[5323]-11

M.Sc. - I

PHYSICAL CHEMISTRY

CH - 110 : Physical Chemistry - I

(2008 Pattern) (Semester - I) (Old)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) *Answers to the TWO sections should be written in SEPARATE answer books.*
2) *ALL questions are COMPULSORY.*
3) *Figures to the RIGHT SIDE indicate FULL marks.*
4) *Use of logarithmic table/calculator is ALLOWED.*
5) *Neat diagrams must be drawn WHEREVER necessary.*

Physico - Chemical Constants

1.	Avogadro Number	N =	6.022×10^{23} mol^{-1}
2.	Boltzmann Constant	k =	1.38×10^{-16} erg K^{-1} molecule^{-1}
		=	1.38×10^{-23} J K^{-1} molecule^{-1}
3.	Planck Constant	h =	6.626×10^{-27} erg s
		=	6.626×10^{-34} J s
4.	Electronic Charge	e =	4.803×10^{-10} esu
		=	1.602×10^{-19} C
5.	1 eV	=	23.06 k cal mol^{-1}
		=	1.602×10^{-12} erg
		=	1.602×10^{-19} J
		=	8065.5 cm^{-1}
6.	Gas Constant	R =	8.314×10^{7} erg K^{-1} mol^{-1}
		=	8.314 J K^{-1} mol^{-1}
		=	1.987 cal K^{-1} mol^{-1}
7.	Faraday Constant	F =	96487 C equiv^{-1}
8.	Speed of light	c =	2.997×10^{10} cm s^{-1}
		=	2.997×10^{8} m s^{-1}
9.	1 cal	=	4.184×10^{7} erg
		=	4.184 J
10.	1 amu	=	1.673×10^{-27} kg
11.	Bohr magneton	β_e =	-9.274×10^{-24} J T^{-1}
12.	Nuclear magneton	β_n =	5.051×10^{-27} J T^{-1}
13.	Mass of an electron	m_e =	9.11×10^{-31} kg

P.T.O.

SECTION - I

Q1) Attempt <u>any three</u> of the following: **[15]**

a) Explain the experimental procedure to verify Heisenberg's Uncertainity Principle.

b) Using chemical Potential derive the expression for entropy change in mixing of two ideal gases.

c) Derive the time independent Schrodinger wave equation.

d) What is Gibb's function? Explain the dependence of Gibb's function on temperature.

e) Define the term Osmosis and Osmotic pressure. Show that osmotic pressure is a colligative property on the basis of chemical potential.

Q2) Attempt <u>any three</u> of the following: **[15]**

a) Derive the workdone in a reversible adiabatic expansion of an ideal gas.

b) Explain Einsteins photoelectric effect. How does it support plank's hypothesis of quantization of energy?

c) Derive the Gibb's-Duhem equation. What are its applications?

d) State and explain Raoult's law. What is its applications?

e) What is partial molar quantity? Describe any one method to determine the partial molar quantity.

Q3) Solve <u>any two</u> of the following: **[10]**

a) A water alcohol mixture is 40% in alcohol by mass, the density of water is 1 gram/cc and density of alcohol is 0.785 gram/cc. Find the total volume of 1 kg mixture [Given : Partial molar volume of water = 17.5 cc mole^{-1}, and partial molar volume of ethanol = 55.0 cc mole^{-1}].

b) Calculate the velocity of ejected electrons from Barium Surface $\phi = 2.48$ *ev*. When light of 400 nm is irradiated on Barium cathode.

c) Calculate the entropy change of mixing when 16 gram of 'NO' and 32 gram of 'O_3' at 200K.

[Given Atomic Weight : N = 14, O = 16].

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2

SECTION - II

Q4) Attempt <u>any three</u> of the following: **[15]**

   a)   How can half-life period of a reaction be used to determine its order?

   b)   Derive Eyring's equation using activated complex theory.

   c)   Write a note on the electronic partition function.

   d)   Describe the kinetics of a reaction approaching equilibrium.

   e)   What are the fast reactions? Describe flow method to study reaction kinetics.

Q5) Attempt <u>any three</u> of the following: **[15]**

   a)   What is stirling's approximation? Describe its importance in statistical mechanics.

   b)   Write a note on Bose-Einstein statistics.

   c)   Explain the significance of Lineweaver and Eadie plots.

   d)   Describe Lindemann theory of unimolecular reactions.

   e)   What is steady state approximation? Explain using suitable example.

Q6) Solve <u>any two</u> of the following. **[10]**

   a)   A first order solution phase reaction is 25% complete in 290.8 seconds, show that it will never be 100% complete.

   b)   What is the rotational partition function of H_2 molecule at 300 K(Given: Rotational constant, $B=60.864$ cm^{-1} for H_2).

   c)   Calculate the rate constant of a diffusion controlled reaction at 300 K if the viscosity of the reaction medium is 0.89 cP.

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M.Sc. - I

INORGANIC CHEMISTRY

CH-130: Molecular Symmetry and Chemistry of P-block Elements

(2008 Pattern) (Semester - I)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1)   Answer to the two sections should be written in separate answer books.

2)   All questions are compulsory.

3)   Figures to the right indicate full marks.

4)   Use of logarithmic table/calculator is allowed.

SECTION-I

Q1) Attempt <u>any</u> <u>three</u> of the following: **[15]**

a)   What are the conditions of a mathematical point group?

b)   Assign appropriate point group for any two of the following:

  i)   Naphthalene

  ii) IF_5

  iii) NH_3

c)   Define plane of symmetry. With a schematic diagram explain different types of planes in allene.

d)   What is a glide plane? Illustrate different types of glides and their symbols.

e)   On the basis of symmetry, what is the criterion for the molecule to be optically active? Which of the following molecules is/are optically active?

  i) BF_3

  ii) $CHClF_2$

Q2) Attempt <u>any</u> <u>three</u> of the following: **[15]**

a) Using matrix multiplication find the product of

   i) $C \times \sigma_n^{xy}$

   ii) $\sigma_n^{xy} \times C_2^z$

b) Sketch and describe all the symmetry operations in $[AuCl_4]^-$ complex ion and classify it into appropriate point group.

c) Using Great orthogonality theorem, derive the character table for C_{3v} point group. The classes are E, $2C_3$, $3\sigma_v$.

d) Give the group multiplication table for H_2O molecule.

e) Differentiate between point symmetry and space symmetry.

Q3) Attempt <u>any two</u> of the following: **[10]**

a) Prove that the presence of a S_n axis in a molecule implies the presence of n distinct elements if n is even and 2n distinct elements if n is odd.

b) Label the following irreducible representations with appropriate Mulliken symbols stating the rules.

	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$
Γ_1	1	1	1	1	1	1
Γ_2	1	1	−1	1	1	−1
Γ_3	2	−1	0	2	−1	0
Γ_4	1	1	1	−1	−1	−1
Γ_5	1	1	−1	−1	−1	1

c) What are the point groups possible for a linear molecule? Explain in detail giving suitable examples.

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Q4) Attempt <u>any three</u> of the following: [15]

   a) Give an account of hydrides of boron.

   b) What are crown ethers? Explain the use of crown ethers in separation of alkali metals.

   c) Give an account of Borazole.

   d) What are interhalogen compounds? Explain with suitable example.

   e) Write a note on reaction of RMgX.
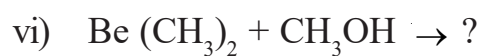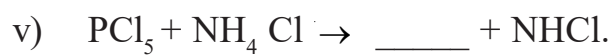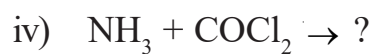
Q5) Attempt <u>any three</u> of the following: [15]

   a) What are aluminosilicates? Explain with suitable examples.

   b) Write a note on activation of nitrogen.

   c) Explain characteristic reactions of PCl_5.

   d) Write a short note on carbon nanotubes.

   e) Write a short note on sulphur oxoanions.

Q6) a) Draw <u>any five</u> structures: [5]

      i) $S_2 F_{10}$

      ii) $P_4 S_{10}$

      iii) $[B_6 H_6]^{2-}$

      iv) $Li_4 (CH_3)_4$

      v) $[Cl_2 PN]_3$

      vi) $Xe O_2 F_2$

b) Complete the following reactions (any five): [5]

i) $BCl_3 + HN(CH(CH_3)_2) \rightarrow ? + HCl$

ii) $RLi + R'CHO \xrightarrow{H_2O} ?$

iii) $Na + C_{10}H_8 \text{ (THF)} \rightarrow ?$

iv) $NH_3 + COCl_2 \rightarrow ?$

v) $PCl_5 + NH_4Cl \rightarrow \underline{\hspace{1cm}} + NHCl.$

vi) $Be(CH_3)_2 + CH_3OH \rightarrow ?$

$\mathcal{EEE}$

Total No. of Questions :6]

P1845

SEAT No. :

[**Total No. of Pages : 5**

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M.Sc. - I

ORGANIC CHEMISTRY

CH - 150 : Organic Reaction Mechanism and stereochemistry

(2008 Pattern) (Semester - I)

Time : 3 Hours]   *[Max. Marks :80*

Instructions to the candidates:

   1)   *All questions are compulsory.*

   2)   *Figures to the right indicate full marks.*

   3)   *Answer to the <u>two sections</u> should be written in separate answer book.*

SECTION - I

Q1) Explain <u>any four</u> of the following.   **[16]**

   a)   PKa value of 4 - nitro anisole is less than 3-nitro anisole.

   b)   Anti elimination occur readily than syn elimination.

   c)   Ph $COCH_2Cl$ reacts with KI in acetone about 32000 time faster than n-butylchloride.

   d)   M- Chloroanisole on reaction with sodamide in liquid ammonia gives P-anisidine.

   e)   Addition of Br_2 to cis 2 - butene is stereospecific.
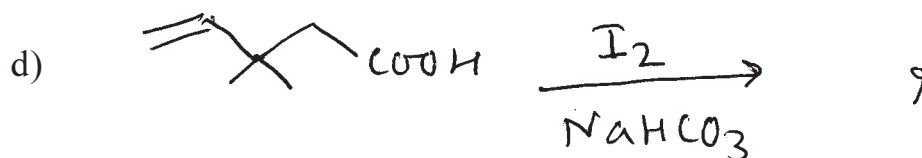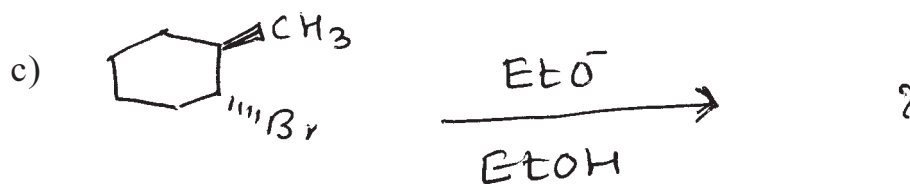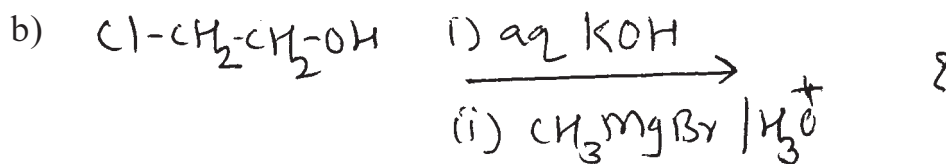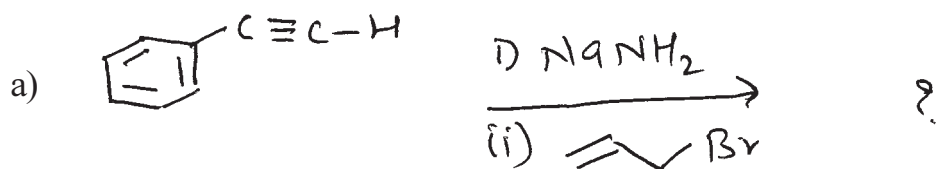
Q2) Write a short note on any three of the following: **[12]**

   a)   Crown ether.

   b)   SNi mechanism.

   c)   Proton Sponges.
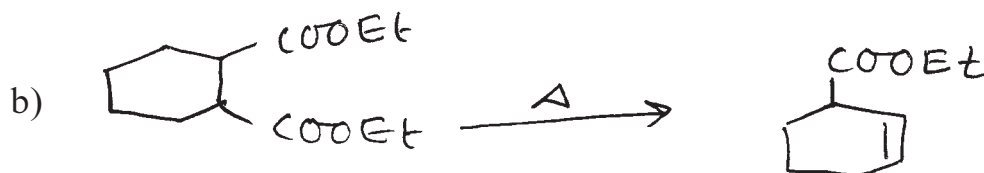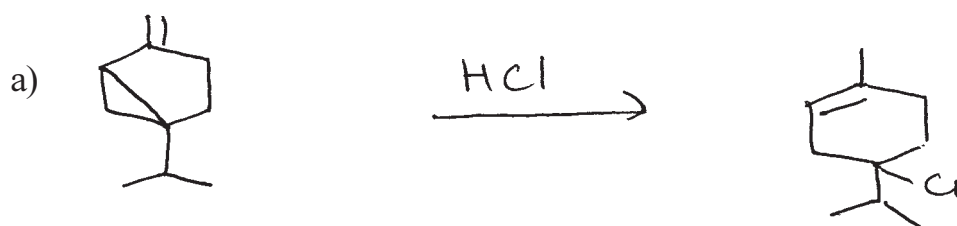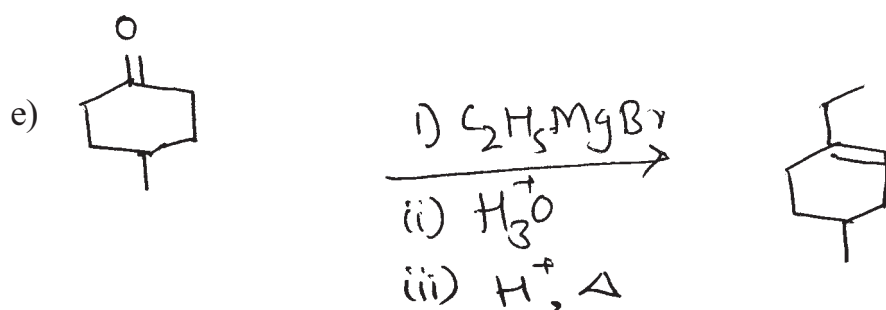
   d)   Non classical carbocation.

