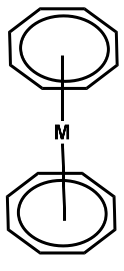
M.Sc. Examination, 2025
Semester-IV
Chemistry
Course: MCH41-I (Optional Inorganic)

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

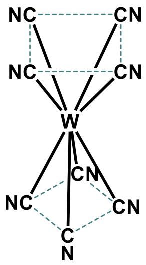
Questions are equal value as indicated in the margin.

*Answer **any four** questions*

1. (a) Deduce the point group for the following molecules **A** and **B**: (2)



(A)



(B)

(b) Arrange the following ligands in order of increasing nephelauxetic effect and nephelauxetic constant with justification: F^-, I^-, NH_3, H_2O, CN^-. (3)

(c) What do you mean by Cotton effect? How does it differ from the Faraday effect? (2)

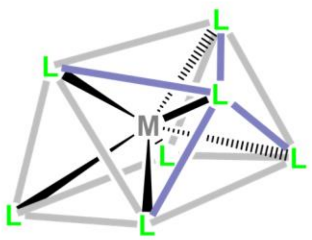
(d) In the electronic spectra of $[Co(en)_3]^{3+}$, two peaks are observed at 21400 and 29400 cm^{-1}, but the CD spectra exhibit three Cotton effects at 20300, 23400, and 29400 cm^{-1}, respectively. Explain the observed electronic transitions and the Cotton effect. (3)

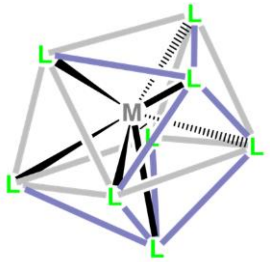
2. (a) Estimate the free ion and spectroscopic ground state term symbol for a low-spin Fe(III) system. (2)

(b) Explain with the help of the character table and MO diagram of a tetrahedral complex why tetrahedral complexes are 100 - 1000 times more intensely colored than octahedral complexes. (3)

(c) Illustrate the correlation diagram for a d^2 electronic configuration in an octahedral crystal field, and then show the increasing order of energy level of the triplet electronic states under strong field conditions using the Tanabe-Sugano diagram. (4+1)

3. (a) Write down the coordination number and coordination geometry around the metal center for the following coordination polyhedra. (2)





(b) '$[Co(ox)_3]^{3-}$ and $[Co(en)_3]^{3+}$ have similar absorption spectra and show two broad peaks at 330 & 480 nm and 420 & 600 nm, respectively, however the absorption spectra of these two complexes differ in intensity and peak spacing.' Justify. (2.5)

(c) Among the following electronic transitions, ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and ${}^2E_g \leftarrow {}^4A_{2g}$, which will be sharper and which will be more intense transition for $[Cr(H_2O)_6]^{3+}$? Justify. (1.5)

(d) Compare and explain the number of expected absorption bands in $[CrF_6]^{3-}$, $[Cr(en)_3]^{3+}$ and trans-$[Cr(en)_2F_2]^+$. Arrange the molar extinction coefficient in increasing order for the above complexes. (3+1)

4. (a) Prove that the spin-allowed transitions for $Cs[VCl_4]$ contain both electronically and vibronically allowed transitions, whereas all spin-allowed electronic transitions for $K_3[CrF_6]$ are only vibronically allowed. (3)

(b) High spin $[CoF_6]^{4-}$ shows three bands at 7,150, 15,200 and 19,200 cm^{-1}. Find the 10Dq value, β and B'. (Given: $B_0 = 970$ cm^{-1}) (2.5)

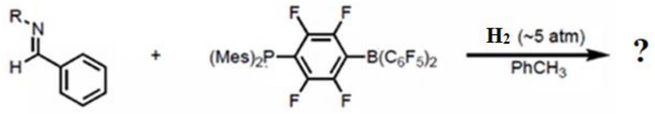
(c) What are the differences and similarities between 3c-4e and 3c-2e bonds? (2)

(d) Explain the bonding and stability of XeF_2 and SF_6 using molecular orbital diagrams, without considering the involvement of *d* orbitals. (2.5)

5. (a) What do you mean by frustrated Lewis pairs (FLP)? Write down the mechanism of H_2 activation by a frustrated Lewis pair. (1+2)

(b) Complete the following reactions: (2)

(i)



(ii)

$$HP(Mes)_2 + B(C_6H_5)_3 \xrightarrow{CO_2} ?$$

(c) Write down the products **A**, **B**, and **C**. Draw structures of **A** and **B**. (3)

(i)

$$\mathbf{B} \xleftarrow{AsF_5} XeF_6 \xrightarrow{CsF} \mathbf{A}$$

(ii)

$$Au + KrF_2 \xrightarrow{60\ ^{\circ}C} \mathbf{C}$$

(d) Write down the shape and N-X-L notations for the following molecules. (2)

(i) $XeOF_4$ (ii) XeO_2F_2

6. (a) What do you mean by a fluxional molecule? Explain the fluxional behaviour of hypervalent PCl_2F_3 with the help of NMR spectroscopy at room and low temperatures. (3)

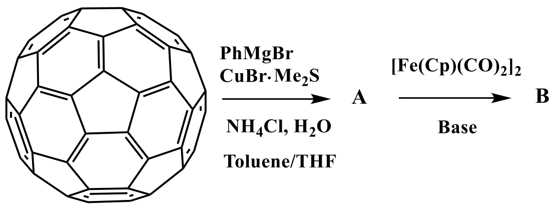
(b) Briefly describe the key steps involved in synthesizing graphene using Hummers' method. (1.5)

(c) Explain why C_{60} shows unusual stability compared to other higher or lower fullerenes. (2)

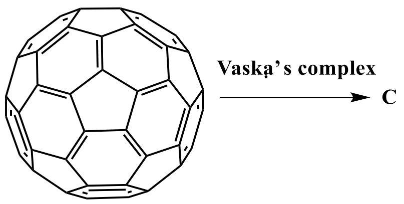
(d) What is the molecular term symbol for an O_2 molecule with opposite electron spins in an excited electronic state $[2\pi_g]^1\,[6\sigma_u]^1$. (1.5)

(e) Write down the products **A**, **B** and **C** for the following reactions: (2)

(i)

