R0084	Sub. Code
	536101

M.Sc. DEGREE EXAMINATION, NOVEMBER – 2023

First Semester

Chemistry

INORGANIC CHEMISTRY – I

(CBCS – 2022 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A $(10 \times 1 = 10)$

Answer **all** the following objective questions by choosing the correct options.

1. According to VSEPR theory, the molecule having ideal tetrahedral shape is (CO1, K1)

   (a) SF_4 (b) SO_4^{2-}

   (c) S_2Cl_2 (d) SO_2Cl_2

2. Select the correct order of ionic radii. (CO1, K1)

   (a) $O^{2-} > S^{2-} > Se^{2-} > Te^{2-}$

   (b) $Te^{2-} > S^{2-} > O^{2-} > Se^{2-}$

   (c) $O^{2-} > Te^{2-} > S^{2-} > Se^{2-}$

   (d) $Te^{2-} > Se^{2-} > S^{2-} > O^{2-}$

3. The compound which exhibit John-Teller distortion is (CO2, K1)

   (a) $[Mn(H_2O)_6]^{2+}$ (b) $[Mn(H2O)_6]^{3+}$

   (c) $[Cr\ (H_2O)_6]^{3+}$ (d) $[Fe(CN)6]^{4-}$

4. The crystal field stabilization energy (CFSE) of complex $[CoF_3(H_2O)_3]$ (CO2, K1)

   (a) $0\Delta_o$ (b) $0.4\Delta_o$

   (c) $0.8\Delta_o$ (d) $1.8\Delta_o$

5. Stabilization of highest oxidation states of transition metals by strong electronegative ligands due to (CO3, K1)

(a) $d\pi(L) \rightarrow d\pi(M)$ bonding

(b) $p\pi\ (L) \rightarrow d\pi\ (M)$ bonding

(c) $d\pi\ (L) \rightarrow p\pi\ (M)$ bonding

(d) $d\pi\ (M) \rightarrow d\pi\ (L)$ bonding

6. Considering σ-bonding only in the MO diagram of metal complex with Trigonal Bipyramidal (TBP) geometry the d-orbital which remain non-bonding are (CO3, K2)

(a) d_{z^2} and d_{xy} (b) d_{xy} and d_{yz}

(c) $d_{x^2-y^2}$ and d_{xy} (d) d_{z^2} and d_{yz}

7. Co-ordination number in simple cubic crystal structure (CO4, K2)

(a) 1 (b) 3

(c) 2 (d) 4

8. The ratio between the number of closed packed atoms and the number of tetrahedral hole in cubic close packing (CO4, K1)

(a) 1 : 1 (b) 2 : 1

(c) 1 : 3 (d) 1 : 2

9. The lanthanide ion that exhibit colour in aqueous solution is (CO5, K1)

(a) Eu(III) (b) La(III)

(c) Gd(III) (d) Lu(III)

10. The pair in which both actinide shows +3 oxidation state only is (CO5, K1)

(a) Ac and Lr (b) Ac and No

(c) Cm and Bk (d) Cm and Lr

Part B (5 × 5 = 25)

Answer **all** the questions not more than 500 words each.

11. (a) Explain the concept of hybridization with reference to sp^3 and sp^3d. Give examples. (CO1, K2)

Or

(b) On the basis of HSAB principle explain why HgS is insoluble and $Hg(OH)_3$ is soluble in dil.HCl. (CO1, K2)

12. (a) How does the d-orbital splitting change on octahedral become square planar complex. Explain. (CO2, K3)

Or

(b) Explain John-Teller theorem and discuss how it is helpful to deal with distortion on Cu(II) complex. (CO2, K3)

13. (a) Explain the effect of π-bonding and change the value of Δ_0 with examples. (CO3, K3)

Or

(b) Draw MO diagram of $[Pt(NH_3)_4]^{2+}$ ion. (CO3, K3)

14. (a) Calculate the limiting radius ratio (r^+/r^-) for tetrahedral coordination of a cations in an ionic lattice (CO4, K3)

Or

(b) Explain the crystal structure of cesium chloride. (CO4, K3)

15. (a) What is lanthanide contractions? Give any two its consequences. (CO5, K2)

Or

(b) Write the difference between lanthanides and actinides. (CO5, K2)

Part C (5 × 8 = 40)

Answer **all** the questions not more than 1000 words each.

16. (a) Using the following data, calculate enthalpy of formation of CaF(s) and explain its stability. Estimated lattice energy of CaF(s) = –745 $KJmol^{-1}$; enthalpy of atomization Ca(s) = 201 KJmol'; 1st ionization energy of Ca(g) = 590 $KJmol^{-1}$; enthalpy of atomization of F(g) = 79 $KJmol^{-1}$; electron affinity of F(g) = –335$KJmol^{-1}$; enthalpy of $CaF_2(s)$ = –1243 $KJmol^{-1}$. (CO1, K3)

Or

(b) Write on account of MO theory apply to hetero-nuclear diatomic molecules of NO and find the bond order. (CO1, K3)

17. (a) Explain the postulates of VB theory. Discuss the geometry of $[Co(NHs)_6]^{3-}$ complex. (CO2, K3)

Or

(b) What are factors on which affect the magnitude of crystal field stabilization energy (CFSE). (CO2, K3)

18. (a) Discuss the salient features of MO theory. (CO3, K4)

Or

(b) Draw and discuss the MO diagram for $[Co(CN)_6]^{3-}$ without it-bonding . (CO3, K4)

19. (a) Explain fluoride types of structure with examples. (CO4, K4)

Or

(b) Based on their crystal structure give an comparative account of the properties of diamond and graphite. (CO4, K4)

20. (a) Explain the principles behind the separation of lanthanide by ion-exchange method. (CO5, K3)

Or

(b) Evaluate colour and spectral behavior of actinides. (CO5, K3)

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R0085	Sub. Code 536102

M.Sc. DEGREE EXAMINATION, NOVEMBER – 2023

First Semester

Chemistry

ORGANIC CHEMISTRY – I

(CBCS – 2022 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A (10 × 1 = 10)

Answer **all** the following objective questions by choosing correct option.