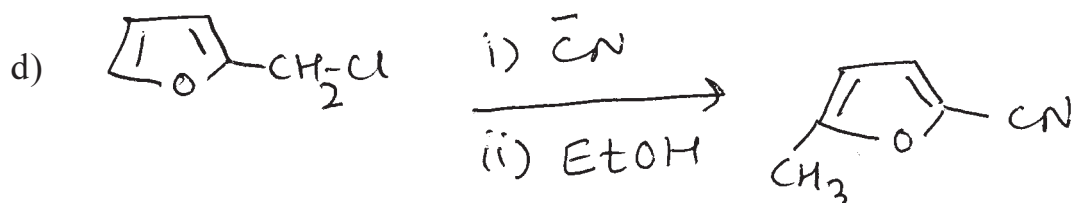*P.T.O.*

Q3) Predict the product/s with mechanism for <u>any three</u> of the following: **[12]**

a) Phenylacetylene ($C\equiv C-H$ on benzene ring)
$$\xrightarrow[\text{ii)} \diagup\!\!\diagdown Br]{\text{i) } NaNH_2} \quad ?$$

b) $Cl-CH_2-CH_2-OH$
$$\xrightarrow[\text{ii) } CH_3MgBr \,|\, H_3O^+]{\text{i) aq KOH}} \quad ?$$

c) (cyclohexane with CH_3 and Br substituents)
$$\xrightarrow[\text{EtOH}]{EtO^-} \quad ?$$

d) (alkene-substituted $COOH$ compound)
$$\xrightarrow[NaHCO_3]{I_2} \quad ?$$

<div align="center"><u>SECTION - II</u></div>

Q4) Suggest the mechanism for <u>any four</u> of the following. **[12]**

a) (bicyclic structure with isopropyl group)
$$\xrightarrow{HCl}$$
(cyclohexene structure with Cl and isopropyl group)

b) (cyclohexane with two $COOEt$ groups)
$$\xrightarrow{\Delta}$$
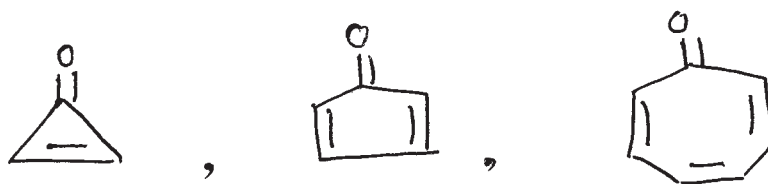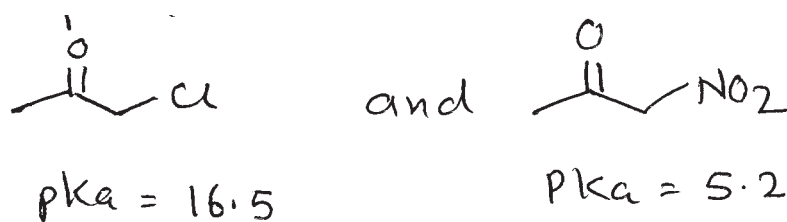(cyclopentene with $COOEt$ group)

c)

d)

e)

Q5) Attempt any four of the following: [12]

a) Explain stability order of the following compounds.


b) Explain the PKa values of the following compounds.

pka = 16.5   Pka = 5.2

c) Cis 4 - hydroxy cyclohexane carboxylic acid lactorized on heating but trans does not explain.

d) What are Lewis acids? Give uses of Lewis acids in organic synthesis.

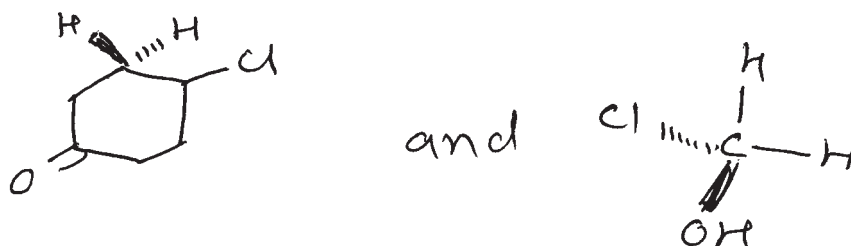e) Electrophilic as well as nucleophilic substitutions of naphthalene occurs at α- position. Explain.

Q6) Attempt any eight of the following. [16]
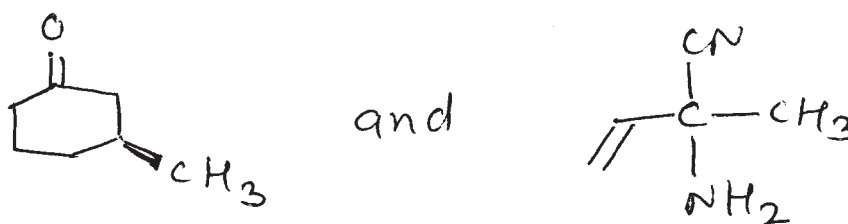
a) Assign EIZ confiquration of the following.
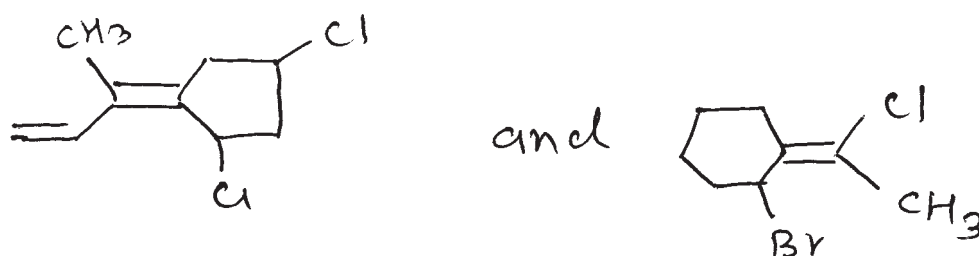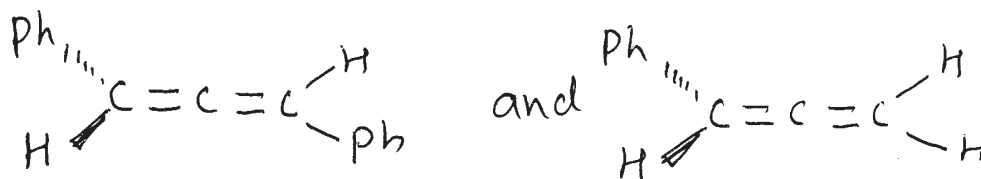

b) Assign pro R/S of the following.
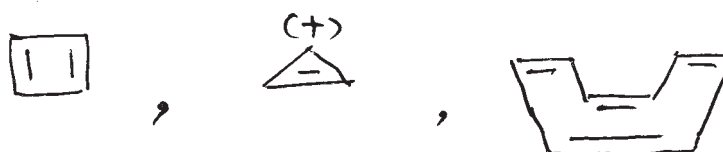

c) Assign R/S confiquration of the following.

d) Draw the resonance structures of the following.

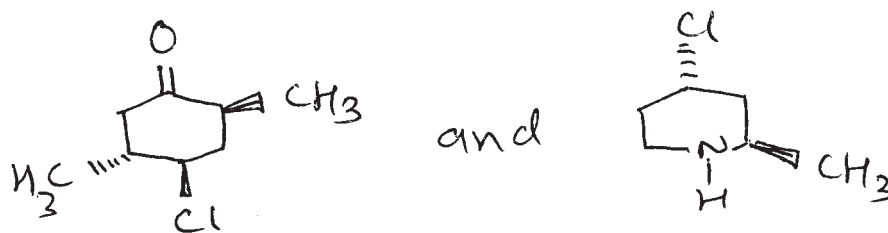e) Which of the following compound is optically active?

f) Identify aromatic, antiaromatic and nonaromatic compounds of the following.

g) Write a short note on hydrogen banding.

h) Acetamide is neutral but pthalamide is acidic. Explain.

i) Assign total number of sterco - isomers of the following.

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M.Sc. - I

PHYSICAL CHEMISTRY

CH - 210 : Physical Chemistry - II

(2008 Pattern) (Semester - II) (Old)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) Answers to the two sections should be written in separate answer books.

2) All questions are compulsory.

3) Figures to the right side indicate full marks.

4) Use of Logarithmic table / calculator is allowed.

5) Neat diagrams must be drawn wherever necessary.

<u>Physico - Chemical Constants</u>

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6.	Gas Constant	R	=	8.314×10^{7} erg K^{-1} mol^{-1}
			=	8.314 J K^{-1} mol^{-1}
			=	1.987 cal K^{-1} mol^{-1}
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			=	2.997×10^{8} m s^{-1}
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11.	Bohr magneton	β_e	=	-9.274×10^{-24} J T^{-1}
12.	Nuclear magneton	β_n	=	5.051×10^{-27} J T^{-1}
13.	Mass of an electron	m_e	=	9.11×10^{-31} kg

SECTION - I

Q1) Attempt any three of the following: **[15]**

a) What do you mean by beak broadening? Explain collision and Doppler broadening.

b) Distinguish between simple harmonic oscillator and anharmonic oscillator with respect to energy equation, section rule and energy curve.

c) Discuss the principles of fluorescence, phosphore scence and ESR.

d) What is Raman Scattering? Describe the quantum theory of Raman effect.

e) How many fundamental modes of vibrations are there for a linear and non-linear molecule made up of 'N' atoms? Depict the change in dipole proanced by each vibration of water molecule.

Q2) Attempt any three of the following: **[15]**

a) Discuss the different processes by which an electronically excreted molecule can lose energy.

b) State and explain the Franck-Condon principle. How can one explain the intensity of vibrational electronic spectra.

c) Derive the equation $I = \mu v^2$ for a rigid diatomic molecule and sketch the allowed rotational energy levels.

d) Explain the principle of NMR spectroscopy and give its application.

e) Discuss the Raman activity of vibrations with the help of polarizability ellipsoid and polarizability plots of CO_2 molecule.

Q3) Solve any two of the following: **[10]**

a) The fundamental vibration frequency of HCl is 2989 cm^{-1}. Find the force constant of HCl bond.

b) The average spacing between successive rotational lines of CO molecule is 3.8662 cm^{-1}. Determine the transitions which gives the most intense spectral line at 318K.

c) When 30.61 ev radiation is used to produce photo electron spectra of neon, photoelectrons of kinetic energy 1.5 eV have been emitted calculate the ionization energy of these electrons in R J mol^{-1}.

(Given : 1 eV = 9.635×10^4 J mol^{-1})

SECTION - II

Q4) Attempt any three of the following: **[15]**

    a) Give an account of compton effect.

    b) Explain the principle of neutron activation analysis. Give its applications.

    c) Write a note on India's nuclear energy programme.

    d) Derive Fermi's four factor formula for a nuclear reactor.

    e) Explain scintillation counter.

Q5) Attempt any three of the following: **[15]**

    a) Write a note on radiolysis of water.

    b) Explain isotope dilution and reverse isotope dilution analysis.

    c) What is diffusion? Explain zone diffusion technique.

    d) How can radio-isotopes be employed to understand extent of wear and tear of machines?

    e) Explain natural and artificial synthesis of ^{14}C.