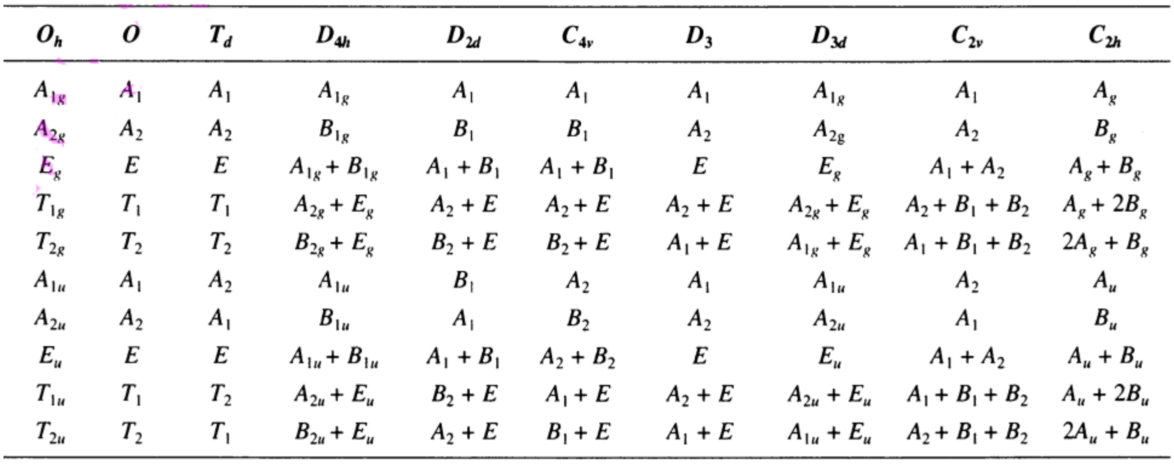


(ii)



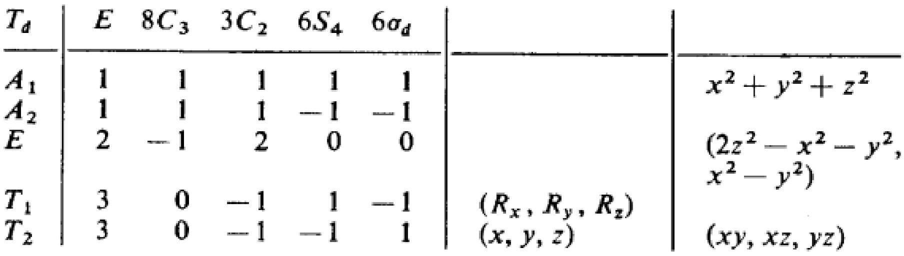
- . -

Table 1. Correlation Table for the O_h Point Group



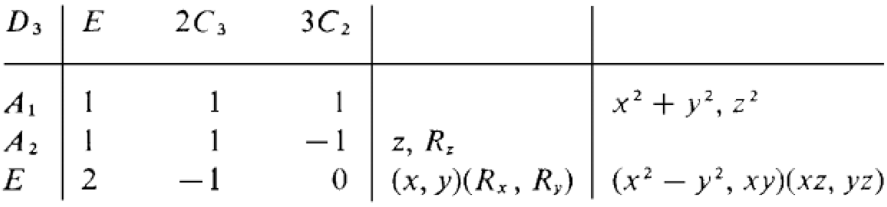
O_h	O	T_d	D_{4h}	D_{2d}	C_{4v}	D_3	D_{3d}	C_{2v}	C_{2h}
A_{1g}	A_1	A_1	A_{1g}	A_1	A_1	A_1	A_{1g}	A_1	A_g
A_{2g}	A_2	A_2	B_{1g}	B_1	B_1	A_2	A_{2g}	A_2	B_g
E_g	E	E	$A_{1g}+B_{1g}$	A_1+B_1	A_1+B_1	E	E_g	A_1+A_2	A_g+B_g
T_{1g}	T_1	T_1	$A_{2g}+E_g$	A_2+E	A_2+E	A_2+E	$A_{2g}+E_g$	$A_2+B_1+B_2$	A_g+2B_g
T_{2g}	T_2	T_2	$B_{2g}+E_g$	B_2+E	B_2+E	A_1+E	$A_{1g}+E_g$	$A_1+B_1+B_2$	$2A_g+B_g$
A_{1u}	A_1	A_2	A_{1u}	B_1	A_2	A_1	A_{1u}	A_2	A_u
A_{2u}	A_2	A_1	B_{1u}	A_1	B_2	A_2	A_{2u}	A_1	B_u
E_u	E	E	$A_{1u}+B_{1u}$	A_1+B_1	A_2+B_2	E	E_u	A_1+A_2	A_u+B_u
T_{1u}	T_1	T_2	$A_{2u}+E_u$	B_2+E	A_1+E	A_2+E	$A_{2u}+E_u$	$A_1+B_1+B_2$	A_u+2B_u
T_{2u}	T_2	T_1	$B_{2u}+E_u$	A_2+E	B_1+E	A_1+E	$A_{1u}+E_u$	$A_2+B_1+B_2$	$2A_u+B_u$

Table 2. Character Table of Tetrahedral Point Group



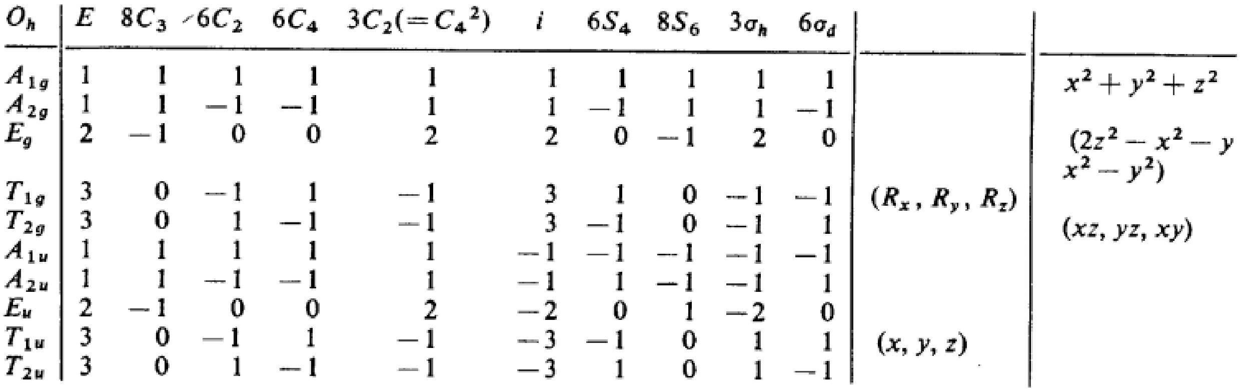
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