1. The order of decreasing strength of acid is (CO1, K4)

   (a) $HCl > NH_4^+ > H_3O^+ > H_2O$

   (b) $HCl > H_3O^+ > NH_4^+ > H_2O$

   (c) $H_3O^+ > NH_4^+ > HCl > H_2O$

   (d) $H_2O > H_3O^+ > NH_4^+ > HCl$

2. What is the correct structure of Spiro [2,4]-hept-1-ene (CO1, K2)

   (a)  (b) 

   (c)  (d) 

3. The decreasing order of stability of carbanion is (CO2, K4)

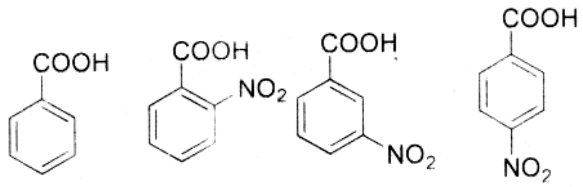
(a) Benzyl>Diphenylmethyl>Triphenylmethyl

(b) Diphenylmethyl> Benzyl>Triphenylmethyl

(c) Triphenylmethyl>Diphenylmethyl>Benzyl

(d) Triphenylmethyl> Benzyl>Diphenylmethyl

4. The correct order of acidity among the following compound I-IV is (CO2, K4)



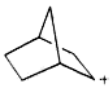
I II III IV

(a) II>III>IV>I (b) IV>II>III>I

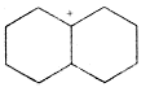
(c) II>IV>III>I (d) IV>III>II>I

5. Which of the following carbocation violates Bredt's rules? (CO3, K1)

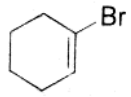
(a) 

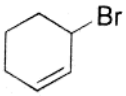
(b) 

(c) 

(d) 

6. Which is the final main product of the following reaction of trans-1,2-dibromocyclohexane is (CO3, K4)

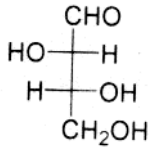
(a) 

(b) 

(c) 

(d) 

7. Predict the R/S configuration of the given compound is (CO4, K4)



(a) 2S,3R

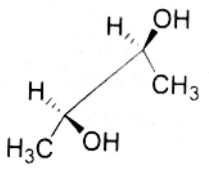
(b) 2R,3S

(c) 2R,3R

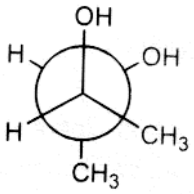
(d) 2S,3S

R0085

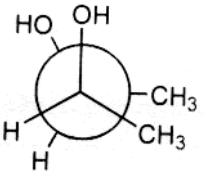
8. Chose the correct Newman projection formula of the given compound from Sawhorse (CO4, K3)



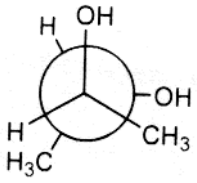
(a)



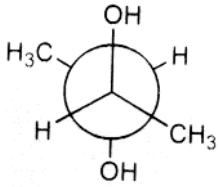
(b)



(c)



(d)



9. Which of the following conformations of butane has the lowest energy? (CO5, K4)

(a) Anti (b) Gauche
(c) Eclipsed (d) Staggered

10. In hydroxylation of alkenes under Prevost conditions the product is formed in the form of (CO5, K2)

(a) Erytho (b) Racemic
(c) Thero (d) meso

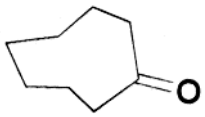
Part B (5 × 5 = 25)

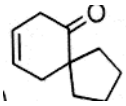
Answer **all** the questions not exceeding more than 500 words each.

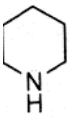
11. (a) Write difference between No bonding resonance and Mesomeric effect. (CO1, K1)

Or

(b) Give the IUPAC name of the following compounds (CO1, K1)

(i) 

(ii) 

(iii) 

(iv) 

12. (a) Explain Curtin-Hammett principle. (CO2, K3)

Or

(b) Illustrate potential energy diagrams and types of reactions. (CO2, K2)

13. (a) Examine stereo chemical path ways are possible in $S_N{}^2$ reaction. (CO3, K4)

Or

(b) Comparison between Hoffmann and Saytzeff rules with examples. (CO3, K4)

14. (a) Explain detail about Cram's rule. (CO4, K2)

Or

(b) Write a note on Erythro and Threo isomers with examples. (CO4, K2)

15. (a) Demonstrate the conformation and relative stability of Butane. (CO5, K3)

Or

(b) How to open epoxide in cyclohexyl system in Furst Plattner rule. (CO5, K3)

Part C $(5 \times 8 = 40)$

Answer **all** the questions not more than 1000 words each.