Q6) Solve any two of the following: **[10]**

    a) A radioactive sample decays to 40% of its original in 12.6 days calculate the radioactivity of 0.69 g of sample if the only isotope present in the sample is 32p.

    b) One litre halide mixture was analyzed for its iodide content 2cm^3 of labelled Iodine having a specific activity 21 cps/cm^3 was added to this mixture. After proper mixing 2 cm^3 of pure iodide was separated which showed the activity of 400 counts for 10 minutes. Find the percentage of iodide in the mixture.

    c) Fission energy due to single atom of 235 U is 200 MeV. Calculate the power released during the fission of 1 kg 235 U in 1 day.

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[5323] - 22

M.Sc.-I (Inorganic Chemistry)
CH - 230 : INORGANIC CHEMISTRY - II
(2008 Pattern) (Semester - II)

Time : 3 Hours]   *[Max. Marks : 80*
Instructions to the candidates:
1) *All questions are compulsory.*
2) *Answers to the two sections should be written in separate answer books.*
3) *Use of log tables and calculator is allowed.*
4) *Figures to the right indicate full marks.*
5) *Draw neat diagrams wherever necessary.*

SECTION-I

Q1) Attempt any three of the following :   **[15]**

   a)   Calculate the total degeneracy of the following :

       i) $S'P'$

       ii) 5_H

       iii) 6_G

       iv) 5_D

       v) $2\ {}^6T_{29}$

   b)   What is Laporte selection rule for electronic transitions? Explain relaxation in it using example.

   c) $[NiCl_4]^{2-}$ complex ion is more intense in colour than $[Ni(H_2O)_6]^{2+}$. Explain.

   d)   Prepare a microstate table for P^2 configuration and find at G.S.

   e)   Give the splitting of 5_D form in weak cubic field using character table for pure rotational point group 'O'.

Q2) Attempt any three of the following :   **[15]**

   a)   Give the full spectroscopic symbol for the G.S. term for following ions :

       i) V^{2+}

       ii) Cr^{2+}

       iii) Mn^{2+}

       iv) Co^{2+}

       v) Zn^{2+}

b) Write a note on chemiluminescence in compounds.

c) Explain which of the following complexes show orbital contribution to magnetic moment. Justify.

   i) $[Mn\ F_6]^{4-}$

   ii) $[Fe(H_2O)_6]^{2+}$

d) Classify the following configurations as A, E or T in complexes having oh symmetry.

   i) $t2g^6, eg^1$

   ii) $t2g^2$

   iii) $t2g^1$

   iv) $t2g^3, eg^2$

e) What will be the possible transitions in the complexes?

   i) $[Ti\ (H_2O)_6]^{2+}$

   ii) $[Cr\ (NO_2)_6]^{3-}$

Q3) Attempt any two of the following : **[10]**

a) Write a note on 'charge transfer spectra'.

b) The octahedral complex of Cu(II) shows effective magnetic moment of 2.018 B.M. Calculate 10Dq if $\lambda = -830\ cm^{-1}$.

c) Calculate the values of Dq, B, β and $\beta°$, if the electronic spectrum of Ni(II) octahedral complexes shows $v_1 = 10750$, $v_2 = 17500$ and $v_3 = 28200\ cm^{-1}$. (B° = 1030 cm^{-1})

SECTION-II

Q4) Attempt any three of the following : **[15]**

a) What are the functions of metalloproteins?

b) What are the binding sites of amino acids which are used for metal binding?

c) Explain the importance of porphyrin and corrin as ligands.

d) Comment on natural selection of element used in bioinorganic chemistry.

e) Describe the chelate effect with respect to complexes.

Q5) Write short notes : any three of the following :   [15]
  a)   Siderophores
  b)   Calmodulin
  c)   Mo cofactor
  d)   Apotransferin
  e)   Irving-William series

Q6) Draw the structure of any five :   [10]
  a)   Adenin
  b)   4 Fe – 4s
  c)   Uracil
  d)   Porphyrin
  e)   Oxyhaemoglobin

Direct Products

1. **Group of the form G xi or G x σh**
   The g, u, or '," additions to the IR symbol in this group satisfy
   g x g = u x u = g, g x u = u, 'x' = "x"=

2. **Product of the form A x A, B x B, A x B**
   For all groups:
   Letter Symbol: A x A =A, B x B = A , A x B = B
   Subscript: 1 x 1 = 1, 2 x 2 = 1, 1 x 2 = 2
   Except for the B representations of D_2 and D_2 where
   B x B = B, and 1 x 2 = 3, 2 x 3 = 1, 3 x 1 = 2

3. **Products of the forms: A x E, B x E:**
   (a) For all groups $A \times E_k = E_k$ irrespective of the suffix on A.
   (b) For all groups except D_4d, D_4d, S_8:
   $B \times E_1 = E_2$, $B \times E_2 = E_1$
   irrespective of the suffix on B (If the group has only one B representative
   put $E_1 = E_2 = E$)
   (c) For D_4h:
   $B \times E_1 = E_3$, $E \times E_2 = E_3$, $B \times E_3 = E_3$, $B \times E_2 = E_2$, $B \times E_3 = E_1$
   Irrespective of the suffix on B:
   (d) For D_4d, S_8:
   $B \times E_1 = E_3$, $B \times E_2 = E_2$, $B \times E_3 = E_1$
   Irrespective of the suffix on B:

4. **Products of the form E x E:**
   (For groups which have A, B, or E symbols without suffixes put $A_1 = A_2 = A$,
   etc in the equation below)
   (a) For Oh, O, T_3, D_6h, D_2, C_6v, C_6h, C_6, S_6, D_2d, D_2h, D_3, C_2, C_3h, C_3:
   $E_1 \times E_1 = E_2 \times E_2 = A_1 + A_2 + B_2$; $B_1 \times E_2 = B_1 + B_2 + E_1$
   (b) For D_4h, D_4, C_4v, C_4h, C_4, S_4, D_2d:
   $E \times E = A_1 + A_2 + B_1 + B_2$.
   (c) For D_6d:
   $E_1 \times E_1 = E_3 \times E_3 = A_1 + A_2 + Eg$
   $E_2 \times E_2 = E_4 \times E_4 = A_1 + A_2 + Eg$
   $E_3 \times E_3 = A_1 + A_1 + B_1 + B_2$
   $E_1 + E_2 = E_4 + E_3 = E_1 + E_3$, $E_1 \times E_3 = E_3 \times E_1 = E_2 + E_1$,
   $E_1 + E_4 = E_2 + E_3 = E_3 + E_3$, $E_2 \times E_3 = E_3 \times E_4 = E_1 + E_3$,
   $E_1 + E_3 = B_4 + B_2 + E_4$, $E_2 \times E_4 = B_1 + B_2 + E_2$.
   (d) D_5d, D_2h, D_3, C_3v, C_3h, C_3:
   $E_1 \times E_1 = A_1 + A_2 + E_2$, $E_2 \times E_2 = A_1 + A_2 + E_1$
   $E_1 \times E_2 = E_1 + E_2$
   (e) For D_4d, S_8
   $E_1 \times E_1 = E_3 \times E_3 = A_1 + A_2 + E_2$
   $E_2 \times E_2 = A_1 + A_2 + B_1 + B_2$
   $E_1 \times E_2 = E_2 \times E_3 = E_1 + E_3$, $E_1 \times E_3 = B_1 + B_2 + E_2$

5. **Product involving the T (or F) representation of Oh, O, Td:**
   $A_1 \times T_1 = T_1$, $A_1 \times T_2 = T_2$, $A_2 \times T_1 = T_2$, $A_2 \times T_2 = T_1'$
   $E \times T_1 = E \times T_2 = T_1 + T_2$,
   $T_1 \times T_2 = A_2 + E + T_1 + T_2$.

   $T_1 \times T_1 = T_2 \times T_2 = A_1 + E + T_1 + T_2$

6. To Complete result for O are

O	A_1	A_2	E	T_1	T_2
A_1	A_1	A_2	E	T_1	T_2
A_2	A_2	A_1	E	T_2	T_1
E	E	E	A_1+A_2+E	T_1+T_2	T_1+T_2
T_1	T_1	T_2	T_1+T_2	$A_1+E+T_1+T_2$	$A_2+E+T_1+T_2$
T_2	T_2	T_1	T_1+T_2	$A_2+E+T_1+T_2$	$A_1+E+T_1+T_2$

Character Table for O rotational group

O	E	$6C_4$	$3C_2(=C_4^2)$	$8C_3$	$6C_2$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	-1	1	1	-1		
E	2	0	2	-1	0		$(x^2-y^2, 2z^2-x^2-y^2)$
T_1	3	1	-1	0	-1	$(R_x,R_y,R_z);(x,y,z)$	
T_2	3	-1	-1	0	1		(xy, xz, yz)

Correlation table for group Oh

Oh	O	Td	D_4h	D_2d	C_4v	C_2v	D_3d	D_3	C_2h
A_1g	A_1	A_1	A_1g	A_1	A_1	A_1	A_1g	A_1	Ag
A_2g	A_2	A_2	B_1g	B_1	B_1	A_2	A_2g	A_2	Bg
Eg	E	E	A_1g+B_1g	A_1+B_1	A_1+B_1	A_1+A_2	Eg	E	Ag+Bg
T_1g	T_1	T_1	A_2g+E_g	A_2+E	A_2+E	$A_2+B_1+B_2$	A_2g+Eg	A_2+E	Ag+2Bg
T_2g	T_2	T_2	B_2g+Eg	B_2+E	B_2+E	$A_1+B_1+B_2$	A_1g+Eg	A_1+E	2Ag+Bg
A_1u	A_1	A_1	A_1u	B_1	A_2	A_2	A_1u	A_1	Au
A_2u	A_2	A_1	B_1u	A_1	B_2	A_1	A_2u	A_2	Bu
Eu	E	E	A_1u+B_1u	A_1+B_1	A_2+B_2	A_1+A_2	Eu	E	Au+Bu
T_1u	T_1	T_2	A_2u+Eu	B_2+E	A_1+E	$A_1+B_1+B_2$	A_2u+Eu	A_1+E	Au+2Bu
T_2u	T_2	T_1	B_2u+Eu	A_2+E	B_1+E	$A_2+B_1+B_2$	A_1u+Eu	A_1+E	2Au+Bu

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M.Sc. - I

ORGANIC CHEMISTRY

CH-250: Synthetic Organic Chemistry and Spectroscopy

(2008 Pattern) (Semester - II)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

   1)   *All questions are compulsory.*

   2)   *Figures to the right indicate full marks.*

   3)   *Answers to the two sections to be written in separate answer books.*

SECTION - I

Q1) Explain <u>any four</u> of the following: **[16]**

   a)   Explain the role of peracid in epoxidation and lactonization reactions.

   b)   Give the significance of Reformatsky reaction.

   c)   What are phosphorous ylides? Explain with suitable example.

   d)   Wolf rearrangement is used to prepare higher homologue of carboxylic acid. Explain.

   e)   Explain 'Swern Oxidation'.

Q2) Write short notes on any three of the following: **[12]**

   a)   Generation and reactivity of carbene.

   b)   Organo copper reagents in organic synthesis.

   c)   Simmon-Smith reaction.

   d)   Synthetic applications of DIBAL-H.