Table 3. Character Table of D_3 Point Group



D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

Table 4. Character table of O_h Point Group



O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y$ $x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Table 5. Normal modes of vibrations

O_h([ML$_6$]): $A_{1g}+E_g+T_{2g}+2T_{1u}+T_{2u}$; **$T_d$([ML$_4$]):** A_1+E+2T_2

D_{4h}([ML$_4$]): $A_{1g}+B_{1g}+B_{2g}+A_{2u}+B_{2u}+2E_u$; **$D_3$:** $3A_1+2A_2+5E$

M. Sc Examination, 2025
Semester-IV
Chemistry
Course: MCH42-I (Optional)
(Inorganic Chemistry)

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

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

1. (a) Comment on the stability of +2 and +4 oxidation states of Lanthanide metal ions.
(b) Give the brief idea of different coordination numbers of Lanthanide ion-based systems.
(c) Discuss about electronic spectroscopic findings of Lanthanide complexes.
(d) Write a short note on any two organometallic compounds of Lanthanide elements.
(4×2.5)

2. (a) "The number of Raman peaks for CO_2 and CS_2 are different." - Justify the fact.
(b) How can you distinguish physical and chemical absorption of CO_2 by means of Raman spectroscopy?
(c) Describe about carbonyl insertion reaction of Actinide compound.
(d) Calculate the magnetic moment of Dy^{+3} and Pr^{+3}.
(4×2.5)

3. (a) Discuss the spectroscopic method for the analysis of SO_2 in an air sample.
(b) Show the involved route of formation of photochemical smog.
(c) Write the mechanistic path of biomethylation of Hg^{2+}. Show a biochemical process involved in Lead poisoning.
(d) Write the principle involved in the estimation of COD in a polluted water sample.
(4×2.5)

4. (a) Establish the relationship between the chemical potential and the surface curvature.
(b) Calculate the minimum number of pentagonal faces present in C_{60} molecules using Euler's theorem for polyhedra.
(c) What is a carbon nanotube? Mention different types of carbon nanotubes?
(d) Give the reason behind peak broadening in nanostructures with proper explanation.
(4×2.5)

5. (a). Discuss about synthesis, symmetry and structural arrangement of Uranocene.
(b) Write about the concept of 'Atom Economy'. Give proper example. Why is it so important as a principle of green chemistry?
(b) What do you mean by dark and bright field imaging in electron microscopy?
(c) Discuss about the Samarium Barbier reaction.
(4×2.5)

6. (a) Write down the Brus equation and mention the different terms involved.
(b) Show the different paths of ozone depletion in stratosphere.
(c) Account the special role of symmetry factors of AB_2 type molecules in the Raman spectroscopic outcomes.
(d) Write a note on hydride formation reaction of actinide compound.
(4×2.5)

M. Sc Examination, 2025
Semester-IV
Chemistry
Course: MCH43-I (Optional)
(Inorganic Chemistry)

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

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

1. (a) Draw the Marcus plot in both the normal and inverted regions.
   (b) Explain the difference in electron exchange rate for the pairs $[Ru(NH_3)_6]^{3+}/[Ru(NH_3)_6]^{2+}$ and $[Fe(OH_2)_6]^{3+}/[Fe(OH_2)_6]^{2+}$.
   (c) Predict the mechanism with justification of the following electron transfer reaction.
   $$[Fe(CN)_6]^{3-} + [Co(CN)_5]^{3-} \rightarrow \text{product?}$$
   (3+4+3=10)
2. (a) EPR spectral analysis shows that $g_{\parallel} > g_{\perp}$. Justify this observation with suitable example of Cu(II) complex.
   (b) Explore the possible EPR spectral outcome of $[Mn(H_2O)_6]^{2+}$ system at room temperature.
   (c) Cite one radical type metal-chelating organic ligand (L) and explore the EPR pattern of PdL_2 complex.
   (d) How can you explain the redox process of $[Cu(2,2'\text{-bipyridine})_2]^{2+}$ by the help of EPR study ?
   (4×2.5=10)
3. (a) What is hydroformylation reaction? Mention one catalyst and its active form involved in the reaction. How do you improve 'n/I' ratio in the hydroformylation reaction?
   (b) What is Wilkinson's catalyst? Is it an organometallic compound? Justify your statement in the light of the catalytic cycle involving Wilkinson's catalyst. Critically analyze the cycle.
   ((1+1+3)+(1+1+3)=10)
4. (a) Briefly describe the effect of dynamic Jahn-Teller distortion on magnetic property in hole doped manganites.
   (b) What is colossal magnetoresistance? Why it exhibits maxima near ferromagnetic T_C?
   (c) Schematically illustrate the trimeron in Fe_3O_4.
   (4+(1+2)+3=10)
5. (a) Explain the mechanism (with evidence) of reduction of $[Fe(CN)_6]^{4-}$ by $HCrO_4^-$.
   (b) In the inner sphere electron transfer (ISET) process, the $\sigma \rightarrow \sigma^*$ net electron transfer is highly favored—explain.
   (c) Comment on the magnetic ground state of d^5—O—d^5 90°-superexchange interaction with plausible explanation.
   (d) What do you mean by thermoelectrics? What are power factor and figure of merit?
   (4×2.5=10)

6. (a) Write a brief note on anisotropic EPR spectral process.
   (b) Write the impact of Zero Filed Splitting factor for explaining the EPR pattern of photo-excited naphthalene radical.
   (c) Discuss the different steps involved in Fisher-Tropsch synthesis of gasoline. What is hydrosilyllation? Describe the Chalk-Harrod mechanism of hydrosilylation.
   3+2+(2+1+2)=10

M. Sc. Examination, 2025
Semester-IV
Subject: Chemistry
Paper: MCH41-P (Optional Physical)

Time: Three Hours Full Marks: 40

Questions are of value as indicated in the margin.