16. (a) Comment the aromatic nature of following annuenes (CO1, K1)

(i) [14] annulene

(ii) [8] annulene

(iii) [16] annulene (3+3+2)

Or

(b) State that Huckel's $(4n+2)$ e^- rules to explain the aromatic character of organic compounds. How will you explain the aromatic characters of pyrrole and thiophene. (CO1, K1)

17. (a) List out primary kinetic isotope effect and secondary isotope effect. (CO2, K3)

Or

(b) Distinguish kinetic controlled and thermodynamically controlled chemical reactions. (CO2, K3)

18. (a) Justify stereochemistry of E_2 reaction. (CO3, K2)

Or

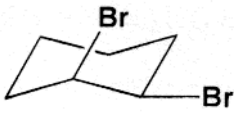
(b) Explain the following reaction mechanisms (CO3, K2)

(i) Friedel crafts acylation

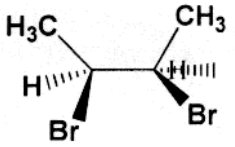
(ii) Diazonium coupling

19. (a) Write R and S nomenclature using Cahn-Ingold-Prelog rules for following compounds (CO4, K4)

(i)



(ii)



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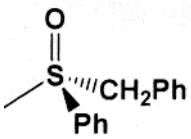
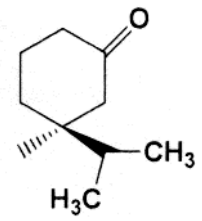


(iv)



Or

(b) Comment on the number of possible stereoisomers of 2,3-dibromobutane and 2,3-dihydroxybutneodioic acid (CO4, K4)

20. (a) Explain the conformation analysis of cyclohexane (CO5, K3)

Or

(b) Neighboring group participation by Woodward and provost method. (CO5, K3)

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R0086	Sub. Code 536103

M.Sc. DEGREE EXAMINATION, NOVEMBER – 2023

First Semester

Chemistry

PHYSICAL CHEMISTRY – I

(CBCS – 2022 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A $(10 \times 1 = 10)$

Answer **all** the following objective questions by choosing the correct options.

1. If Ae^{-3x} is an elgen function of the operator d^2/dx^2, its eigen value is (CO1, K1)

   (a) 3 (b) 6

   (c) –6 (d) 9

2. The energy of Bohr orbit is given by (CO1, K2)

   (a) $E_n = -13.6\frac{Z^2}{n^2}eV$

   (b) $E_n = -13.6\frac{Z^2}{n}eV$

   (c) $E_n = -13.6\frac{Z}{n^2}eV$

   (d) $E_n = -13.6\frac{n^2}{Z^2}eV$

3. The trace or character σ_{xy} is (CO2, K2)

(a) 3 (b) –3

(c) 1 (d) –1

4. The point group of BCl_3 is (CO2, K2)

(a) C_{3v} (b) C_{3h}

(c) D_{3h} (d) D_{3d}

5. From the Erying equation, the plot of ln (k/T) versus 1/T will give a straight line. From the slope of the straight line, ———————— can be calculated. (CO3, K1)

(a) Entropy of the reaction

(b) Enthalpy of the reaction

(c) Entropy of activation

(d) Enthalpy of activation

6. The unit of zeroth order reaction is given by (CO3, K2)

(a) s^{-1}

(b) Mol L^{-1} s^{-1}

(c) L Mol^{-1} s^{-1}

(d) No unit

7. If the temperature of the source in increased, the efficiency of the Carnot engine (CO4, K1)

(a) Increases

(b) Decreases

(c) Remains constant

(d) Becomes zero

8. Which is true for the entropy of a spontaneous reaction? (CO4, K1)

(a) $\Delta S(\text{system}) - \Delta S(\text{surroundings}) > 0$

(b) $AS(\text{system}) + \Delta S(\text{surroundings}) > 0$

(c) $\Delta S(\text{surroundings}) > 0$ only

(d) $\Delta S(\text{system}) > 0$ only

9. Spin inversion takes place in which of the following process (CO5, K1)

(a) Photosensitization

(b) Internal conversion

(c) Fluorescence

(d) Phosphorescence

10. Which of the following electronic transition require less energy? (CO5, K1)

(a) π to π^* (b) σ to σ^*

(c) σ to π^* (d) n to σ^*

Part B $(5 \times 5 = 25)$

Answer **all** the questions not more than 500 words each.

11. (a) Explain black body radiation and photoelectric effect. (CO1, K3)

Or

(b) State and explain the postulates of quantum mechanics. (CO1, K3)

12. (a) Write the group multiplication table for water molecule and prove that water belongs to abelian group. (CO1, K3)

Or

(b) (i) Explain improper axis of rotation using an example. (CO2, K3)

(ii) Predict the point group of the following.

- Inorganic benzene
- Cis ML_4X_2
- CO_2

13. (a) Explain the effect of added salt on the rates of ionic reactions in solution. (CO3, K3)

Or

(b) Show that the energy of activation calculated by collision theory is less than that calculated by Arrhenius equation. (CO3, K3)

14. (a) Derive Gibbs-Helmholtz equation. (CO4, K2)

Or

(b) Obtain Maxwell's relation of thermodynamic variables. (CO4, K2)

15. (a) Explain the Marcus theory of electron transfer reactions. (CO5, K2)

Or

(b) (i) Define quantum yield. (CO5, K2)

(ii) Discuss any one mechanism for photon up conversion.

Part C (5 × 8 = 40)

Answer **all** the questions not more than 1000 words each.