Q3) Predict the products and suggest the mechanism for any four of the following: **[12]**
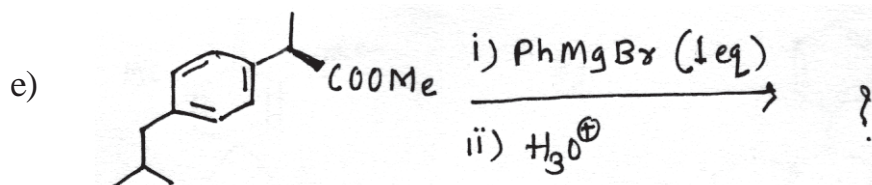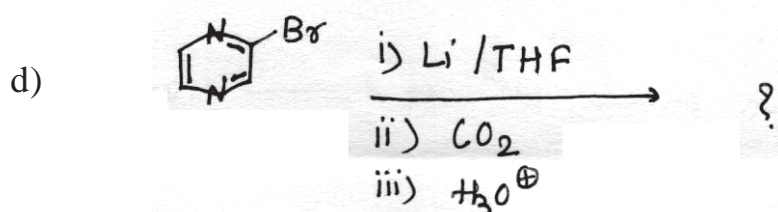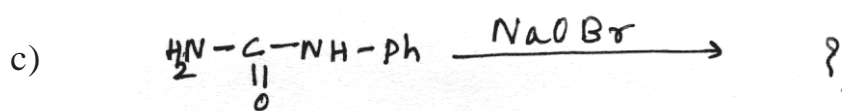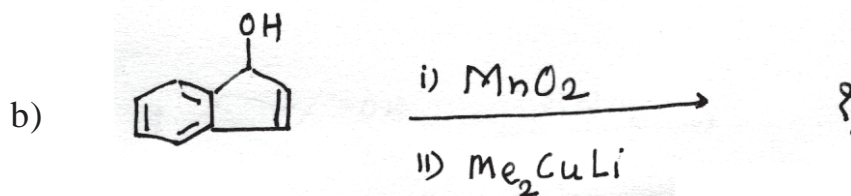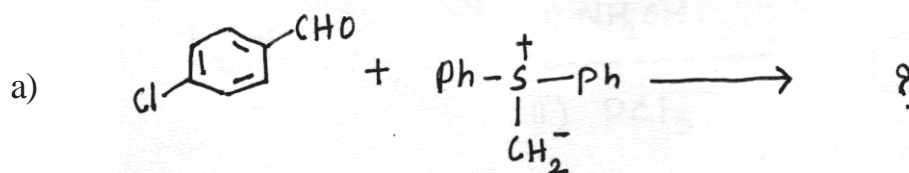
a)

4-Cl-C₆H₄-CHO + $Ph-\overset{+}{\underset{CH_2^-}{S}}-Ph$ ⟶ ?

b)

OH (indenol)
$\xrightarrow{\begin{array}{c} i)\ MnO_2 \\ ii)\ Me_2CuLi \end{array}}$?

c)

$H_2N-\overset{O}{\underset{\|}{C}}-NH-Ph \xrightarrow{NaOBr}$?

d)

(pyridine-Br) $\xrightarrow{\begin{array}{c} i)\ Li\ /THF \\ ii)\ CO_2 \\ iii)\ H_3O^{\oplus} \end{array}}$?

e)

COOMe $\xrightarrow{\begin{array}{c} i)\ PhMgBr\ (1\ eq) \\ ii)\ H_3O^{\oplus} \end{array}}$?

SECTION - II

Q4) Suggest the mechanism for <u>any four</u> of the following: **[12]**

a)

$\xrightarrow{O_3}$ CHO ... CHO

b)

Br $\xrightarrow{\begin{array}{c} Bu_3SnH \\ AIBN \end{array}}$

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c)

d)

e)
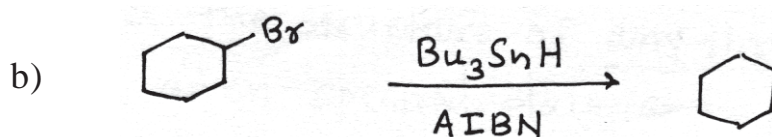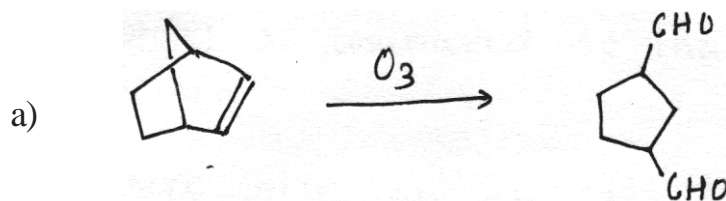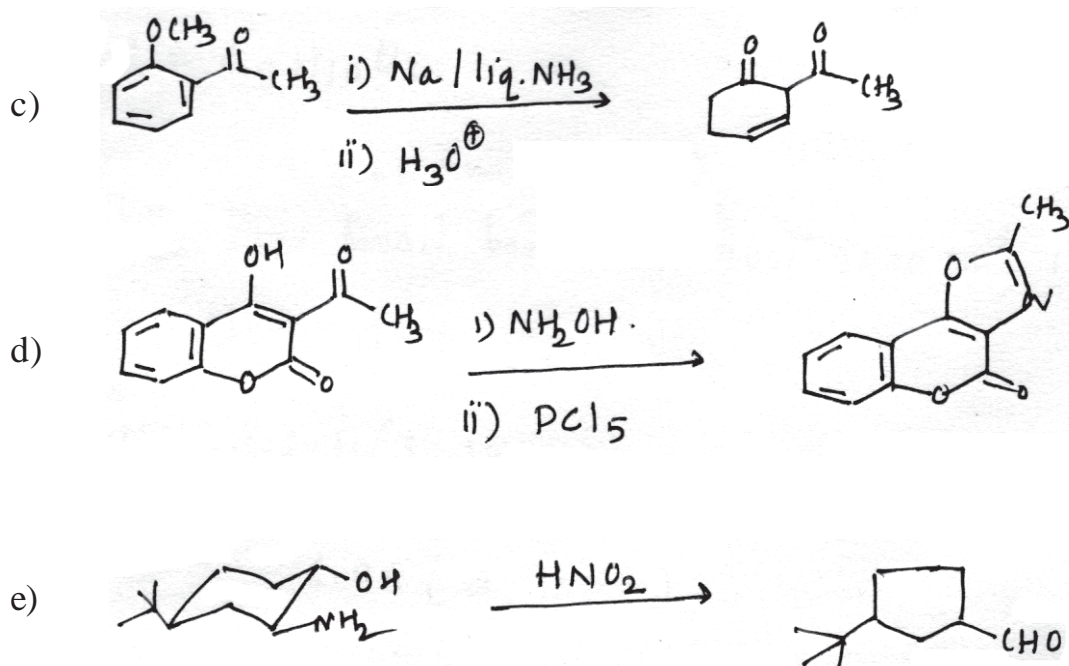
Q5) Attempt <u>any four</u> of the following: **[16]**

a) How will you monitor the following conversion by IR.
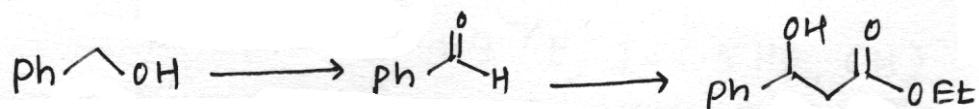
b) Calculate λ_{max} for the following compounds.

i)   ii)
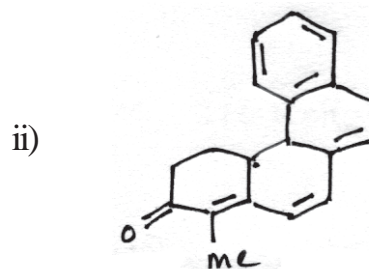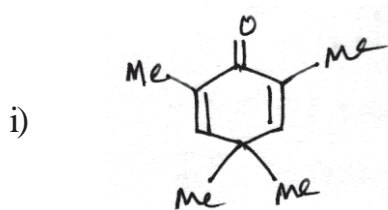
c) Explain fundamental vibrations and overtones.

d) ^{1}H-NMR spectrum of acetonitrile shows shielded protons as compared to that of dichloromethane. Explain.

e) Write note on anisotropic effect.

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Q6) Deduce the structure of <u>any three</u> of the following using given spectral data and justify your answer. **[12]**

a) M.F. = $C_9H_{10}O_2$
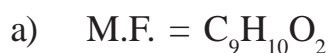
UV = 253, 265 nm ($\in$ 220)

IR = Very broad bands at 3000-3400 cm^{-1}, 1710, 1600, 1500, 924 cm^{-1}.

^{1}H-NMR: δ = 2.11(s, 15 mm)

3.48 (s, 10 mm)

6.98 (d, 10 mm)

7.12 (d, 10 mm)

12.4 (s, 5 mm, D_2O Exchangeable).

b) M.F. = $C_7H_{12}O_4$
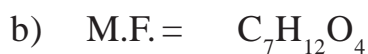
IR = 1742 cm^{-1}

^{1}HNMR: δ = 1.3 (t, J = 6.5 Hz, 6H)

2.6 (s, 2H)

4.16 (q, J = 6.5 Hz, 4H)

c) M.F. = $C_4H_5O_2N$
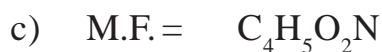
UV = Featherless above 210 nm.

IR = 2250, 1750 cm^{-1}

^{1}HNMR : δ = 3.5 (s, 2H)

3.8 (s, 3H)

d) M.F. = $C_6H_{18}O$
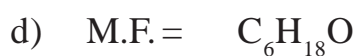
IR = 1700, 1620 cm^{-1}

PMR: δ =1.90 (s, 3H)

2.10 (s, 6H)

6.0 (s, 1H)

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M.Sc.-II
PHYSICAL CHEMISTRY
CH-310: Quantum Chemistry & Solid State Chemistry
(2008 Pattern) (Semester-III) (Old)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:
1) *Answer to the TWO sections should be written in SEPARATE answer books.*
2) *All questions are COMPULSORY.*
3) *Figures to the RIGHT SIDE indicate full marks.*
4) *Use of logarithmic table, calculator is ALLOWED.*
5) *Neat diagrams must be drawn WHEREVER necessary.*

Physico-Chemical Constants

1)	Avogadro Number	N $= 6.022 \times 10^{23}$ mol^{-1}
2)	Boltzmann Constant	k $= 1.38 \times 10^{-16}$ erg K^{-1} molecule^{-1}
		$= 1.38 \times 10^{-23}$ JK^{-1} molecule^{-1}
3)	Planck Constant	h $= 6.626 \times 10^{-27}$ erg s
		6.626×10^{-34} Js
4)	Electronic Charge	e $= 4.803 \times 10^{-10}$ esu
5)	1 eV	$= 1.602 \times 10^{-19}$ C
		$= 23.06$k cal mol^{-1}
		$= 1.602 \times 10^{-12}$ erg
		$= 1.602 \times 10^{-19}$ J
		$= 8065.5$ cm^{-1}
6)	Gas Constant	R $= 8.314 \times 10^{-7}$ ergK^{-1} mol^{-1}
		$= 8.314$ JK^{-1}mol^{-1}
		$= 1.987$ cal K^{-1}mol^{-1}
7)	Faraday Constant	F $= 96487$ equiv^{-1}
8)	Speed of light	c $= 2.997 \times 10^{10}$ cm s^{-1}
		$= 2.997 \times 10^{8}$ cm s^{-1}
9)	1 cal	$= 4.184 \times 10^{7}$ erg
		$= 4.184$ J
10)	1 amu	$= 1.673 \times 10^{-27}$ kg
11)	Bohr magneton	$\beta_e = -9.274 \times 10^{-24}$ J T^{-1}
12)	Nuclear magneton	$\beta_n = 5.051 \times 10^{-27}$ J T^{-1}

P.T.O.

13) Mass of an electron $m_e = 9.11 \times 10^{-31}$ kg

SECTION-I

Q1) Attempt any four of the following : [20]

a) Explain the properties of ladder operators

b) Formulate the energy operators for H_2 molecule and H_2^- ion

c) Show that $[\hat{L}_x, \hat{L}_z] = -i\hbar \hat{L}_y$ for a set of angular momentum operators $\hat{L}_x, \hat{L}_y$ and $\hat{L}_z$.

d) Which of the following functions are eigen functions of the operator $\frac{d^2}{dx^2}$?

   i) $\text{Sin } 4x$

   ii) $\text{Cos } 3x$

   iii) x^{-3}

   Give the corresponding eigen values.

e) State and prove the variation theorem.

f) State the fundamental postulates of quantum mechanics.

Q2) Attempt any four of the following : [20]

a) Discuss Huckel's 4m+2 rule citing benzene and cyclo-octatetraene as examples.

b) Comment giving examples on the positive or negative nature of REPE value for a molecule.

c) Give the comparison between perturbation and variation methods.

d) Deduce the secular determinant for ethene and Obtain the HMO energy values for molecule.

e) How Hess and schaad improved Huckel's calculations for M.O. energies?

f) Derive the expression for the first order correction to the energy of the

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non degenerate unperturbed level.

SECTION-II

Q3) Attempt any three of the following : **[15]**

a) Derive the expression for the Frenkel defects in a crystal at a given temperature.

b) Comment on the effect of temperature on carrier density and conductivity of n-type extrinsicsemiconductor.

c) Write a note on-mechanism of a photographic process.

d) Discuss the mechanism of diffusion in crystalline solids.

e) Distinguish between the resistivities of annealed and on annealed Cu-Au alloys.

Q4) Attempt any three of the following : **[15]**

a) State and explain the various methods of electric breakdown in insulators.

b) Explain the parabolic rate low used to explain the mechanism of gas-solid reactions.

c) The fast growing faces are eliminated whereas slow growing faces persist in a crystal, prove this statement on the basis of geometrical considerations.

d) Write a note on : Taylor-Orowan dislocations.

e) Define 'Colour centre' and explain the fermation of F and V colour centres in crystal.