Answer any four questions

1. (a) Define a traveling wave in words. Based on your definition, comment on the functional form of a traveling wave. Identify which of the following correspond to traveling waves, (i) $f(x,t)=A\cos[b(x-vt)]$, (ii) $f(x,t)= A\exp[-b(x-vt)^2]$ (iii) $f(x,t)=A/(1+b(x-vt)^2)$ (iv) $f(x,t)=A\text{cox}(bvt)^2\sin(bx)$. Here the symbols have usual meaning. 1+1.5+2

(b) Derive the wave equation for a one dimensional mechanical wave. Based on your comment in the above question, check the validity of the wave equation for any one dimensional travelling wave. 3+2.5

2. (a) To write the atomic or the molecular Hamiltonian function we consider the relevant Coulomb potential. Is it expected and consistent with the experimental results? 2

(b) Coulomb's law of force is consistent with the principle of superposition of forces. Comment on the statement. 2

(c) Demonstrate a standing wave using a traveling wave and its reflection. Find the mathematical form of the standing wave for your case. Check that it is consistent with your demonstration. Then comment on the stationary solutions of the Schrodinger's equation for the bounded motion. 2+1+ 1+2

(3) Derive the Einstein's result on the specific heat of solid with appropriate approximation and assumption. Check its validity with appropriate explanation. If any modification of the result is necessary then arrive at the modified result. 2+4+4

4. State the result of the Compton effect. How it depends on the characteristics of the incident radiation and the target? Based on your answer, propose the relevant model and arrive at the result. Finally, comment on the outcome of the Compton effect. 1.5+1+2+5+0.5

5. (a) Based on the properties of the Schrödinger equation and the interpretation of wave function one may account for eigenfunction and eigenvalues qualitatively. Comment on the statement with a suitable example. 5

(b) State the first principle of quantum mechanics and discuss its application in chemistry(if any). 2+3

6. (a) Define the Dirac representation of a state. What is the goal of this representation? State the properties of a ket vector. A bra vector and its associated ket vector are said to be duals of one another. Comment on the statement. 1+1+1.5+1.5

(b) Any vector in the Hilbert space may be a ket vector but the reverse is not true. Comment on the statement. 1.5

(c) Show that there is an analogy between the Heisenbeg equations of motion of a quantum system and the Hamilton's equation motion of its classical analog. It gives a clue to the motivation for the quantization postulate. Comment on the statement. 2.5+1

M. Sc. Examination, 2025
Semester-IV
Chemistry
Optional Course: MCH42-P
(Physical Chemistry)

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

Questions are of value as indicated in the margin.

*Answer **any four** questions*

1. Derive an expression for the variation of potential with distance from the semiconductor surface for a semiconductor-solution interface. In this context also discuss the potential variation across space-charge domain. What is the total differential capacity of the semiconductor-solution interface? [5+2+3]

2. (a) What is "*Fermi level*"? How do the locations of Fermi levels vary in case of intrinsic and doped semiconductors. How an intrinsic semiconductor conducts electricity? [1+2+2]

(b) Show that a corroding metal is analogous to a short-circuited energy-producing cell. [2]

(c) How air and pH influence the rate of corrosion of a metal? [2]

(d) What is the corrosion inhibition method to increase the stability of the metals? [1]

3. (a) Define equilibrium exchange current density (i_0). Can the equilibrium exchange current density be measured by an instrument? [1+2]

(b) Show that, at equilibrium, the Butler-Volmer equation settles down to the Nernst Equation and at far away from equilibrium it reduces to an exponential i vs. η law for interface. [3+2]

(c) How linear low-field approximation explains that an interface is polarizable or non-polarizable? [2]

4. (a) Write down the Poisson's summation formula and define the terms involved in it. Using this, show that the Fourier transformation of a direct lattice is a reciprocal lattice. [2+2]

(b) Calculate the volume of the reciprocal primitive cell. [2]

(c) State and prove Bloch's theorem in relation to the wave function in a periodic lattice. [1+3]

5. (a) Define the terms centrifugal energy and impact parameter in molecular reaction dynamics. Based on conservation of energy in an elastic collision, derive a relation between them. [2+2]

(b) The centrifugal energy helps the colliding partners to surmount the activation barrier for the reaction - Comment on the statement. [2]

(c) What are the essential features of the spectator model? Explain how this model account the experimental observation that the exoergicity of the reaction $Cl + HI \rightarrow HCl + I$ has been found in the vibration of HCl molecule. [1+3]

6. (a) Define angular deflection. What do you understand by rainbow and glory impact parameters? Show the variation of angular deflection (χ) as a function of the impact parameter and identify the rainbow and glory impact parameters. [1+1+1+1]

(b) The experimental data of 'σ (v)', i.e. the velocity dependent reaction cross section may give idea about the long range potential- Justify this statement. [You may assume the high energy approximation for the angular deflection i.e. $\chi(E_T,b)= V(b)/E_T$]. [3]

(c) Consider the following two reactions:

(i) $CH_3I + K \rightarrow KI + CH_3$ (ii) $K + I_2 \rightarrow KI + I$

Draw the picture of the product angular distribution of the above reactions as found in experiments and interpret the results. What can be said about the reaction cross sections? [3]

.

M. Sc. Examination, 2025
Semester-IV
Chemistry
Course: MCH-43-O
Optional (Organic Chemistry)

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

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

1. (a) Predict the major products formed when following compounds are irradiated with UV light: (i) 2-pentanone (ii) 3-hexanone (iii) cyclopentanone (iv) 2-methylcyclohexanone. For each case, indicate whether the major product(s) arise from a Norrish type I or type II pathway (or both). 4x2.0

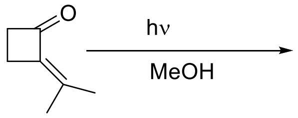
(b) Draw the structure of the ketone that would yield cyclobutanol derivative as a major product upon UV irradiation via a Norrish type II reaction. Provide the mechanism for its formation. 2.0

2. (a) How does photoisomerization occur in alkenes? Illustrate the mechanism with a specific example and detail the various photochemical processes that can take place in the excited state during this reaction. 3.0+3.0

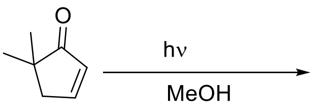
(b) Discuss the photochemical cis-trans isomerization of cycloalkenes, considering the unique constraints and characteristics imposed by the cyclic structure. Explain the mechanism by which this isomerization occurs upon light absorption and highlight any specific considerations or limitations that arise due to the cyclic nature of the alkene. 4.0

3. Predict the product (with appropriate stereochemistry, if applicable) in each case. Explain formation of the products with the help of suitable mechanistic pathways. 5x2.0

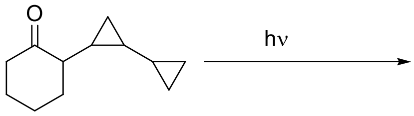
(i)