16. (a) (i) Explain the emission line spectrum of H-atom with neat sketch. (5)

(ii) What is the wavelength of an electron moving at 5.31×10^6 m/sec? Given: mass of electron = 9.11×10^{-31} kg; h = 6.626×10^{-34} Js. (3)

(CO1, K2)

Or

(b) Derive the energy of hydrogen atom using Bohr's theory. (CO1, K2)

17. (a) Using GOT, construct the character table of C_{3v} point group. (CO2, K3)

Or

(b) (i) Prove that $S_n^n = E$ (When n is even) and $S =_n^{2n} = E$ (When n is odd). (4)

(ii) List out the symmetry elements present in XeF_4. (2)

(iii) Using matrix multiplication, prove that $S_2 = I$. (2)

(CO2, K3)

18. (a) Explain Lindemann-Hinshelwood mechanism of unimolecular reactions. (CO3, K2)

Or

(b) Derive the expressions for the concentrations of A, B and C at time't' for the simplest consecutive reaction, $A \rightarrow B \rightarrow C$. (CO3, K2)

19. (a) With the help of Carnot cycle. Show that $w = q_2 (T_2 - T_1)/T_2$. (CO4, K3)

Or

(b) Discuss Einstein and Debye models of a vibrating solids. (CO4, K3)

20. (a) Discuss the principle, materials, construction and efficiency of solar energy conversion using dye sensitized solar cells. (CO5, K2)

Or

(b) Explain the mechanism of various photophysical processes using Jablonski Diagram. (CO5, K2)

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R0087	Sub. Code
	536052

M.Sc. DEGREE EXAMINATION, NOVEMBER – 2023

First Semester

Chemistry

Elective : INSTRUMENTAL METHODS OF ANALYSIS

(CBCS – 2022 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A $(10 \times 1 = 10)$

Answer **all** the following objective questions by choosing the correct option.

1. In which chromatograph, stationary phase held in a narrow tube and mobile phase is forced through it under pressure? (CO1, K1)

   (a) Paper (b) column

   (c) gas (d) liquid

2. In TLC, stationary phase is made of ———————— and mobile phase is made of ————————. (CO2, K1)

   (a) Solid, liquid (b) Liquid, liquid

   (c) Liquid, gas (d) Solid, gas

3. While using an instrument for some measurement if we place it in wrong manner, then the error will be (CO2, K3)

   (a) Instrument error (b) Systematic error

   (c) Environment error (d) Random error

4. The difference between the indicated value and true value of a quantity is (CO3, K3)

(a) Gross error (b) absolute error

(c) dynamic error (d) relative error

5. The pair of light source and atomizer resulting highest sensitivity in AAS measurement is (CO3, K2)

(a) Hg lamp, nitric oxide flame

(b) Hg lamp, graphite furnace

(c) Hallow cathode lamp, graphite furnace

(d) Hallow cathode lamp, acetylene-nitric oxide flame

6. A mass spectrometer separates ions based on which of the following factors? (CO3, K2)

(a) Mass (b) Charge

(c) Molecular weight (d) Mass to charge ratio

7. Which of the following techniques is used to study the contour of proteins (CO4, K4)

(a) SEM (b) TEM

(c) AFM (d) confocal microscope

8. Electron microscope can give magnification upto (CO4, K4)

(a) 40X (b) 4000X

(c) 40000X (d) 4,00,000X

9. Monitoring the current at an electrolytic electrochemical cell that is generated at a fixed voltage and is proportional to the concentration of analyte present in the test sample in solution is referred to as (CO5, K5)

(a) Voltammetry (b) Potentiometry

(c) Amperometry (d) Colulometry

10. Which transducers is the most comprehensive and mostly used by research group in biosensing analysis? (CO5, K5)

(a) Voltammetric (b) Conductive

(c) Potentiometric (d) Volumetric

Part B ($5 \times 5 = 25$)

Answer **all** the following questions not more than 500 words each.

11. (a) Write the principle of GC-MS. (CO1, K1)

Or

(b) Write the mechanism of ion exchange chromatography. (CO1, K1)

12. (a) How will you minimize errors? (CO2, K2)

Or

(b) Compare linear regression and correlation coefficient. (CO2, K1)

13. (a) Write the principles of atomic fluorescence spectroscopy. (CO3, K2)

Or

(b) Write the applications of atomic mass spectroscopy. (CO3, K1)

14. (a) Write the principles of DSC. (CO4, K2)

Or

(b) Write the applications of thermo mechanic analysis. (CO4, K1)

15. (a) Compare anodic and cathodic stripping voltammetry. (CO5, K2)

Or

(b) Compare voltammetry and potentiometry. (CO5, K2)

Part C (5 × 8 = 40)

Answer **all** the following questions not more than 1000 words each.

16. (a) Discuss the theory and applications of thin layer chromatography. (CO1, K1)

Or

(b) Discuss the theory and applications of LC-MS. (CO1, K1)

17. (a) Compare mean and standard deviation. (CO2, K2)

Or

(b) Analyze the student t-test and comparison of results. (CO2, K2)

18. (a) Compare AAS and AES. (CO3, K1)

Or

(b) Discuss the principles and applications of flame photometry. (CO3, K1)

19. (a) Compare TGA and DTA. (CO4, K2)

Or

(b) Differentiate between AFM and TEM. (CO4, K1)

20. (a) Discuss the principles and applications of electrogravimetry. (CO5, K2)

Or

(b) Discuss the biological applications of electrochemical sensors. (CO5, K1)

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R0088	Sub. Code 536301

M.Sc. DEGREE EXAMINATION, NOVEMBER – 2023

Third Semester

Chemistry

ADVANCED INORGANIC CHEMISTRY

(CBCS – 2022 onwards)

Time : 3 Hours Maximum : 75 Marks

Section A (10 × 1 = 10)