Q5) Solve any two of the following : **[10]**

a) Calculate the dislocation density for a cubic crystal having 10^{-6} cm edge length and total dislocation length of 10^{-12} cm.

b) Calculate the number of electrons per cm^3 in the conduction band of semiconductor having a bandgap of 0.72 eV at 27°C.

c) If 2 eV is the energy required for the pair of ions to move from the crystal's interior to the surface, What is the proportion of vacancies (n/N) present at 400K?

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M.Sc.

PHYSICAL CHEMISTRY

CH-311: Nuclear and Radiation Chemistry

(2008 Pattern) (Semester - III)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) *Answers to the two sections should be written in separate answer books.*
2) *All questions are compulsory.*
3) *Figures to the right side indicate full marks.*
4) *Use of logarithmic table/calculator is allowed.*
5) *Neat diagrams must be drawn wherever necessary.*

Physico - Chemical Constants

1.	Avogadro Number	N	$= 6.022 \times 10^{23} \text{ mol}^{-1}$
2.	Boltzmann Constant	k	$= 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1}$
			$= 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1}$
3.	Planck Constant	h	$= 6.626 \times 10^{-27} \text{ erg s}$
			$= 6.626 \times 10^{-34} \text{ J s}$
4.	Electronic Charge	e	$= 4.803 \times 10^{-10} \text{ esu}$
			$= 1.602 \times 10^{-19} \text{ C}$
5.	1 eV		$= 23.06 \text{ k cal mol}^{-1}$
			$= 1.602 \times 10^{-12} \text{ erg}$
			$= 1.602 \times 10^{-19} \text{ J}$
			$= 8065.5 \text{ cm}^{-1}$
6.	Gas Constant	R	$= 8.314 \times 10^{7} \text{ erg K}^{-1} \text{ mol}^{-1}$
			$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
			$= 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$
7.	Faraday Constant	F	$= 96487 \text{ C equiv}^{-1}$
8.	Speed of light	c	$= 2.997 \times 10^{10} \text{ cm s}^{-1}$
			$= 2.997 \times 10^{8} \text{ m s}^{-1}$
9.	1 cal		$= 4.184 \times 10^{7} \text{ erg}$
			$= 4.184 \text{ J}$
10.	1 amu		$= 1.673 \times 10^{-27} \text{ kg}$
11.	Bohr magneton	β_e	$= -9.274 \times 10^{-24} \text{ J T}^{-1}$
12.	Nuclear magneton	β_n	$= 5.051 \times 10^{-27} \text{ J T}^{-1}$
13.	Mass of an electron	m_e	$= 9.11 \times 10^{-31} \text{ kg}$

SECTION-I

Q1) Attempt <u>any three</u> of the following: **[15]**

    a)   Discuss the applications of semiempirical mass equation.

    b)   Describe the process of nuclear fission. What are the prompt & delayed neutrons?

    c)   Derive an expression for infinite medium multiplication factor.

    d)   Discuss the characteristics of thermal, fast & intermediate reactors.

    e)   Discuss the principle & working of breeder reactor.

Q2) Attempt <u>any three</u> of the following: **[15]**

    a)   What are the basic components of accelerator?

    b)   Discuss with suitable examples various types of nuclear reactions.

    c)   Discuss the various types of moderators & coolants used in nuclear reactors.

    d)   Discuss the portulates of Bohr's theory of compound nucleus.

    e)   Discuss the principle of particle induced 'χ' ray emission technique.

Q3) Attempt <u>any two</u> of the following: **[10]**

    a)   Calculate the binding energy of the two last neutrons in ^{37}Cl. [Given: the mass difference bet^{h} $^{35}_{63}$Cl & ^{37}Cl is 1.9970 amu].

    b)   Calculate the spin & parity of $^{63}_{30}$Zn & $^{52}_{23}$V .

    c)   Calculate the energy level density in ^{63}Cu excited to 8MeV. Given: Fermi gas model constant c = 0.3 MeV^{-1} & α = 2.0 MeV^{-1}.

SECTION-II

Q4) Attempt <u>any three</u> of the following: **[15]**

a) Discuss the mechanism of radiation annealing.

b) Write a note on "Chernobyl accident".

c) Discuss the various stages of interaction of radiation with biological cells.

d) Discuss the role of pulse height analyzer in scintillation counter.

e) Explain the working of Cockeroft-Walton accelerator.

Q5) Attempt any three of the following: **[15]**

a) Explain the role of cupric ions in ferrous sulphate-cupric sulphate dosimeter.

b) Describe the working of any one personal dosimeter.

c) Enlist various radiation protecting material. How thickness of the protecting material is calculated for reduction of dose.

d) What are the somatic effects of radiations? Give an account of short term and long term effects of radiation.

e) Describe various modes of nuclear retention.

Q6) Solve any two of the following: **[10]**

a) Find out the dose due to 200 mci ^{99m}Tc at a distance of 2m.

   Given: E_r = 140 keV.

b) Find out the thickness of lead needed to decrease the activity of 50,000 cpm from CS-137 source to 12,000 cpm.

   Given: e^{μ} = 0.211 b/e, Z of pb = 82, A of pb = 207, density of lead = 11.35 g cm^{-3}.

c) Find out the dose absorbed by methanol in 2h when exposed to gamma radiation in terms of rads.

   Given: dose absorbed by Fricke solution at same position = 3.2 Gy/min. (Z/A) of Fricke solution = 0.553.

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M.Sc. - II

PHYSICAL CHEMISTRY

CH - 312 : Advanced Instrumental Methods of analysis

(2008 Pattern) (Semester - III)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

    1)   *Answers to the two sections should be written in separate answer books.*

    2)   *All questions are compulsory.*

    3)   *Figures to the right side indicate full marks.*

    4)   *Use of logarithmic table calculator is allowed.*

    5)   *Neat diagrams must be drawn wherever necessary.*

Physico - Chemical Constants

1.	Avogadro Number	N	=	6.022×10^{23} mol^{-1}
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3.	Planck Constant	h	=	6.626×10^{-27} erg s
			=	6.626×10^{-34} J s
4.	Electronic Charge	e	=	4.803×10^{-10} esu
			=	1.602×10^{-19} C
5.	1 eV		=	23.06 k cal mol^{-1}
			=	1.602×10^{-12} erg
			=	1.602×10^{-19} J
			=	8065.5 cm^{-1}
6.	Gas Constant	R	=	8.314×10^{7} erg K^{-1} mol^{-1}
			=	8.314 J K^{-1} mol^{-1}
			=	1.987 cal K^{-1} mol^{-1}
7.	Faraday Constant	F	=	96487 C equiv^{-1}
8.	Speed of light	c	=	2.997×10^{10} cm s^{-1}
			=	2.997×10^{8} m s^{-1}
9.	1 cal		=	4.184×10^{7} erg
			=	4.184 J
10.	1 amu		=	1.673×10^{-27} kg
11.	Bohr magneton	β_e	=	-9.274×10^{-24} J T^{-1}
12.	Nuclear magneton	β_n	=	5.051×10^{-27} J T^{-1}
13.	Mass of an electron	m_e	=	9.11×10^{-31} kg

P.T.O.

SECTION - I

Q1) Attempt any three of the following : **[15]**

  a) Describe a typical *x*-ray absorption spectrum and write Beer's law for *x*-ray absorption.

  b) What is photoluminescene? Describe the apparatus for it.

  c) Explain the 'S' route and 'T' route mechanism for electro-chemiluminescene.

  d) Write activation equation of NAA and explain the terms involved in it.

  e) What is *x*-ray fluorescence? Describe the apparatus for measuring x-ray fluorescence.

Q2) Answer any three of the following : **[15]**

  a) Explain the working of time of flight analyzer used in mass spectrometry.

  b) Describe electron-bombardment ionization source in mass spectrometer.

  c) What are the parameters considered while selecting an optimum nuclear reaction in NAA.

  d) Describe in brief the applications of photoluminescene.

  e) What is energy dispersive device? Explain briefly genionization detector.

Q3) Solve any two of the following : **[10]**

  a) The mass absorption coefficient for Ni measured with CuKα line is 49.2 cm^2/g. Calculate the thickness of nickel, nickel foil that was found to transmit 47.8% of incident power of beam of CuKα radiation. The density of Ni is 8.90 g/cm^2.

  b) What weight of the alloy should be taken which contain 2% gold if the irradiation period is 2 days in a neutron flux of 1.8 x 10^7 n cm^{-2} s^{-1} and desired activity after a cooling period of 1 day is 500 [given - γ = 100%, σ = 98.8 b, ty$_2$ of 198 Au = 2.7 days counting efficiency = 20%].

  c) Calculate the kinetic energy that a singly charged ion (z = 1) will acquire if it is accelerated through potential of 10^{3}V in electron bombardment ion source.

SECTION - II

Q4) Answer any three of the following : **[15]**

a) What is plasma ? Describe with neat diagram a typical ICP source.

b) Write a note on power compensated DSC.

c) What is cyclic voltammetry ? Draw and explain the typical cyclic voltammogram.

d) Describe the applications of coulometric titrations.

e) Describe energy level diagram for the sample and spectrometer in ESCA.

Q5) Answer any three of the following : **[15]**

a) Explain the terms
   i) Binding energy
   ii) Fermi energy
   iii) Work function
   iv) Kinetic energy of ejected electron with suitable energy level diagram.

b) Discuss the factors affecting DTA curves.

c) Discuss current voltage relationship in coulometric technique.

d) Write a short note on hydrodynamic voltammetry.

e) Discuss briefly applications of ICP - AES techniques

Q6) Solve any two of the following : **[10]**

a) Calculate time required for constant current of 0.75 A to deposit 0.270 g of $C_O(II)$ as an element on cathode assuming 100% current efficiency.

b) The work function of a spectrometer is 50 eV. The binding energy of the emitted electron is 1070 eV. If the kinetic energy of the emitted electron is 1.77 eV. Find the wave length of incident - x - ray.

c) The thermal curve of 125.5 mg sample that contained mixture of $MgC_2O_4H_2O$ and thermally stable salt had mass loss of 6.98 mg at an onset temperature of about 140°C corresponding to vaporization of water determine percentage of $MgC_2O_4H_2O$ is sample.

[atomic weight - Mg = 24, C=12, O=16, H-1.0]

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M.Sc. - II
PHYSICAL CHEMISTRY
CH - 314 : Polymer Chemistry
(2008 Pattern) (Semester - III) (Old)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

  1) *Answers to the two sections should be written in separate answer books.*
  2) *All questions are compulsory.*
  3) *Figures to the right side indicate full marks.*
  4) *Use of logarithmic table / calculator is allowed.*
  5) *Neat diagrams must be drawn wherever necessary.*

Physico - Chemical Constants

1.	Avogadro Number	N	=	6.022×10^{23} mol^{-1}
2.	Boltzmann Constant	k	=	1.38×10^{-16} erg K^{-1} molecule^{-1}
			=	1.38×10^{-23} J K^{-1} molecule^{-1}
3.	Planck Constant	h	=	6.626×10^{-27} erg s
			=	6.626×10^{-34} J s
4.	Electronic Charge	e	=	4.803×10^{-10} esu
			=	1.602×10^{-19} C
5.	1 eV		=	23.06 k cal mol^{-1}
			=	1.602×10^{-12} erg
			=	1.602×10^{-19} J
			=	8065.5 cm^{-1}
6.	Gas Constant	R	=	8.314×10^{7} erg K^{-1} mol^{-1}
			=	8.314 J K^{-1} mol^{-1}
			=	1.987 cal K^{-1} mol^{-1}
7.	Faraday Constant	F	=	96487 C equiv^{-1}
8.	Speed of light	c	=	2.997×10^{10} cm s^{-1}
			=	2.997×10^{8} m s^{-1}
9.	1 cal		=	4.184×10^{7} erg
			=	4.184 J
10.	1 amu		=	1.673×10^{-27} kg
11.	Bohr magneton	β_e	=	-9.274×10^{-24} J T^{-1}
12.	Nuclear magneton	β_n	=	5.051×10^{-27} J T^{-1}
13.	Mass of an electron	m_e	=	9.11×10^{-31} kg

SECTION - I

Q1) Attempt any three of the following: **[15]**

a) Define and explain secondary fond forces in a polymer.

b) Define polydispersity index with a sketch.

c) What is instantaneous polymer composition?

d) Discuss elastomes forming properties of a polymer.

e) Write a note on Zeigler-Natta Catalyst.

Q2) Attempt any three of the following: **[15]**

a) Discuss what is glass transition temperature.

b) Write a note in block and graft co-polymer.

c) Describe the kinetics of condensation polymer.

d) Derive the rate equation for step polymerization in the presence of a catalyst.

e) Distinguish between homopolymers and heteropolymers.

