**M. Sc. Examination, 2025**
**Semester-II**
**Chemistry**
**Course: MCH-21-I (Inorganic Chemistry)**

**Time: Three Hours** **Full Marks: 40**

Questions are of value as indicated in the margin.
Answer any *four* questions

1. (a) $[Cr(OH_2)_6]^{3+}$ reacts through the $I_a$-path in the ligand substitution process while $[Cr(NH_3)_5(OH_2)]^{3+}$ reacts through the $I_d$-path –explain.
(b) For the solvent exchange process, $\Delta V^{\neq}$ is positive for $[Mn(DMF)_6]^{2+}$ while it is negative for $[Mn(OH_2)_6]^{2+}$—explain.
(c) $[Co^{III}Cl(en)_2(L)]^{n+} + H_2O \rightarrow [Co^{III}(OH_2)(en)_2(L)]^{(n+1)+} + Cl^-$. In the above reaction (L = $\pi$-donor ligands), the *cis*-complex reacts faster than the *trans*-complex (i.e. $k_{cis} >> k_{trans}$): The cis-complex leads to 100% retention of stereochemistry while the *trans*-complex leads to *cis-trans* isomerisation. Explain.

(3+3+4)=10

2. (a) Compare and explain the relative rates of acid hydrolysis and base hydrolysis of $[M(NH_3)_5X]^{2+}$ (M = Co and Cr; $X^-$ = $Cl^-$, $Br^-$, $NCS^-$).

$$[M(NH_3)_5X]^{2+} \xrightarrow{hydrolysis} [M(NH_3)_5(OH_2)]^{3+} \text{ (acid hydrolysis product)}$$
$$[M(NH_3)_5(OH)]^{2+} \text{ (base hydrolysis product)}$$

(b) Draw the geometrical isomers of $[CoCl(NH_3)(tren)]^{2+}$ and give their relative rates of base hydrolysis (without any explanation)..
(c) Discuss the role of distal histidine in hemoglobin/myoglobin in reducing the CO toxicity.
(d) Draw (only) the $O_2$-binding curves of hemoglobin (Hb) and myoglobin (Mb).

(4+2+3+1)=10

3. (a) Write down the Hill equations for Mb—$O_2$ and Hb—$O_2$ interactions. Illustrate cooperativity and non-cooperativity in $O_2$ binding of Hb and Mb resoectively in terms of the Hill plot.
(b) *In vitro*, the Cu(II)/cysteine (R—SH) system is unstable in terms of redox activity but in the electron transport blue proteins, this interaction is not unstable. Explain.
(c) Show the redox couples involved for the $Fe_4S_4$ clusters acting as the HiPIP (high potential iron protein) and ferredoxin (Fd). Explain the reason behind the difference in redox potentials of HiPIP and Fd.

(4+3+3)=10

4. *Attempt any four*
(i) Comment on the structure of $NiAl_2O_4$.
(ii) Give the structure (normal or inverse) of the tetragonal spinels $CuFe_2O_4$ and $CuCr_2O_4$ with proper reason.
(iii) $CdI_2$ can be considered as a giant molecule: why?
(iv) Compare the defect clusters in fcc-Pt and bcc $\alpha$-Fe.
(v) Which one of $CaCO_3$ and $CaTiO_3$ is perovskite and why?

(2.5×4)

5. *Attempt any four*

(i) In the expression of intrinsic carrier density of a semiconductor (symbols have usual meaning)

$$n_i = N_C \left(\frac{m_h^*}{m_e^*}\right)^{3/4} exp\left[{-E_g}/{2kT}\right]$$

The exponential contains ${E_g}/{2}$ and not $E_g$. Why? A small difference in band gap results in several order changes in $n_i$s at a fixed temperature: why?

(ii) $BaTiO_3$ is ferroelectric but not $CaTiO_3$: why?

(iii) Briefly explain ferromagnetism in Fe, Co and Ni using Bethe-Slate curve.

(iv) Give Langevin function and hence deduce the Curie law.

(v) What do you mean by London penetration depth of a superconductor?

(2.5×4)

6. *Attempt any four*

(i) In thermogravimetric analysis ΔM is fundamental, not ΔT: why?

(ii) Why do we need a reference in DTA technique?

(iii) Briefly compare TGA and DTA.

(iv) Compare topotactic and epitactic reactions.

(v) The calcium content in a 200 mL sample of natural water was determined by precipitating the cation as $CaC_2O_4$. The precipitate was filtered, washed, and ignited in a crucible with an empty mass of 26.6002 g. The mass of the crucible plus CaO (56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (40.078 g/mol) in water in units of grams per 1000 mL of the water.