Answer **all** the following objective questions by choosing the correct option

1. The correct statement for a Fischer carbine complex is (CO1, K1)

   (a) The carbine carbon is electrophilic in nature

   (b) Metal exists in high oxidation state

   (c) Metal fragment and carbine are in the triplet states

   (d) Co-ligands destabilize the complex

2. The correct order of energy level of d-orbitals in ferrocene is (CO1, K1)

   (a) $d_{x}^{2}{}_{-y,}^{2}d_{xy} < d_{z}^{2} < d_{xy,}d_{y}^{2}$

   (b) $d_{z}^{2} < d_{x,y,}d_{yz} < d_{x}^{2}{}_{-y}^{2},d_{xy}$

   (c) $d_{x}^{2}{}_{-y,}^{2}d_{xy} < d_{xz,}d_{yz} < d_{z}{}^{2}$

   (d) $d_{xz,}d_{yz} < d_{x}{}^{2}y^{2},d_{xy} < d_{z}{}^{2}$

3. Which of the following is not suitable catalyst for hydroformylation. (CO2, K1)

(a) $HCo(CO)_4$ (b) $HCo(CO)_4PBu_3$

(c) $HRh(CO)(PPh_3)_3$ (d) $H_2Rh(PPh_3)_2Cl$

4. Reductive - elimination is reverse of reaction. (CO2, K1)

(a) Insertion (b) Nucleophilic

(c) Electrophilic (d) Oxidative-addition

5. Spectroscopic ground state term symbols of $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2+}$ respectively. (CO3, K2)

(a) ^2T_1g and $^4A_1$ (b) ^2T_2g and $^4T_1$

(c) ^2T_3g and $^4T_1$ (d) $^2T_1$ and $^4A_1$

6. The energy separation of spectroscopic terms are expressed as (CO3, K2)

(a) Nephelauxetic ratio

(b) Racha parameter

(c) Δ_o

(d) v

7. In biological system, the metal ion involved in electron transport are (CO4, K2)

(a) Na^+ and K^+ (b) Zn^{2+} and Mg^{2+}

(c) Ca^{2+} and Mg^{2+} (d) Cu^{2+} and Fe^{2+}

8. In photosynthesis, predominant metal present in the reaction center of photosystem II is (CO4, K2)

(a) Zn (b) Cu

(c) Mn (d) Fe

9. In oxyhaemoglobin the iron center best described by which of the following? (CO5, K1)

(a) High spin Fe(II) (b) High spin Fe(III)

(c) Low spin Fe(III) (d) Low spin Fe(II)

10. Carboxypeptidase contains (CO5, K1)

(a) Zn(II) and hydrolysis CO_2

(b) Mg(II) and hydrolysis CO_2

(c) Zn(II) and hydrolysis peptide bond

(d) Mg(II) and hydrolysis peptide bond

Part B ($5 \times 5 = 25$)

Answer **all** the questions not more than 500 words each.

11. (a) What are the Schrock type carbene? Give two example. How Fischer type carbene differ from Schrock carbene? (CO1, K2)

Or

(b) Treatment of $Cr(CO)_6$ with $LiCH_3$ followed by $[(CH_3)_3O]BF_4$, give the carbene complex $(OC)_5Cr=C(OCH_3)CH_3$, propose a mechanism for this synthesis. (CO1, K2)

12. (a) Draw the catalytic cycle for the Ziegler-Natta polymerization of propene, Comment about the polymer that are formed. (CO2, K3)

Or

(b) Explain hydroformylation reaction with suitable example. (CO2, K3)

13. (a) The three absorption band for $[CrF_6]^{3-}$ are observed in an electronic spectrum at 14900 cm^{-1} and 22700 cm^{-1} and 34400 cm^{-1}. Determine the value of B^1 and Δ_o. (CO3, K4)

Or

(b) Ferromagnetic material are more magnetic than paramagnetic material. Analyze it. (CO3, K4)

14. (a) Mention the use of Gd(III) complexes as MRI contrast agents. (CO4, K3)

Or

(b) Trans-platin has no anticancer activity, though cis-platin is a promising anticancer drug. Explain. (CO4, K3)

15. (a) Illustrate the structure and functions of haemoglobin. (CO5, K2)

Or

(b) Classify copper protein in terms of structural features. (CO5, K2)

Part C (5 × 8 = 40)

Answer **all** the questions not more than 1000 words each.

16. (a) Write down the structure of ferrocene and explain the nature of bonding in it. (CO1, K3)

Or

(b) Distinguish ring closing and ring opening metathesis reaction. (CO1, K3)

17. (a) Examine the fluxionality in cyclic polyene complexes. (CO2, K4)

Or

(b) Analyze the following reaction mechanism with suitable catalyst $C_2H_4 + 1/2\ O_2 \rightarrow CH_3CHO$. (CO2, K4)

18. (a) Write d-orbital configuration and use Tannabe-Sugano diagram for d^2 and d^8 octahedral complex. (CO3, K3)

Or

(b) Explain the following (i) Nephelauxetic effect (ii) Spin cross over. (CO3, K3)

19. (a) What is mean by active transport in Na/K pump? Give a diagrammatic representation of the process and explain the mechanism involved in it. (CO4, K4)

Or

(b) Give the light phase and dark phase reaction in photosynthesis. (CO4, K4)

20. (a) Comment the structure and activity of carboxypeptidase A. (CO5, K4)

Or

(b) Outline the probable mechanism pathway for nitrogenase activity in N_2-fixation. (CO5, K4)

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R0089	Sub. Code
	536302

M.Sc. DEGREE EXAMINATION, NOVEMBER – 2023

Third Semester

Chemistry

ADVANCED ORGANIC CHEMISTRY

(CBCS – 2022 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A $(10 \times 1 = 10)$

Answer **all** the following objective questions by choosing the correct option.