Q3) Solve any two: **[10]**

a) Find the viscosity of a polymer having C = 0.4 g/dl Huggin constant = 0.33.

K = 1.2×10^{-4} α = 0.73 m = 1.2×10^5

b) The relative viscosities of a fraction of polystyrene of $\bar{M}_n = 275000$, in teralin at 20°C were

% conc	0.01	0.05	0.10	0.25
η_r	1.05	1.25	1.59	2.70

Find α.

c) 3 moles of 1, 3 butadiene and 2 moles of vinylchloride are co-polymerized. Find polymar composition at 8.8 : 0.035 reactivity ratios respectively.

[At. wts : C = 12 H = 1 Cl = 35.5]

Q4) Attempt any four of the following: [20]

   a)   Distinguish between condensation and addition polymers.

   b)   Discuss the membrane osmometry technique.

   c)   Describe compression molding.

   d)   Write a note on melt spinning.

   e)   Discuss the use of DTA in polymer analysis. Compare it with IR as an analytical tool.

   f)   How is reinforced plastic made?

Q5) Attempt any four of the following: [20]

   a)   Describe the process of Calendering.

   b)   Write a note on XRD use in polymer analysis.

   c)   Discuss the effects of radiation exposure on polymers.

   d)   Describe the process of dying a fibre.

   e)   Explain what are conducting polymers.

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[5323]-35

M.Sc. - II

PHYSICAL CHEMISTRY

CH - 315 : Special Topics in Physical Chemistry

(2008 Pattern) (Semester - III)

Time : 3 Hours]　　　　　　　　　　　　　　　　　　　*[Max. Marks : 80*

Instructions to the candidates:

　1)　Answers to the two sections should be written in separate answer books.

　2)　All questions are compulsory.

　3)　Figures to the right side indicate full marks.

　4)　Use of logarithmic table / calculator is allowed.

　5)　Neat diagrams must be drawn wherever necessary.

<u>Physico - Chemical Constants</u>

1.	Avogadro Number	N =	6.022×10^{23} mol^{-1}
2.	Boltzmann Constant	k =	1.38×10^{-16} erg K^{-1} molecule^{-1}
		=	1.38×10^{-23} J K^{-1} molecule^{-1}
3.	Planck Constant	h =	6.626×10^{-27} erg s
		=	6.626×10^{-34} J s
4.	Electronic Charge	e =	4.803×10^{-10} esu
		=	1.602×10^{-19} C
5.	1 eV	=	23.06 k cal mol^{-1}
		=	1.602×10^{-12} erg
		=	1.602×10^{-19} J
		=	8065.5 cm^{-1}
6.	Gas Constant	R =	8.314×10^{7} erg K^{-1} mol^{-1}
		=	8.314 J K^{-1} mol^{-1}
		=	1.987 cal K^{-1} mol^{-1}
7.	Faraday Constant	F =	96487 C equiv^{-1}
8.	Speed of light	c =	2.997×10^{10} cm s^{-1}
		=	2.997×10^{8} m s^{-1}
9.	1 cal	=	4.184×10^{7} erg
		=	4.184 J
10.	1 amu	=	1.673×10^{-27} kg
11.	Bohr magneton	β_e =	-9.274×10^{-24} J T^{-1}
12.	Nuclear magneton	β_n =	5.051×10^{-27} J T^{-1}
13.	Mass of an electron	m_e =	9.11×10^{-31} kg

SECTION - I

Q1) Attempt any four of the following: **[20]**

a) Define the terms-catalyst, activity, selectivity, stability and inhibitor.

b) Draw and discuss the mechanism of the phenol acetone condensation reaction to give bisphenol A.

c) Explain the catalysis in concentrated strong acid solution.

d) Discuss the influence of the oxygen medium on the properties of surface and ceramic grain boundaries in porous ceramics.

e) Explain the basis of classification of sensors according to the material used and principle of conversion.

f) Write a note on conductimetric sensors.

Q2) Attempt any four of the following: **[20]**

a) Discuss the catalysis in gas phase with suitable example.

b) What are active and passive sensors?

c) Calculate the pH and concentration of all species in 0.01 M Na_2CO_3 (Given : $ka_1 = 4.47 \times 10^{-7}$ and $ka_2 = 5.62 \times 10^{-11}$)

d) Write the proton condition for H_3PD_4 and $NaHCO_3$.

e) Write the charge balance for 0.1 M NaCN and 0.01 M HCl.

f) Write mass balance on sodium and carbonate in 0.1M Na_2CO_3 and acetate in 0.1 M acetic acid.

SECTION - II

Q3) Attempt any four of the following: **[20]**

a) Discuss the sol-gel method of preparation of nanoparticles.

b) Describe different forms of smart composites.

c) Write a note on Pachinko Machine.

d) Calculate the wavelength of an electron emitted in cathode ray tube operating at 10,000V.

e) Explain the uses of nanomaterials.

f) Write a note on ferrofluids.

Q4) Attempt any four of the following: [20]

   a) Describe the phase diagram of the water system.

   b) Write a note on Fullerin.

   c) How are the rubber like ceramics prepared? Discuss their applications.

   d) Explain the terms with example:

       i) Phase and   ii) Component

   e) Discuss the application of phase rule to sulphur system.

   f) Describe the anomalous properties of nanoparticles.

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M.Sc. - II

INORGANIC CHEMISTRY

CH - 326 : Organometallic Compounds of Transition Metals and Homogeneous Catalysis

(2008 Pattern) (Semester - III)

Time : 3 Hours]   *[Max. Marks : 80*
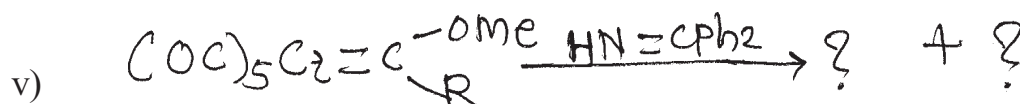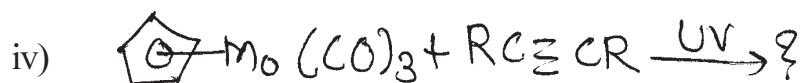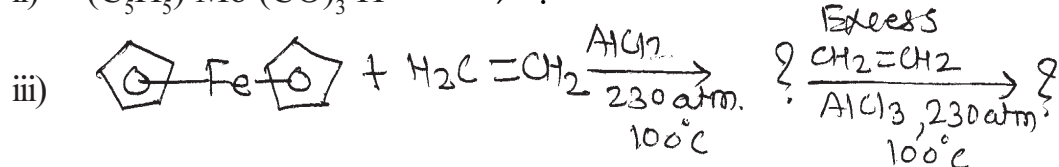
Instructions to the candidates:
1) *All questions are compulsory and carry equal marks.*
2) *Figures to the right indicates full marks.*
3) *At-No- Fe = 26, Mn = 25, Co = 27, Pd = 46, Mo = 42.*

Q1) Attempt any four of the following: **[20]**

  a)   Give the systematic classification of σ-bonded T.M. hydrocarbyls.

  b)   What are the structural features of simple metalcarbonyls.

  c)   Give the typical reactions of zeise's salt.

  d)   What are the alkyne complexes? Discuss bonding in such complexes.

  e)   What is EAN rule? Which of the following obey EAN rule?

   i) $Fe_2 (CO)_9$,   ii) $[Mn (CO)_4 NO]^-$

   iii) $[Co (\eta^5-C_5H_5)_2]$,   iv) $Cpd (NO)_2 W^- H$

   v) $\left[\bigcirc\!\!-\!Mo (CO)_3 \right]^+$

Q2) Attempt any four of the following: **[20]**

  a)   Predict the product in the following reactions.

   i) $Na [R Fe (CO)_4] + CO \longrightarrow$?

   ii) $(C_5H_5) Mo (CO)_3 H \xrightarrow{NO}$?

   iii) $+ H_2C=CH_2 \xrightarrow[230 \text{ atm.}]{AlCl_3} $? $\xrightarrow[AlCl_3, 230\text{atm}]{\text{Excess} \atop CH_2=CH_2 \atop 100°C}$?

   iv) $Mo (CO)_3 + RC \equiv CR \xrightarrow{UV}$?

   v) $(CO)_5 C_2 = C \underset{R}{\overset{-OMe}{\big<}} \xrightarrow{HN=CPh_2}$? + ?

                     P.T.O.

b) Discuss the ^{1}Hnmz of $Fe(CO)_3$ ($\eta^4-C_8H_8$) at zoom temperature and $-145°C$.

c) Explain the effect of organometallic compounds on environment.

d) Write the factor favourable for the oxidative addition reactions.

e) How organometallic compounds are useful in isomerisation, explain with example.

Q3) Attempt any four of the following: **[20]**

a) Name the organometallic compounds which can active small molecules such as O_2, H_2, CS_2 etc. Explain the reaction involved.

b) Write an account of applications of OMC'S in agriculture and horticulture.

c) Give the principal steps in the catalystic cycle for the hydrogenation of an alkene using Wilkinsons catalyst.

d) Explain : IR spectroscopy is important method to establish the structure of compounds with formula $M (PPh_3)_2 (CO)_4$.

e) Draw the structures

   i) $OS_3 (CO)_{12}$ ii) $MO(CO)_3 (\eta^6 - C_7H_8)$

   iii) $Fe(CO)_5$ iv) $CO_4 (CO)_{12}$

   v) $\mu\text{-CO}-\mu\ CRR' -[-Cp^* Rh]_2$

Q4) Write short notes on any four: **[20]**

a) Organometallic compounds as protecting agents.

b) Fluxional behaviour of organometallics.

c) Group IV OMC'S in medicine.

d) Metal-arene compounds.

e) Industrial applications of the Heck reaction.

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[5323]-37

M.Sc. -II

INORGANIC CHEMISTRY

CH - 330: Coordination Chemistry, Magnetism and Inorganic Reaction Mechanism

(2008 Pattern) (Semester - III)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

    1)   *All questions are compulsory and carry equal marks.*

    2)   *Neat diagrams must be drawn wherever necessary.*

    3)   *Use of logarithmentic table and calculator is allowed.*

Q1) Answer any four of the following.   **[20]**

    a)   Draw the crystal field splitting of d orbitals of a central metal ion in the symmetric octahedral, tetrahedral and square - planar complexes.

    b)   Explain the magnetic properties in dimeric copper (II) acetate monohydrate.

    c)   Explain the terms:

         i)   Solute - sovent interaction.

         ii)   M-O-M bridge angle.

    d)   Why is it that oxovanadium (IV) forms complexes which are involved in a weak ferromagnetic exhange.

    e)   Explain the experimental magnetic moment of the following ions:

         i) Mn^{3+} µ B.m. expt = ~ 4.9 B.m., At. No. Mn=25

         ii) Fe^{2+} µ B.m. expt = ~ 5.5 B.m., At. No. Fe =26

P.T.O.

Q2) Answer any four of the following: **[20]**

a) Explain the difference between antiferromagnetic spin - spin exchange and spin pairing.

b) Explain the terms:

i) Magnetic domain

ii) Canting

c) What are mixed valence compounds? What is the nature of electronic spectra of these compounds?

d) The extent of exchange interaction in the Cu_2O_2 ring system is greater than that in Cr_2O_2 ring system. Explain.

e) Explain why $Fe_2(CO)_9$ is diamagnetic?

Q3) Answer any four of the following: **[20]**

a) Explain how the solvent plays an important role in substitution reaction of square - planar complexes.

b) Differentiate between SN^1 and SN^2 mechanisms.

c) Explain two electron transfer reactions.

d) Discuss the applications of photochemistry of coordination compounds.

e) Give in brief an account of π–bonding theory of trans effect.

Q4) Write short notes on (Any four): **[20]**

a) Acid Hydrolysis.

b) Anation reactions.

c) Reductive elimination reactions.

d) Recemization of tris - chelate complexes.

e) Polarisation theory.

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M.Sc. - II

INORGANIC CHEMISTRY

CH-331: Structural Methods in Inorganic Chemistry

(2008 Pattern) (Semester - III)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

   1)   All questions are compulsory.

   2)   All questions carry equal marks.

   3)   Use of calculator's is allowed.

Q1) Answer the following (any four):   **[20]**

   a)   Explain the Mössbauer spectra of high spin cis and trans $Fe(NH_3)_4Cl_2$.

   b)   Explain the ESR spectra of $^{13}CD_3$ radical.

   c)   Explain the ^{31}P- NMR spectra of HPF_2 molecule.

        Given:

        i) $J_{^{31}P - ^{19}F} > J_{^{31}P - ^1H}$

        ii) $J_{^{31}P - ^1H} > J_{^{31}P - ^{19}F}$

   d)   Explain the cyclic voltammogram of antibiotic chloroamphicol.

   e)   What is NQR spectroscopy? Write the asymmetric parameter involved in NQR spectroscopy.