(2.5×4)

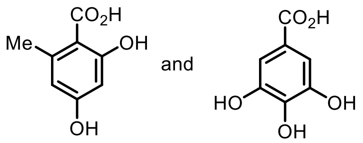
**M. Sc Examination, 2025**
**Semester-II**
**Organic Chemistry (Theory)**
**Course: MCH22-O**

**Time: Three Hours** **Full Marks: 40**

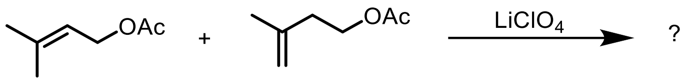
Questions are of value as indicated in the margin

**Answer <u>Four</u> Questions, taking two questions from Q1 to Q3 and two from Q4 to Q6**

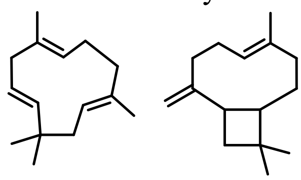
1. a) Recognize the pathways involved in the biosynthesis of the following two compounds and show both biosyntheses from the suitable precursors. 3.5




b) This chemical experiment aims to imitate the biosynthesis of terpenes, a mixture of products results. Identify them. Draw a mechanism for the reaction. To what extent is it biomimetic, and what can the natural system do better? 2.0

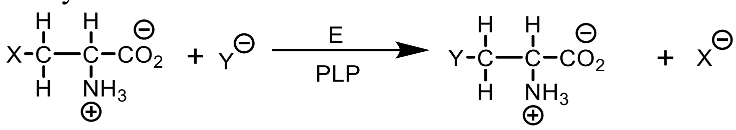



c) Both humulene and caryophyllene are made in nature from farnesyl pyrophosphate (FPP) in different plants. Suggest how they are prepared from FPP, showing the intermediates involved. How do the enzymes control which product is formed? 3.0

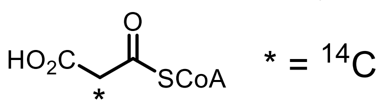


humulene Caryophyllene

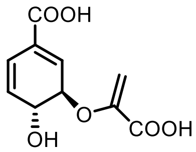
d) PLP can catalyze β-substitution reactions. Propose a mechanism for the following PLP-catalyzed reaction: 1.5




2. a) Predict the distribution of $C^{14}$ labelling in decanoic acid when acetyl-CoA and 4×Malonyl-CoA are utilized for biosynthesis. Discuss the mechanism. 2.0

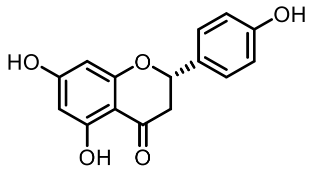



b) Salicylic acid (2-hydroxybenzoic acid) is derived from chorismic acid in microorganisms, but it is obtained from cinnamic acid in plants. Show both the biosynthesis pathway with the mechanism. 2.5

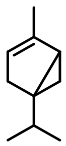


Chorisimic Acid

c) Discuss the biosynthesis of the following flavanone derivative from *L*-phenyl alanine. Compare the stability of the flavanone under acidic and basic conditions. 2.5

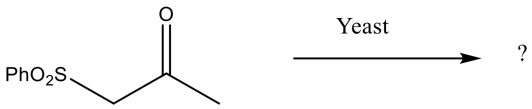



d) Carry out the biosynthesis of thujene from geranyl pyrophosphate (GPP) and discuss the mechanism. 2.0


Thujene

e) Explain why the ability of PLP to catalyse an amino acid transformation is greatly reduced if a PLP-requiring enzymatic reaction is carried out at a pH at which the pyridine nitrogen is not protonated. 1.0

3. a) Write down the structure of $NAD^+$ and indicate the active portion that changes its structure chemically during the catalysis of the oxidation-reduction reaction.
   b) Discuss the stereochemical consequences involved in the interconversion of ethanol and acetaldehyde catalysed by YADH enzyme.
   c) Predict the stereochemical configuration of the reduced product in the following reaction with proper justification.




2+6+2

4. a) Provide one example with the name and structure of each 3.0

   i) Simple lipid
   ii) Complex lipid
   iii) Wax

   b) Write the product(s) when a triglyceride is treated with methanol (3 moles) and NaOH 2.0
   c) Write the structure of ceramide and sphingomyelin 2.0
   d) Describe how the molecules and ions get transported across the cell membrane. 3.0

5. a) What is PLP? What types of reactions are generally catalyzed by PLP-dependent enzymes? Discuss Dunathan hypothesis.
   b) Discuss the mechanism of the enzyme-catalysed decarboxylation. (1+2+3)+4

6. a) What are t-RNA, m-RNA, and r-RNA? Discuss the role of these macromolecules in the translation process of protein biosynthesis. 7.0
   b) Write down the structure and function of the TPCK reagent. 3.0

**M. Sc. Examination, 2025**

**Semester-II**

**Course: MCH23-P**

**Physical Chemistry (Theory)**

**Time: Three Hours** **Full Marks: 40**

Questions are of value as indicated in the margin.