1. An oxidation of benzyl alcohol in the presence of manganese dioxide to give ————————. (CO1, K3)

   (a) Benzoic acid (b) Toluene

   (c) Benzene (d) Benzaldehyde

2. Compound X on reaction with O_3 followed by Zn/H_2O gives formaldehyde and 2-methyl propanal as products. The compound X is (CO1, K2)

   (a) 3-methylbut-1-ene (b) 2-methylbut-1-ene

   (c) 3-methylbut-2-ene (d) 2-methylbut-2-ene

3. Olefin hydrogenation using Wilkinson's catalyse initiates with (CO2, K1)

   (a) Olefin addition to Rh(PPh3)3Cl

   (b) Olefin addition to Rh(PPh3)2Cl

   (c) A phosphine dissociation from Rh(PPh3)3Cl

   (d) A phosphine addition to Rh (PP3)2Cl

4. Why is sodium borohydride an important reagent in reducing a ketone? (CO2, K2)

(a) It is good for hydrolysis type reactions

(b) It can cat as a free radical initiator

(c) It is a good source of the hydride ion

(d) It can act as a base

5. Nef oxidation is used to oxidize (CO3, K3)

(a) Primary and Sec. Nitro compounds

(b) Primary and Sec. alcohols

(c) Cleavage of tertiary alcohols

(d) Terminal alkenes

6. Robinson annulation is (CO3, K3)

(a) Aldol followed by Michael

(b) Michael followed by Aldol

(c) Aldol followed by Mannich

(d) Mannich followed by Aldol

7. Which of the following is not true about the five membered ring? (CO4, K2)

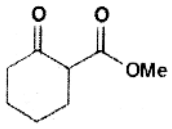
(a) Five membered rings are more stable than four membered ring

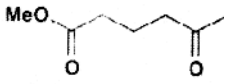
(b) Five membered rings are more stable than six memebred ring

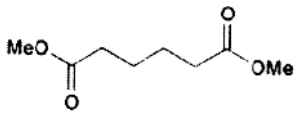
(c) Five membered rings are more stable than seven membered ring

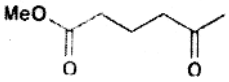
(d) Five membered rings are more stable than eight membered ring

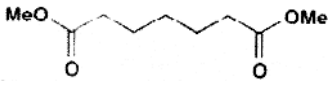
8. Which compound can be used for the synthesis of the following in a cyclization reaction? (CO4, K2)



(a) 

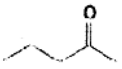
(b) 

(c) 

(d) 

9. Which of the following (to be converted by functional group interconversion, FGI) is not a good alternative target for the synthesis of pentan-2-ol? (CO5, K2)

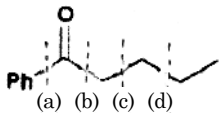
(a) 

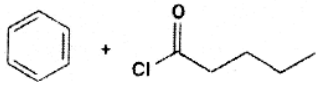
(b) 

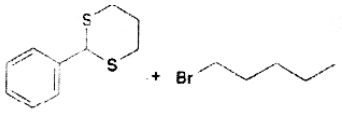
(c) 

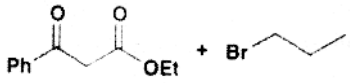
(d) 

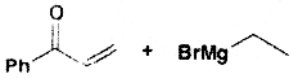
10. Which combination of reagents is wrong for disconnections (a)-(d) in the following? (CO5, K3)



(a) 

(b) 

(c) 

(d) 

R0089

Part B (5 × 5 = 25)

Answer **all** the questions not more than 500 words each.

11. (a) What is Sharpless asymmetric epoxidation? Give me the synthesis and mechanism. (CO1, K4)

Or

(b) Write the hydroboration-oxidation of alkenes. (CO1, K4)

12. (a) Why Wilkinson catalyst is called homogeneous? Explain. (CO2, K4)

Or

(b) Which functional group is reduced by adding the reagent $NaBH_4$? Explain with suitable example. (CO2, K3)

13. (a) Write short note on Baylis-Hillman reaction. (CO3, K4)

Or

(b) Give any five organic synthesis of solid state reaction. (CO3, K2)

14. (a) Write the reaction and mechanism of the Bergman cyclization. (CO4, K3)

Or

(b) Write the different approaches towards the synthesis of three member rings. (CO4, K4)

15. (a) What do you mean by retrosynthesis? Explain with suitable example. (CO5, K4)

Or

(b) Discuss the importance in the protective agents in the organic reactions. (CO5, K5)

Part C (5 × 8 = 40)

Answer **all** the questions not more than 1000 words each.

16. (a) Discuss briefly Sharpless asymmetric dihydroxylation with suitable mechanism. (CO1, K5)

Or

(b) Discuss briefly Woodward Prevost reaction and mechanism. (CO1, K5)

17. (a) Write suitable reaction and mechanism of (CO2, K3)

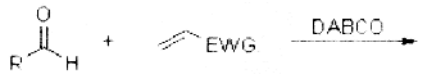
(i) Birch reduction;

(ii) McMurry reaction.

Or

(b) How do you prepare Corey-Bakshi-Shibata reagent? Give any five uses of organic synthesis in the CBS reagent. (CO2, K1)

18. (a) Write the product with suitable mechanism of the following reaction: (CO3, K2)



Or

(b) Write the principle, synthesis and applications of phase transfer catalysis in modern organic synthesis. (CO3, K2)

19. (a) Write the different approaches towards the synthesis of six membered rings. (CO4, K3)

Or

(b) What is Nazarov cyclization? Give the example with mechanism. (CO4, K1)

20. (a) Why synthons are idealized reagents? Explain with suitable example. (CO5, K2)

Or

(b) Suggest the retrosynthetic analysis and total synthesis of the ascorbic acid. (CO5, K3)

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R0090	Sub. Code
	536303

M.Sc. DEGREE EXAMINATION, NOVEMBER – 2023

Third Semester

Chemistry

ADVANCED PHYSICAL CHEMISTRY

(CBCS – 2022 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A $(10 \times 1 = 10)$

Answer **all** the following objective questions by choosing the correct option.