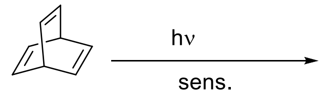
(ii)



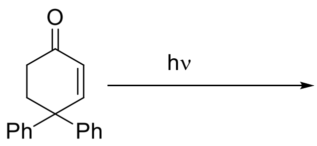
(iii)



(iv)



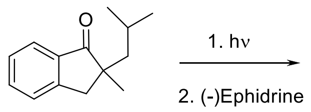
(v)



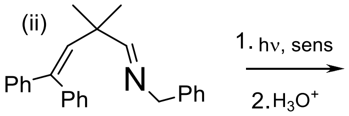
4. 1. (a) Schematically depict the process of organic photosensitization. Illustrate your explanation with a concrete example, clearly identifying the sensitizer, the substrate, and the energy transfer mechanism involved. 5.0

(b) Give the structure of the product(s) with appropriate stereochemistry (if applicable) in each of the following cases and justify your answer with the help of plausible mechanistic pathways. 2x2.5

(i)

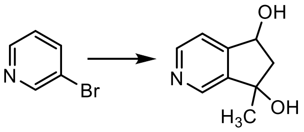


(ii)

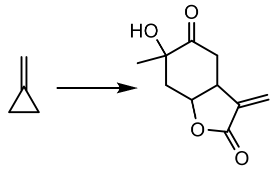


5. Carryout the following transformations with plausible reaction mechanism. 3 +3+2+2

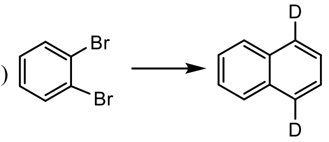
(a)



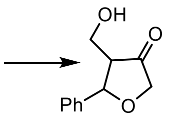
(b)



(c)

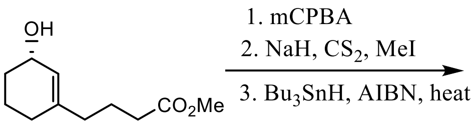


(d) PhCHO

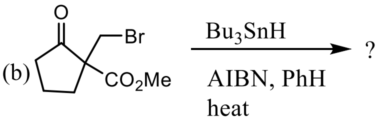


6. Predict the product(s) with plausible reaction mechanism. 2.0 x 5

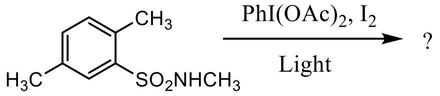
(a)



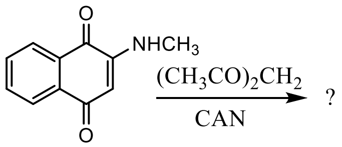
? (b)



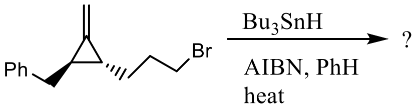
(c)



(d)



(e)



.

M. Sc. Examination, 2025
Semester-IV
Chemistry
Optional Course: MCH43-P
(Physical Chemistry)
Time: Three Hours **Full marks: 40**
Answer any four questions
Questions are of value as indicated in the margin
(Symbols have their usual meaning)

1a) Briefly describe what you mean by Selkov model for glycolysis. Show, how a simple phase space analysis based on this model can explain oscillation around the steady state. 2+4

b) Consider a simple linear kinetic reaction. Derive the expression for steady state concentration and make the stability analysis. 2+2

2. In the context of membrane transport outline how the quantities J_V, L_{VV}, R, ω and L_{DD} can be experimentally determined. Define *reflection coefficient* (R) and discuss how R determines the selectivity of the membrane. 5+2+3

3. Illustrate with a simple chemical model what you mean by *forbidden coupling*. Why it is said that such coupling causes some *apparent violation* of Curie-Prigogine symmetry principle? How forbidden coupling can be correlated with biological active transport processes? 6+2+2

4. (a) From the Hartree-Fock Roothaan equation obtain the matrix form of the same. Hence use Lowdin orthogonalization scheme to express it in eigen value form. 4

(b) Write down the secular determinant for butadiene molecule in HMO theory and hence solve it for the energies of the molecule. Calculate the delocalization energy of butadiene molecule. 4

(c) What do you mean by a saddle point on potential energy surface? How to ascertain whether a stationary point is a minimum or saddle point? 2

5. (a) Prove that the electron density of two different systems whose Hamiltonians are differed by more than a constant can't have the same value. 4

(b) Calculate the functional derivative of the following functionals. 3

$$F[\rho(r),\rho(r')] = \int_0^{\infty}\int_0^{\infty} \frac{\rho(r)\,\rho(r')}{r-r'}\,dr\,dr'$$

(c) Discuss velocity-Verlet algorithm used in MD simulation? 3

6 (a) State and prove the Virial theorem and using this show that the average kinetic and potential energies are same for a Harmonic Oscillator. 1+3+1

(b) By using classical electrostatics obtain an expression for dipole-dipole interaction energy. 3

(c) Sate the Hellmann-Feynmann electrostatic theorem. 2

M. Sc Examination, 2025
Semester-IV
Chemistry
Course: MCH42-O (Optional)
(Organic Chemistry)

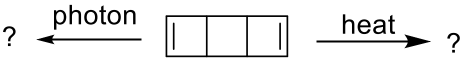
Time: Three Hours **Full Marks: 40**

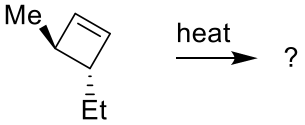
Questions are of value as indicated in the margin.