(All the symbols have their usual meaning.)

Answer ***any four*** questions

1. (a) Identify the point symmetry group of the following molecules/complexes and list the symmetry elements and arrange them according to classes:

(i) $BrF_5$ (ii) Tetrachloroplatinate 2.0+2.0

(b) Construct the Group multiplication table of $C_{2v}$ point symmetry group and using this table show that two symmetry planes of this point group belong to two different classes.

2.0+2.0

(c) What do you mean by an abelian group? Give examples of two such groups.

1.0+1.0

2. (a) Write down the Great Orthogonality theorem and hence obtain the orthogonality theorem in terms of characters. 1.0+3.0

(b) Show that, if $RS = T$, then their corresponding matrix representations $D(R), D(S)$ and $D(T)$ also follow the same combination law i.e. $D(R)D(S) = D(T)$.

3.0

(c) What is the link between Group Theory and Quantum Mechanics? Show that there will always be one totally symmetric representation for each point symmetry group.

1.0+2.0

3. (a) Identify the irreducible representations to which the normal modes of vibration of trans-$N_2F_2$ molecule belongs. Also test the IR and Raman activity of normal modes of vibration of the molecules. The character table of $C_{2h}$ point symmetry group is given below.

4.0+4.0

(b) What should be the values of the following Hamiltonian matrix elements for trans-$N_2F_2$ molecule, where $\psi_i$s are the molecular orbitals and $\psi_1, \psi_2$ and $\psi_3$ belong to $A_g, B_g$ and $B_u$ irreducible representations, respectively?

(i) $\langle\psi_1|\hat{H}|\psi_1\rangle$ (ii) $\langle\psi_1|\hat{H}|\psi_2\rangle$ (iii) $\langle\psi_2|\hat{H}|\psi_2\rangle$ and (iv) $\langle\psi_2|\hat{H}|\psi_3\rangle$

2.0

| $C_{2h}$ | $E$ | $C_2$ | $i$ | $\sigma_h$ | | |
|---|---|---|---|---|---|---|
| $A_g$ | 1 | 1 | 1 | 1 | $R_z$ | $x^2, y^2, z^2, xy$ |
| $B_g$ | 1 | $-1$ | 1 | $-1$ | $R_x, R_y$ | $xz, yz$ |
| $A_u$ | 1 | 1 | $-1$ | $-1$ | $z$ | |
| $B_u$ | 1 | $-1$ | $-1$ | 1 | $x, y$ | |

4. (a) The dimensionless radial Schrödinger equation for the hydrogen-like atoms is given by

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right] R(\rho) = 0,$$

where $\rho = 2\alpha r$ and $\alpha = \frac{Z}{na_0}$. By using suitable mathematical transformation show that the above equation can be reduced to the following form:

$$\rho\frac{d^2U}{d\rho^2} + (2l - \rho + 2)\frac{dU}{d\rho} + (n - l - 1)\,U(\rho) = 0$$

3.0

(b) Show that, in cgs-esu unit, for an electron moving in a circular path

$$\overrightarrow{\mu} = -\frac{|e|}{2m_e c}\overrightarrow{L}$$

In this context define gyromagnetic ratio ($\gamma$) and Bohr magneton ($\mu_B$) and determine the relation between these two quantities. 2.0+1.0+1.0+1.0

(c) Find out the Larmor precession frequency of an electron in a magnetic field of 1.4 tesla. 2.0

5. (a) What do you mean by central potential and central force? Show that the central force is radially directed. 1.0+1.0+3.0

(b) Prove that the eigenvalues of the $z$-component of angular momentum ($\hat{L_z}$) are bounded from above and below in the ladder operator approach. 5.0

6. (a) Evaluate the commutator $[\hat{L_x}, \hat{L_z}]$. 3.0

(b) Show that the eigenfunctions for $l = 0$ state is spherically symmetric.

2.0

(c) A molecule must possess a permanent dipole moment to exhibit rotational spectra–justify the statement. 2.0

(d) In the far infrared spectrum of $H^{79}Br$, there is a series of lines separated by 16.72 $\mathrm{cm}^{-1}$. Calculate the bond length in $H^{79}Br$. 3.0