1. For the d^3 electronic configuration, the ground state term symbol is (CO1, K2)

   (a) $^4F_{1/2}$ (b) $^4F_{3/2}$

   (c) $4F_{7/2}$ (d) $^4F_{9/2}$

2. The energy of antibonding π-molecular orbital by Huckel approximation for ethylene is given by : (CO1, K2)

   (a) A (b) β

   (c) $\alpha + \beta$ (d) $\alpha - \beta$

3. The selection rule of the translational energy levels in the Raman spectrum ΔJ is equal to (CO2, K1)

   (a) ± 1 (b) ± 2

   (c) +1 (d) +2

4. The spectroscopic method used to distinguish the binding modes of M-SCN and M-NCS is (CO2, K1)

(a) NMR (b) Mass

(c) IR (d) NQR

5. The non-polarizable electrodes, the exchange current density values are (CO3, K1)

(a) High (b) Low

(c) Zero (d) Either high or low

6. The emf of the concentration cell with transference is 0.028 V and the emf of the cell without transference is 0.017 V. The liquid junction potential is (CO3, K3)

(a) 0.028 V (b) 0.017 V

(c) 0.045 V (d) 0.011 V

7. The zero point energy of vibrational partition function is expressed as (CO4, K2)

(a) $E_{vib} = 0$ (b) $E_{vib} = 2h\nu$

(c) $E_{vib} = h\nu / 2$ (d) $E_{vib} = 3 / 2\, h\nu$

8. The total number of microstates for 6 identical particles with their occupation numbers $\{1, 2, 3\}$ in three states is (CO4, K3)

(a) 6 (b) 12

(c) 720 (d) 70

9. A crystalline plane has the intercepts $3a, 6b, \infty c$ at X, Y and Z axis, respectively. The Miller indices of the plane is (CO5, K2)

(a) (2 1 0) (b) (3 6 0)

(c) (1 2 0) (d) (2 0 1)

10. Iron belongs to BCC lattice. The Miller indices of the second allowed reflection in the powder diffraction patter of iron would be (CO5, K2)

(a) (1 0 0) (b) (1 1 1)

(c) (2 0 0) (d) (2 1 0)

Part B $(5 \times 5 = 25)$

Answer **all** the questions not more than 500 words each.

11. (a) State the Pauli exclusion principle for electrons and illustrate its use when applied to He atom in its ground state as an example using Slater Determinants. (CO1, K3)

Or

(b) Explain the principle of spin-orbit coupling. (CO1, K3)

12. (a) Describe the importance of asymmetry parameter and quadrupole coupling constant in NQR spectroscopy. (CO2, K2)

Or

(b) Explain the classical theory of Raman effect. (CO2, K2)

13. (a) Describe the construction and working principle of calomel electrode. (CO3, K2)

Or

(b) How is the differential capacitance of the electric double layer determined using the Gouy-Chapman diffuse-charge model? (CO3, K2)

14. (a) Compare the three statistical distributions. (CO4, K4)

Or

(b) Explain the collision theory of reaction rate and compare it with Arrhenius equation. (CO4, K4)

15. (a) State Bragg's law and derive Bragg's equation. (CO5, K3)

Or

(b) Explain the working principle of light emitting diodes with an example. (CO5, K3)

Part C ($5 \times 8 = 40$)

Answer **all** the questions not more than 1000 words each.

16. (a) Write down the secular determinant obtained on applying Huckel's method to *allyl radical*. Obtain the expressions for the energy levels and the wave functions. (CO1, K5)

Or

(b) Discuss the Molecular Orbital treatment of H_2 molecule and explain how the Valance Bond (Heitler-London) method makes up for what MO theory lacks. (CO1, K5)

17. (a) (i) Explain the appearance of P and R branches in the spectrum of a diatomic vibrating rotor. (6)

(ii) State mutual exclusion principle. (2)
(CO2, K4)

Or

(b) Discuss the rotational spectrum of diatomic molecule and derive the rotational energy of it. (CO2, K4)

18. (a) Derive the Butler-Volmer equation for a one electron electrode reaction and explain the low and high field approximations. (CO3, K3)

Or

(b) Explain the salient features of the Stern model of electrified interface. (CO3, K3)

19. (a) Explain the postulates of Maxwell-Boltzmann distribution and derive an expression for most probable distribution. (CO4, K3)

Or

(b) Explain activated complex theory of reaction rates. (CO4, K3)

20. (a) (i) How are primitive, face-centered and body-centered cubic crystals characterized using XRD? (4)

(ii) Explain the properties of covalent solids with examples. (4)

(CO5, K3)

Or

(b) Explain the optical and electrical properties of solids in detail. (CO5, K3)

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R0091	Sub. Code
	536053

M.Sc. DEGREE EXAMINATION, NOVEMBER – 2023

Third Semester

Chemistry

Elective : SPECTROSCOPIC METHODS OF ANALYSIS

(CBCS – 2022 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A $(10 \times 1 = 10)$

Answer **all** the following objective questions by choosing the correct option.