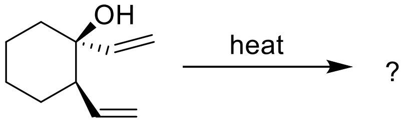
Group A (Answer any two questions)

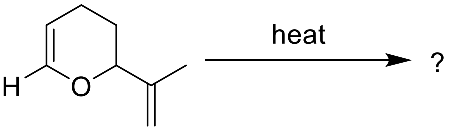
1. (a) Predict with the help of FMO-theory whether conrotatory ring opening of 1,3,5-cyclooctatriene is thermally allowed or not. 2.5
   (b) Explain why the alkyl substituted Dewar benzene is sufficiently stable and does not undergo electroreversion reaction under thermal condition without a catalyst? 2.5
   (c) What is an 'Ene reaction'? Explain with an example. 2.5
   (d) Explain the cheletropic reaction between (2E, 4E)-hexadiene and singlet carbene (:C_{XZ}) by Frontier Molecular orbital theory. 2.5

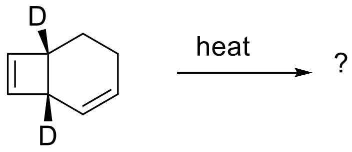
2. Discuss the outcome of the following reactions (***any four***): 2.5×4

a)


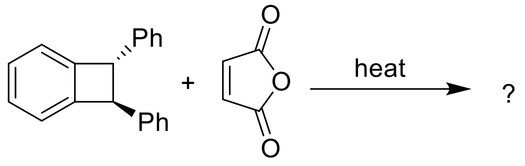
b)


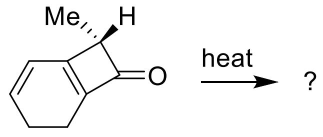
c)


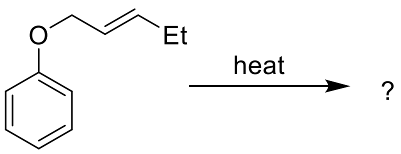
d)


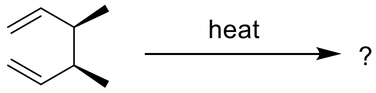
e)


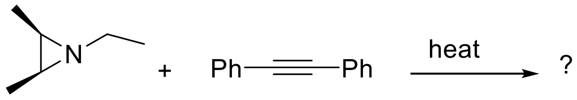
3. Predict the product(s) with plausible mechanism (***any four***): 2.5×4

a)


b)


c)


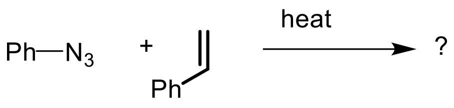
d)


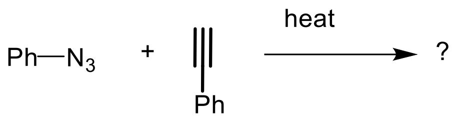
e)


Group B (Answer any two questions)

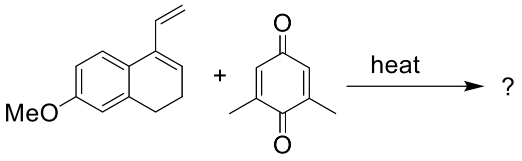
4. (a) Explain the following observation showing the interaction of frontier molecular orbitals: The Diels–Alder reaction between cyclopentadiene and crotonic acid at 10 °C gives 85% endo and 15% exo isomer, but when carried out at 170°C, 40 % endo and 60 % exo adducts are obtained. 2.5

(b) Predict the product(s) of the following thermal reactions explaining your choice. Show all the involved molecular orbitals and energy diagrams. 2.5

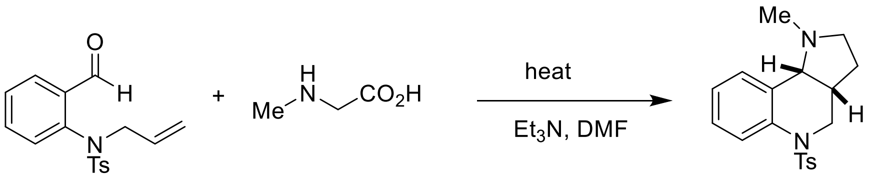




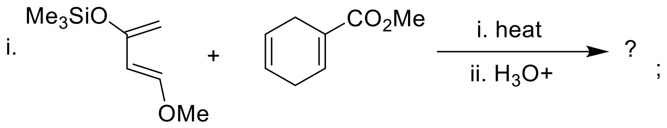
(c) Identify the product of the following reaction. What will happen if the reaction is conducted in the presence of BF_3. Discuss the role of BF_3. Predict the stereochemistry as well. 3.0

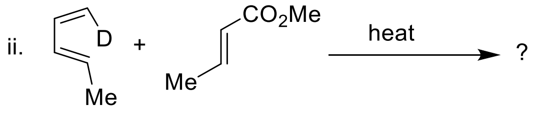


(d) Explain the following observation identifying the right mechanism and the reaction involved. 2.0



5. (a) What is the transition structure aromaticity approach? State the rule. Predict if [4+2] cycloaddition ([$\pi^4_s + \pi^2_s$] and [$\pi^4_s + \pi^2_a$]) are thermally possible by transition structure aromaticity approach. 2.0
(b) With the help of the FMO method predict if [2+2] cycloaddition reaction between alkene and ketene is feasible thermally. 2.0
(c) Predict the product(s) of the following reactions with stereochemistry and justify. 2.0+2.0

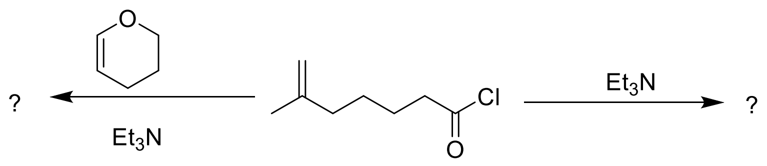




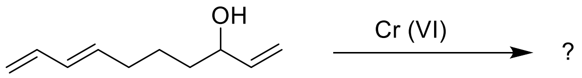
(d) Give the products in the dimerization of 2-phenylbutadiene thermally. Indicate the major product and explain the site selectivity involved. 2.0

6. (a) With the help of correlation diagram, predict whether [2+2] cycloaddition reaction is photochemically feasible. 3.0
(b) Explain the observation that butadiene reacts with vinyl-9-Borabicyclo[3.3.1]nonane (BBN) at room temperature, and the reaction is 200 times faster than the reaction with methyl acrylate. 2.0
(c) Predict the products with proper stereochemistry and explain. 3.0+2.0

i.



ii.



M.Sc. Examinations, 2025
Semester-IV
Chemistry
Course: MCH44-O (Optional Organic)

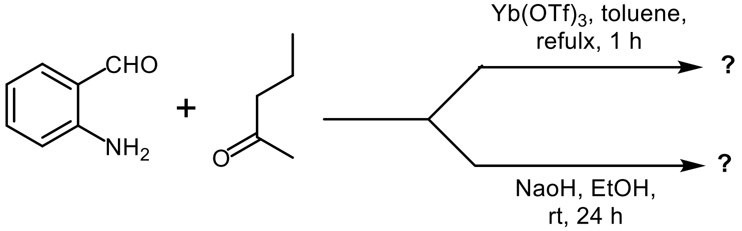
Time: Three Hours **Full Marks: 40**

Questions are of value as indicated in the margin.