Q2) Answer the following (any Four):   **[20]**

   a)   What is XPS? Explain the principle, instrumentation of XPS.

   b)   What is SEM? Explain the working of SEM.

   c)   What is DTA? Draw the DTA curve for $Mn (pH_2O_2) H_2O$ molecule.

P.T.O.

d) What is x-ray diffraction? Explain the difference between single x-ray diffraction and powder x-ray diffraction.

e) What is chemical shift? Explain factors affecting chemical shift in NMR spectra.

Q3) Answer the following (any Four): **[20]**

a) Draw the structure for SnF_4 and explain why quardrupole splitting is observed in this compound but not in $SnCl_4$.

b) What is miller indices? Compute the miller indice for the face having intercepts as-

   i) [1 0 0]   ii) [1 1 1]   iii) [0 1 0]

c) Thermal curve of 250.14 mg sample that containt mixture of $CaC_2O_4.H_2O$ and thermally stable salt had a mass loss Δ m is 13.96 mg at on set temperature about 280°C corresponding to vapourization of H_2O. Determine the % (W/W) of $CaC_2O_4.H_2O$ in the sample.

d) Explain the ESR spectra of $[NF_3]^{\cdot}$ radical.

e) Calculate the energy of nuclei having spin quantum no. I = 3/2 and draw the energy level diagram.

Q4) Write short notes on (any Four): **[20]**

a) Write any two application of DSC.

b) Factors affecting on T&A curve.

c) TEM.

d) Spin- lattice relaxation.

e) Superhyper fine splitting.

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M.Sc. - II

INORGANIC CHEMISTRY

CH-332: Bioinorganic chemistry : Inorganic Elements in the Chemistry of Life

(2008 Pattern) (Semester-III)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) *All questions are compulsory.*

2) *All questions carry equal marks.*

3) *Draw neat diagrams wherever necessary.*

Q1) Answer the following (Any Four):   **[20]**

a) What are radiopharmaceuticals? Which elements are used for radioimaging purpose. Give two examples of metal camplexes used in radiopharmaceuticals.

b) What is MRI ? Explain the making of MRI - contrast agents with a suitable example.

c) Why tyrosinase enzyme is called as mixed-function catalase ? Explain with examples or reactions.

d) Explain the biomethylation reaction of vitamin B_{12}.

e) Explain the active site structure and function of enzyme urease.

Q2) Attempt <u>any four</u> of the following :   **[20]**

a) Explain with mechanism the reaction catalyzed by amine oxidase enzyne.

b) Explain the active site structure and function of carboxy peptidase.

c) What is the difference between blue and non-blue copper oxidases?

Explain the active site structure and function of enzyme galactose oxidase.

P.T.O.

d) Which metal is present at the active site of plastocyanin? What is the geometry around that metal? Which amino acids are bound to metal?

e) Explain in brief, any two techniques used to study metal complex DNA interactions.

Q3) Attempt <u>any four</u> of the following :   **[20]**

a) Give the names of non-covalent binding interactions for metal camplexes with DNA. Explain how tris(phenanthroline) ruthenium complex acts as a spectroscopic probe?

b) Explain the active site structures of enzymes containing copper. Explain the function of Cu-Zn-SOD.

c) Discuss the properties of the species formed during hamolytic and heterolytic cleavage of Co-C band in vitamin B_{12} using diagrams.

d) Explain the role of manganese in photo synthesis.

e) What is meant by chemical nuclease? Explain their functions using suitable examples.

Q4) Write short notes on (any four):   **[20]**

a) Carbonic anhydrase

b) Azurin

c) Catalase

d) Anticancer drug

e) Gold compounds in the treatment of rheumatoid arthritis.

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[5323]-40

M.Sc. - II
ORGANIC CHEMISTRY
CH - 350 : Organic Reaction Mechanism
(2008 Pattern) (Semester - III)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:
1) *All questions are compulsory.*
2) *Figures to the right indicate full marks.*
3) *Answers to the two sections should be written in separate answer books.*

SECTION - I

Q1) Write short notes on (any three) :   **[12]**

   a)   Claisen ester condensation.

   b)   Role of Pyridoxal phosphate in biotransformation.

   c)   Curtius rearrangement.

   d)   BAL1 and BAL2 mechanism.

Q2) Attempt any three of the following: **[12]**

   a)   What is Hammett equation? What is physical significance of rho (ρ)?

   b)   The $-\overset{\oplus}{N}R_3$ group has larger positive δ constant in the meta position than in the para position but it is reverse for $-\overset{\oplus}{N}_2$ group.

   c)   Calculate how much faster p-chloroaniline is benzoylated at 25° then p-nitroaniline using the given data?

   $\rho = -2.78, \sigma_p - c1 = 0.23, \sigma_p - nitro = 0.78$

   d)   Discuss the structure and methods for generation of nitrenes.

Q3) Predict the product with mechanism of any four of the following: **[16]**

a) $\xrightarrow{\Delta}$?

b) $\xrightarrow{CH_2N_2}$?

c) $\xrightarrow{aq.\ AgNO_3}$?

d) $+ Cl_2 \xrightarrow[HOAc]{AcO^-}$?

e) $+ Br_2 \xrightarrow{EtOH}$?
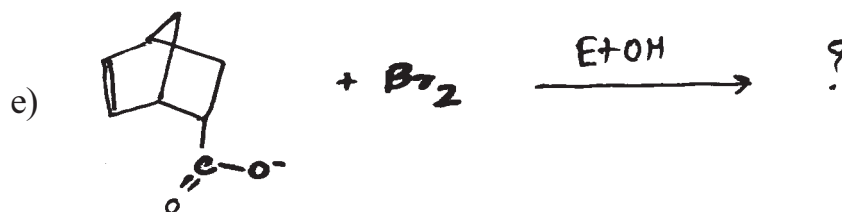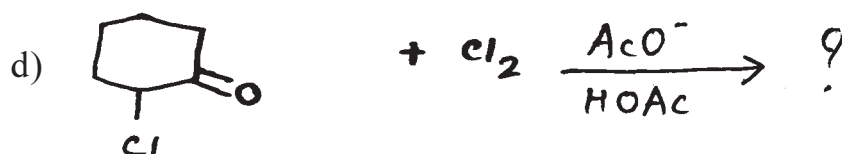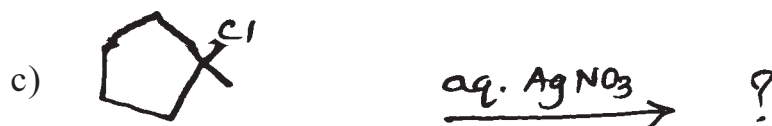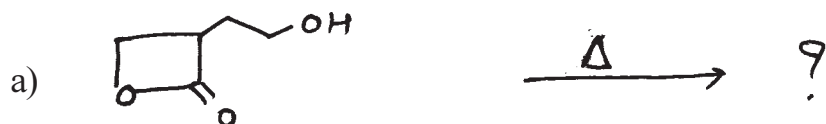
SECTION - II

Q4) Explain any three of the following: **[12]**

a) $(n-Pr)_2$ CH-COOH is esterified more rapidaly than i-Pr-CHE+-COOH.

b) Explain the observed rates of solvolysis of the following compounds:

		Rate
$R = H$	$R' = H$	1
$R = H$	$R' = CH_3$	33.3
$R = CH_3$	$R' = CH_3$	148
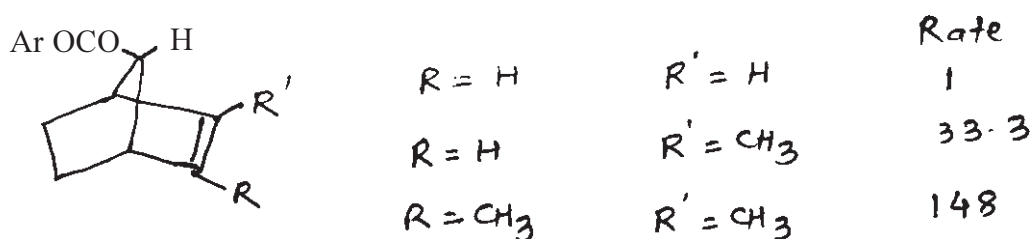
c) The decarboxylation of oxaloacetic acid has been found to be accelerated by Cu^{2+} ions.

d) Phenyl acetone on bromination in acidic and basic medium given same product.

Q5) Suggest the mechanism for the following conversion (any three): **[12]**

a)

b)

c)

d)
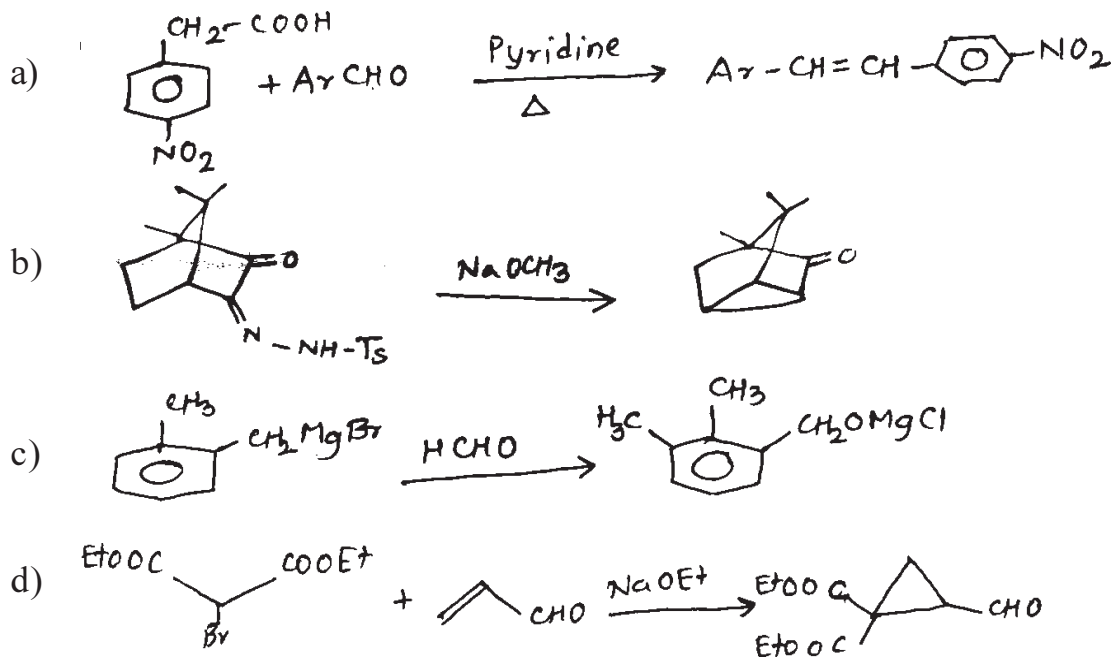
Q6) Attempt any four of the following: **[16]**

a) Acetoxyl acetone is weaker acid than acetyl acetone explain.

b) The decarboxylation of β, γ - unsaturated carboxylic acid occurs readily at higher temperature.

c) Brief account of kinetic isotopic effect.

d) Mesitoic acid is reluctant to undergo esterification under ordinary condition but easily undergoes esterification when dissolved in Conc.H_2SO_4 followed by treatment with alcohol.

e) Discuss any two methods of preparation of enamines, why they are selective in their reactivity.

f) Explain the synthesis of Prephenic acid starting from Shikimic acid.

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M.Sc.

ORGANIC CHEMISTRY

CH - 351 : Spectroscopic Methods in Structure Determination

(2008 Pattern) (Semester - III)

*Time : 3 Hours]*   *[Max. Marks : 80*

Instructions to the candidates:

    1)   All questions are compulsory.

    2)   Figures to the right indicate full marks.

    3)   Answers to two sections should be written in separate answer books.

    4)   Spectroscopic data : IR, PMR, CMR is not provided.

SECTION - I

Q1) Explain any four of the following: **[16]**

    a)   How will you distinguish between following pairs by indicated spectral method.

        i)

        ii)
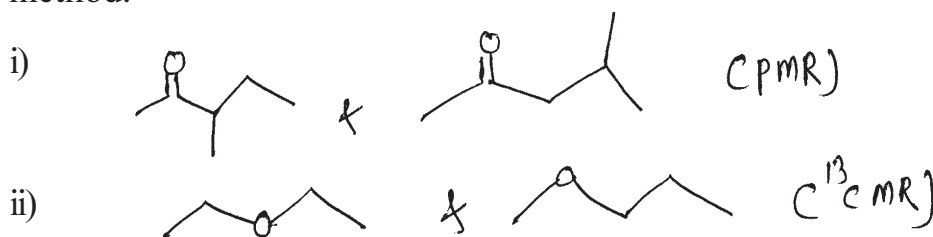
    b)   From the given data, deduce the structures of two isomeric Ketones.

        m.f = $C_7H_{14}O$

Compd. A		Compd. B	
PMR =	1.2 (d) 12 mm	PMR =	1.0 (s) 9 mm
	2.8 (sept.) 2 mm		2.2 (s) 3 mm
			2.31 (S) 2 mm
^{13}CMR =	18 (str.), 38 (m)	^{13}CMR =	30 (str.), 32 (w)
	214 (w)		34 (w), 56 (m), 210 (w)

    c)   Explain chemical ionization technique in mass spectroscopy.

