. (6 + 4 + 6 = 16)

OR

- Q.5.** (a) How do Hund's rules help to arrange the different spectroscopic terms in order of their increasing energies? How does it help to find the term in ground state?
 (b) Draw a combined Orgel diagram for d^1 , d^4 , d^6 and d^9 complexes. (8 + 8 = 16)

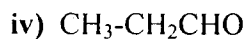
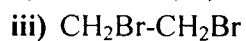
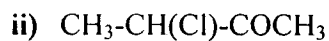
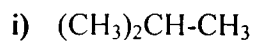
UNIT-III

Q.6. (a) Explain how induced currents affect shielding in protons of ethylene, acetylene and benzene with diagrams.

(b) What is spin-spin coupling? What is meant by (n + 1) rule in spin-spin coupling? (8 + 8 = 16)

OR

Q.7. (a) Sketch the expected PMR spectra of the following compounds taking TMS as the standard reference.



(8)

(b) Explain at least four applications of UV spectroscopy.

(8)