Answer ***two*** questions from ***Question No. 1 to 3*** and ***two*** questions from ***Question No. 4 to 6***

1. a) Outline the suggested mechanism for the Friedländer synthesis. **3**

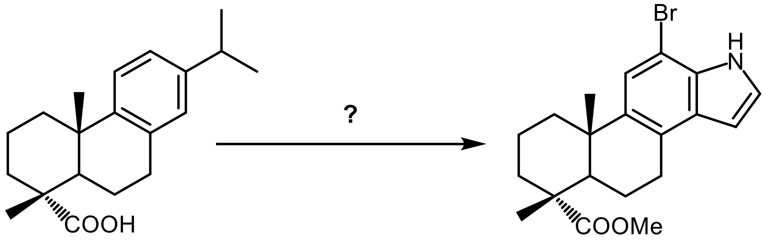
   b) Predict the major product under two different Friedländer conditions (give reasons) **1.5 x 2**



   c) Suggest a synthetic route for Imitrex® **4**

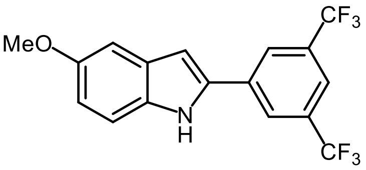
2. a) Outline the photoinduced Bartoli indole synthesis by the oxidative cleavage of alkenes with nitro(hetero)arenes, with the suggested mechanistic aspect. **4**

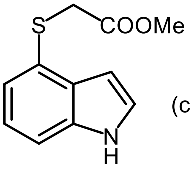
   b) Employing the Bartoli strategy as a key reaction, how can you implement the following transformation? **3**

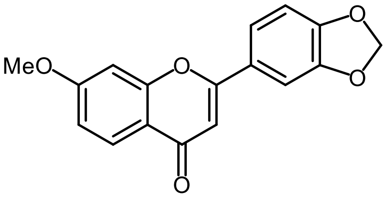


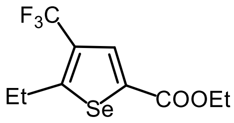
   c) What is Ishikura *et al.*'s modification of Bartoli synthesis? **3**

3. Suggest a suitable synthetic route for each of the following transformations, with a detailed mechanism (**any two**) **5 x 2**

(a)


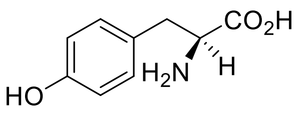
(b)


(c)


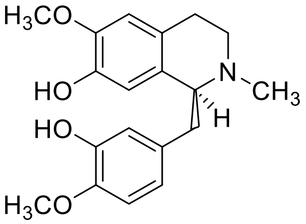
(d)


P.T.O.

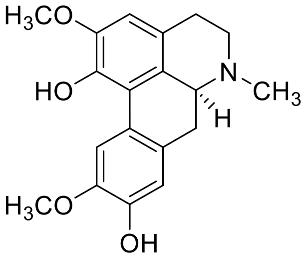
4. a) Suggest a possible biosynthesis of *S*-reticuline from tyrosine and discuss the mechanisms. Show a possible pathway for the transformation of *S*-reticuline to the corresponding *R*-enantiomer. Show the transformation of *S*-reticuline to Isoboldine with the mechanism. **2+1+2**



Tyrosine

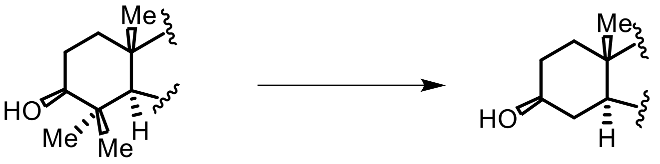


S-reticuline

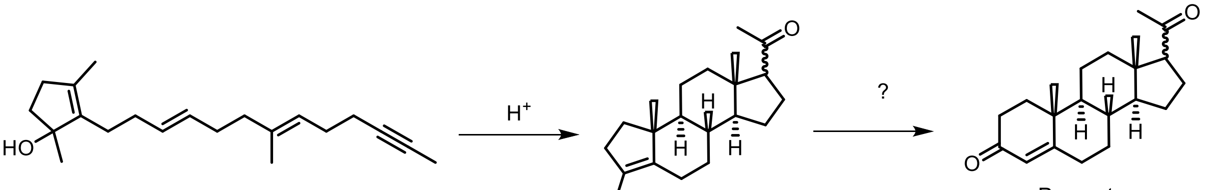


Isoboldine

b) During the biosynthesis of cholesterol from lanosterol, the following two methyl groups are lost. Explain with mechanism how this transformation occurs. Identify the intermediates formed during this transformation. **2.0**

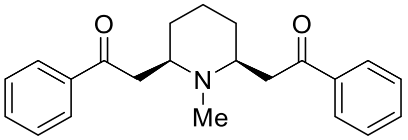


c) Jhonson developed the following scheme for the synthesis of Progesterone. Please explain the transformation with the mechanism and complete the reagents involved during the transformations. Give some more details about cyclization and compare the route with the biosynthesis of steroids. **3.0**

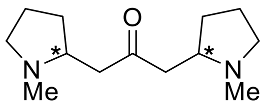


Progesterone

5. a) Outline the synthesis of lobelanine from *l*-lysine and cuscohygrine from *l*-ornithine, showing the reagents and mechanisms involved in each step during biosynthesis. Discuss the stereochemistry of labelled (*) carbons in cuscohygrine. **1.5+1.5+1.0**