1. Identify the microwave inactive molecule (CO2, K2)

   (a) CS (b) HF

   (c) CO_2 (d) HCl

2. Calculate the λ_{max} for 3,4-dimethylpent-3-en-2-one (CO2, K2)

   (a) 237 nm (b) 300 nm

   (c) 239 nm (d) 249 nm

3. The number of allowed transitions for a nucleus with spin 3/2 is (CO2, K2)

   (a) 0 (b) 6

   (c) 2 (d) 3

4. Number of signals in the ^{13}CNMR spectrum of (R)-4-methylpenta-2-ol are (CO1, K2)

   (a) 3 (b) 6

   (c) 5 (d) 4

5. Pulse sequence of COSY is (CO1, K4)

(a) $90x - t_1 - 90x - t_2$

(b) $180x - t_1 - 90x - t_2$

(c) $1800x - t_1 - 180x - t_2$

(d) $90x - t_1 - 180x - t_2$

6. Total number of fine and hyperfine EPR lines expected for octohedral high-spin Mn (II) complexes are respectively (I = 5/2) (CO3, K4)

(a) 5 and 30 (b) 3 and 30

(c) 4 and 24 (d) 3 and 33

7. EI mass spectrum of $CH_3(CH_2)_2CN$ will show a base peak at m/z value of (CO3, K4)

(a) 54 (b) 70

(c) 26 (d) 41

8. Mossbauer and NQR spectra are observed in (CO1, K4)

(a) Liquid state (b) Solid state

(c) Gaseous state (d) Liquid crystalline state

9. In the IR spectrum of p-nitrophenyl acetate, the carbonyl absorption band appears at (CO2, K5)

(a) 1730 cm^{-1} (b) 1670 cm^{-1}

(c) 1700 cm^{-1} (d) 1760 cm^{-1}

10. What is the ^{13}C resonance frequency on a 600 MHz NMR spectrometer? (CO3, K4)

(a) 600 MHz (b) 92 MHz

(c) 60 MHz (d) 150 MHz

Part B $(5 \times 5 = 25)$

Answer **all** the questions not more than 500 words each.

11. (a) How will you distinguish cis stillbene from trans stillbene with the aid of UV-Vis spectroscopy? (CO3, K2)

Or

(b) Discuss the factors that affect the position and intensity of absorption spectrum. (CO1, K2)

12. (a) What is double resonance technique? How it is useful in simplifying the NMR spectra? (CO2, K2)

Or

(b) Write a note on ^{19}F NMR spectroscopy. (CO1, K2)

13. (a) Discuss the J-resolved 2-D spectrum. (CO1, K4)

Or

(b) Highlight the applications of ESR on the Mn and Cu complexes. (CO1, K4)

14. (a) Explain the different types of ionization techniques in mass spectroscopy. (CO1, K4)

Or

(b) Comment on the applications of Mossbauer spectroscopy of iron compounds. (CO2, K4)

15. (a) Sketch all the modes of vibration of CO_2 and H_2O molecule and predict which of the modes are Raman active. (CO3, K4)

Or

(b) Deduce the structure of organic compound with molecular weight 150 which shows the following spectral data :

$UV: \lambda_{max}\ 276nm; IR: 3030 - 2979, 1695, 1692cm^{-1}$

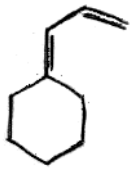
$^1H\ NMR: 2.1(s,3H),\ 3.85(s,3H),\ 7.2(d,2H)$ and $7,65(d,2H)$ (CO3, K5)

Part C $(5 \times 8 = 40)$

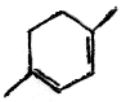
Answer **all** the questions not more than 1000 words each.

16. (a) Following the Woodward Fieser rules, calculate the absorption maximum for each of the following compounds (CO5, K2)

(i) 

(ii) 

(iii) 

(iv) 

Or

(b) (i) The IR absorption spectrum of HCN shows three absorption bands at 3312. 2089, and 712 cm^{-1} Deduce From this whether HCN is linear or bent. Assign the absorption band values.

(ii) Outline the principle of resonance Raman spectroscopy. (CO2, K2)

17. (a) Discuss the origin and significance of the following parameters in NMR spectroscopy : (CO1, K2)

(i) Coupling constant

(ii) NOE

Or

(b) Give a brief note on geminal, vicinal and long range coupling in NMR spectroscopy. (CO1, K2)

18. (a) Using the pulse sequence, describe the INEPT experiments. (CO2, K4)

Or

(b) Discuss the fine structure of ESR spectrum of a triplet state molecule with two unpaired electrons. (CO3, K4)

19. (a) (i) Explain Mc Lafferty rearrangement with an example. (4)

(ii) Discuss the fragmentation pattern of alcohols. (4)

(CO1, K4)

Or

(b) What is the principle of Mossbauer spectroscopy? How does it detect oxidation state? (CO2, K4)

20. (a) The following data was obtained for a pure sample of an unknown organic compound: (CO5, K5)

Combustion analysis : C: 85.7%. H: 6.67%

MS Molecular ion at m/z = 210

^{1}H-NMR : 7.5-7.0, 10 H,m; 5.10, 1 H,S : 2.22, 3H, S ^{13}C-NMR: 206.2 (C) 128.7 (CH) 30.0. (CH_3) 138.4 (C) 127.2 (CH) 129.0 (CH) 65.0 (CH) IR : 1720 cm^{-1} , strong.

Or

(b) (i) How will you differentiate between the following compounds by IR spectroscopy?

Benzylamine and N,N-dimethylacetamide

Propanal and 2-propenal

o-hydroxybenzoic acid and *p*-hydroxybenzoic acid (CO5, K4)

(ii) Sketch off-resonance decoupled and proton decoupled ^{13}C spectra of 4-methyl acetophenone. (CO5, K5)

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