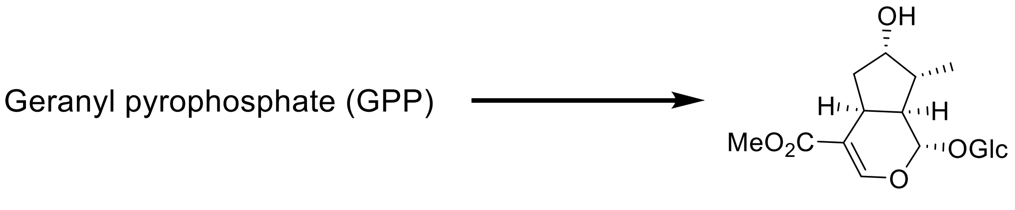


lobelanine



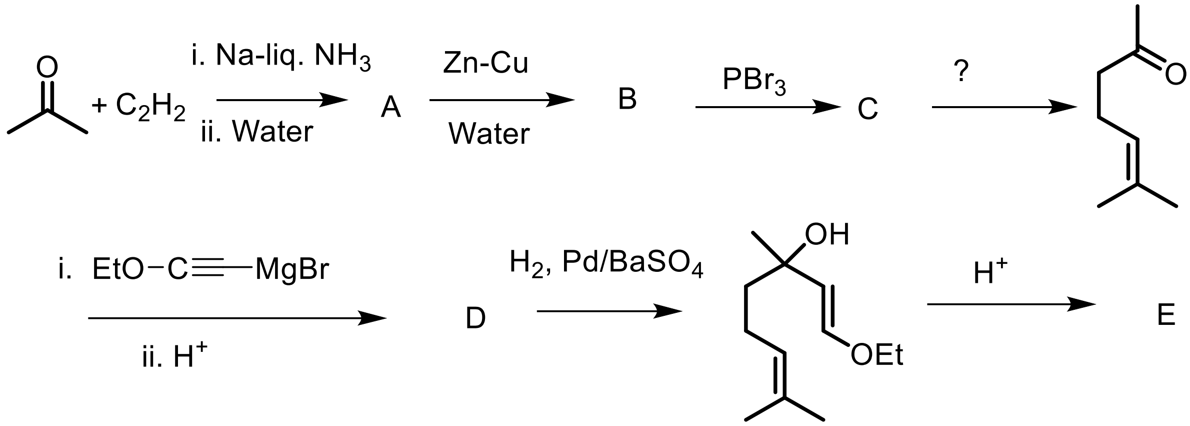
cuscohygrine

b) Discuss the biogenic pathway of the following conversion, showing all the intermediates and reagents involved in each step. **3.0**

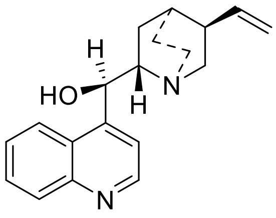


P.T.O.

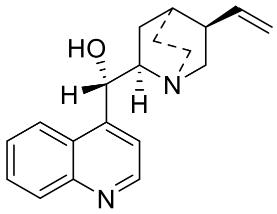
c) Outline the missing reagents involved in each step during the chemical synthesis. Identify A-E. **3.0**



6. a) All cinchona alkaloids contain the same stereochemistry at C-3 and C-4. How could you prove this? **4.0**

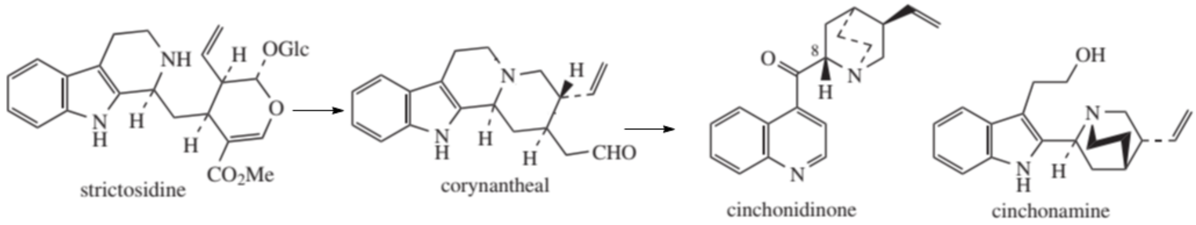


(-)-cinchonidine

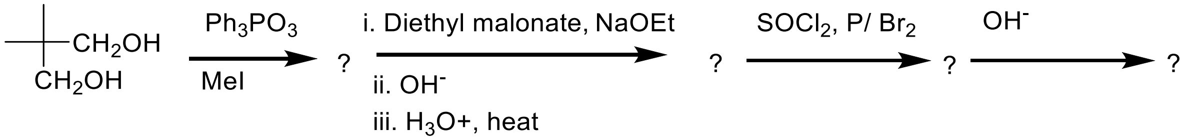


(+)-cinchonine

b) Explain the biosynthesis of chinchodinone from strictosidine with the mechanism. Identify the missing intermediates. Explain the formation of cinchonamine during this biosynthesis. Identify the basic chemistry involved in these transformations. **4.0**



c) Identify the missing intermediates and explain. **2.0**



M. Sc Examination, 2025
Semester-IV
Chemistry
Course: MCH44-I:(Optional)
(Inorganic Chemistry)

Time: 3hrs **Full Marks:40**

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

1. a) Write a short discussion on the basic aspects of Atomic Absorption Spectroscopy.
   b) Write about cationic and anionic interferences observed in Atomic Absorption Spectroscopy. 5+5 = 10
2. (a) Write down the basic principle of "Chromatography".
   (b) What is inert support? In developing the Stationary phase, what are the roles of inert support, activator and ligand? 3+(2+5) = 10
3. (a) Discuss the conservation of energy in nuclear reaction.
   (b) What is Q-value in nuclear reaction? Write the significance(s) of it.
   (c) How is Q-value related to the threshold energy of a nuclear rection?
   (d) The reaction $^{9}Be\ (p, n\ )^{9}B$ has threshold energy of 2.059 MeV. Find the Q-value.
   2+(1+2) + (3+2) = 10
4. a) Comment on luminescent processes and quantum yield. How can you quantitatively identify the concentration of a fluorescent sample?
   b) Write briefly about the ionization suppressor in the Flame photometry. "Mass action law plays a very effective role in the Flame photometry." Justify the statement.
   (2+3) + (2+3) = 10
5. (a) What is "Break Through Capacity" and "Enrichment Factor"? Write down their importance in analytical chemistry.
   (b)What is "Solvent Extraction"? Briefly explain the importance of multiple extractions.
   2+2+2+4 = 10
6. (a) "For the lighter stable nuclides, n/p ≈1, but for the heavier ones, n/p >1"…..explain it from the Fermi gas model.
   (b) What is nuclear reaction Cross Section? Which factor (s) does it depend on?
   (C) The nuclear reaction cross section of ^{113}Cd for capturing thermal neutron is 2×10^{4} b, and the number density of the ^{113}Cd-sheet is 5.57×10^{27} atoms/m^3. What fraction of the incident beam of thermal neutron is absorbed by the Cd-sheet of 0.1mm thickness?
   (d) What is the fission yield? Draw a typical fission yield curve as a function of mass number for a nuclear fission reaction. What inference (s) can one draw from the fission yield curve?

   3+2+2+(1+2) = 10

==================================****=====================================