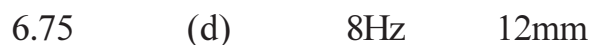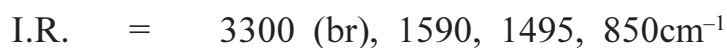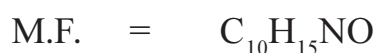d) How will you distinguish between following pair by mass spectroscopy.

i)   ii)
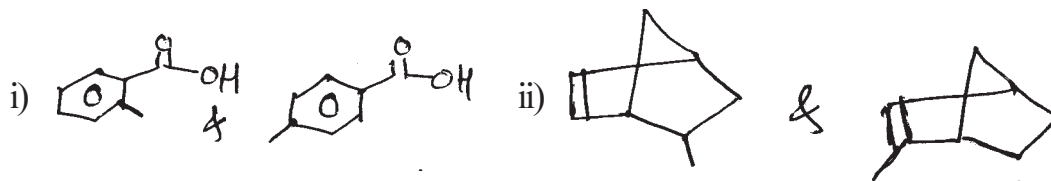
e) Explain : Protonated carbons exhibits stronger signals in ^{13}CMR. Justify with suitable example.

Q2) A) Answer any three. **[9]**

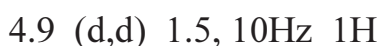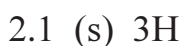a) Deduce the correct structure

   M.F.   = $C_{10}H_{15}NO$

   I.R.   =   3300 (br), 1590, 1495, 850cm^{-1}

   PMR   =   1.85   (Quintet)   8Hz   12mm

                  2.45   (s)   18mm

                  2.60   (f)   6Hz   12mm

                  2.72   (f)   6Hz   12mm

                  4.85   (bs)   Exch.   12mm

                  6.75   (d)   8Hz   12mm

                  7.1   (d)   8Hz   12mm

b) $C_{10}H_{16}O$

   IR = 1690, 1620 cm^{-1}

   PMR   = 1.2 (s) 6H

              1.9 (d) 1.5Hz 3H

              2.1 (s) 3H

              4.9 (d,d) 1.5, 10Hz 1H

              5.1 (d,d) 1.5, 16Hz 1H

              5.2 (d,d) 10, 16Hz 1H

              5.4 (q)   1.5 Hz   1H
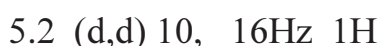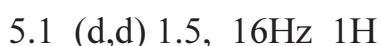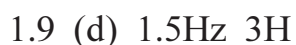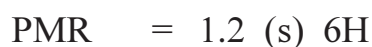
c) $C_{11}H_{10}O_4$ (Compound gives + ve 2,4 DNP Test)

    PMR =   3.96 (s) 12mm

                6.08 (s) 8mm

                6.48 (d) 8Hz 4mm

                6.68 (d) 8Hz 4mm

                6.70 (dd) 16, 8Hz 4mm

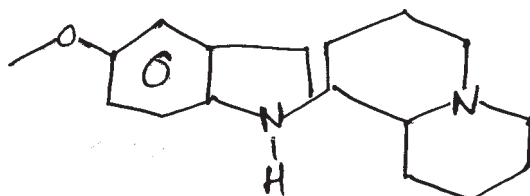   7.38 (d) 16 Hz 4mm

                9.73 (d) 8Hz 4mm

d) $C_{15}H_{14}O$

    IR = $1680cm^{-1}$

    PMR =   2.4 (6H) s ^{13}CMR = 21, 129, 133, 136, 141, 190

                7.2 (4H) d, 8Hz

                7.7 (4H) d, 8Hz

B)   Assign ^{13}CMR signals and justify your answers with justify the assignments.   **[3]**

^{13}CMR :   22 (t), 25 (t), 26 (t), 30 (t), 54 (t), 55 (q), 56 (f), 61 (d), 106 (s), 111 (d), 117 (d), 118 (d), 121 (d), 128 (s), 136 (s), 137 (s).

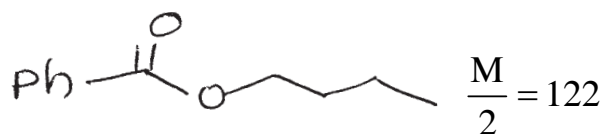*Q3)* Write note on any three of the following.   **[12]**

    a)   Solomon's diagram in NOE.

    b)   Factors affecting vicinal coupling.

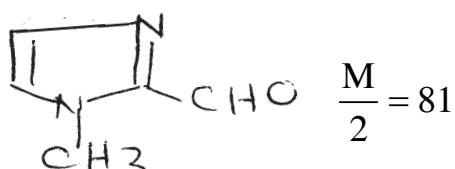   c)   Cosy in spectra interpretation.

    d)   DEPT technique.

SECTION - II

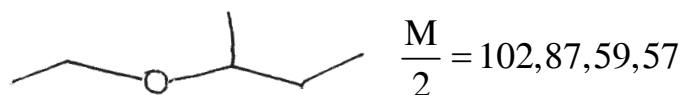**Q4)** a) Explain the genes is of ions for any four of the following. **[8]**

i)

$\dfrac{M}{2} = 122$

ii)

$\dfrac{M}{2} = 81$

iii)

$\dfrac{M}{2} = 102, 87, 59, 57$

iv) $HOCH_2CH_2SH$ $\dfrac{M}{2} = 80, 78, 60, 48$

v) $H_3CCOCH_2CH_2COOH$ $\dfrac{M}{2} = 116, 99, 98, 73$

b) Compound M with molecular formula $C_6H_{12}O$ shows the following fragment ions along with the formation of metastable ions. Assign structure for M. **[4]**

$\dfrac{M}{2}$: 100 (25%), 85 (5%), 57 (27%), 43 (100%), 72 (18%), 41 (27%), 29 (34%), 27 (15%).

Metastable ions : 72.25, 51.84, 25.14, 18.49.

Q5) a) Assign the chemical shifts and comment on the observed coupling constants in compound X. **[8]**

Compound X
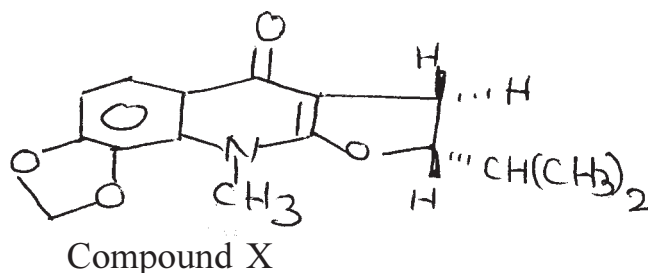
¹HNMR : δ : 0.93 (d, J = 7Hz 3H), 1.03 (d, J = 7Hz, 3H), 2.01 (Eight lines J = 7Hz, 1H), 2.25 (dd, J = 15 & 8Hz, 1H), 2.95 (dd, J = 15 & 10Hz, 1H), 3.80 (s, 3H), 4.76 (m, 1H), 6.02 (s, 2H), 7.03 (d, J = 9Hz, 1H), 8.07 (d, J = 9Hz, 1H)

What will be the change upon irradiation of signal at

i)   2.01 δ and

ii)   2.25 δ ?

b)   Assign the chemical shifts to various carbon atoms in compound y. **[4]**
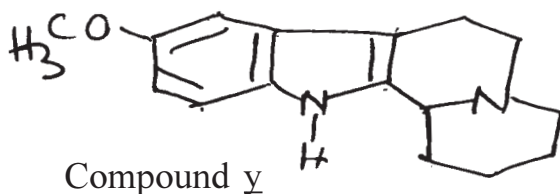
Compound y

¹³CNMR : δ :   137 (s), 136 (s), 128 (s), 121 (d), 118 (d), 117 (d), 111 (d), 106 (s), 61 (d), 56 (t), 55 (q), 54 (t), 30 (t), 26 (t), 25 (t), 22 (t).

c)   Assign the structure to the compound using the following spectral data. **[4]**

Molecular formula : $C_6 H_{11} O_2 B_r$

¹HNMR : δ :   1.25 (t, J = 6Hz, 3H), 2.25 (m, 2H), 2.5 (t, J = 6Hz, 2H), 3.5 (t, J = 6Hz, 2H), 4.15 (q, J = 6Hz, 2H)

¹³CNMR : δ :   15.0 (q), 27.0 (t), 31.2 (t), 31.5 (t), 60.0 (t), 173 (s)

Q6) The spectra of an unknown compound are shown on adjacent pages.   **[12]**

Analyse the spectra and use to arrive at a correct structure of the unknown. Justify.

Molecular Formula:C₅H₉ClO₂

¹H NMR Spectrum
(CDCl₃. 500 MHz)

3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4   ppm

¹³C{¹H} NMR Spectrum
(CDCl₃. 125 MHz)

Solvent

180   160   140   120   100   80   60   40   20   ppm

ppm

¹H–¹H COSY Spectrum
(CDCl₃. 500 MHz)

4.0   3.5   3.0   2.5   2.0   1.5   1.0   ppm

5

¹H–¹³C me-HSQC Spectrum
(CDCl₃, 500 MHz)

¹H–¹³C HMBC Spectrum
(CDCl₃, 500 MHz)

Solvent

⌘⌘⌘

[5323]-42

M.Sc.
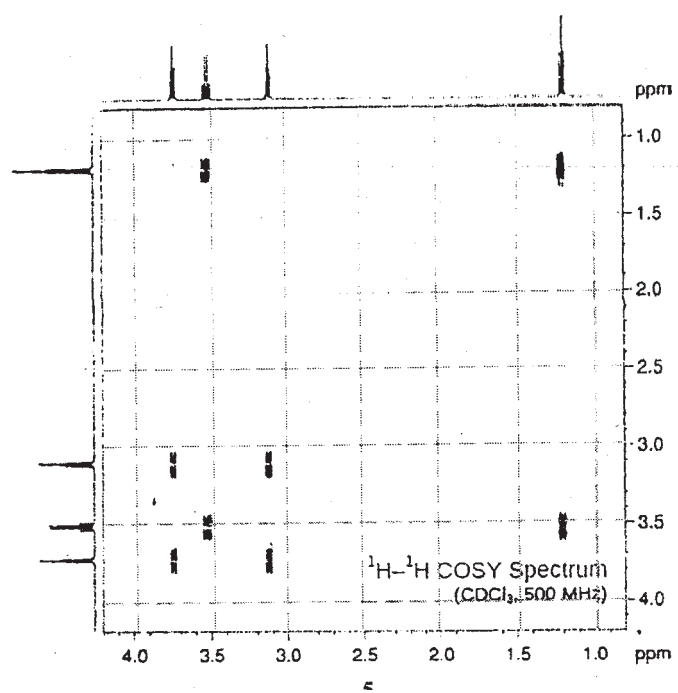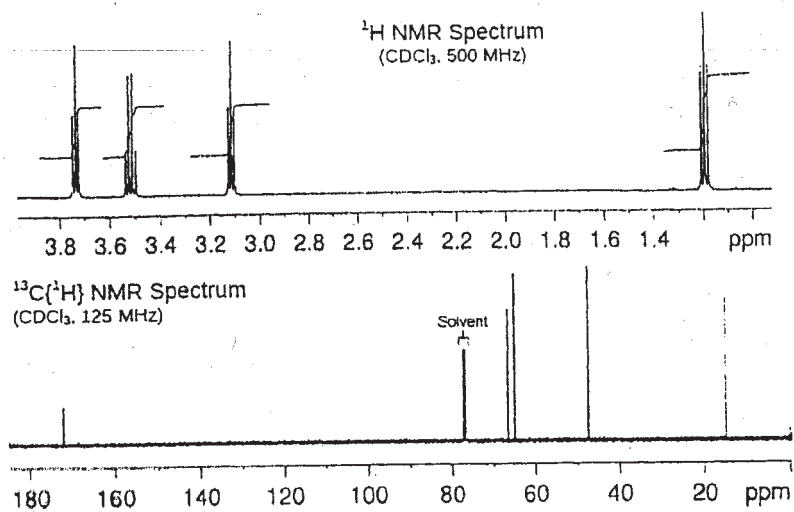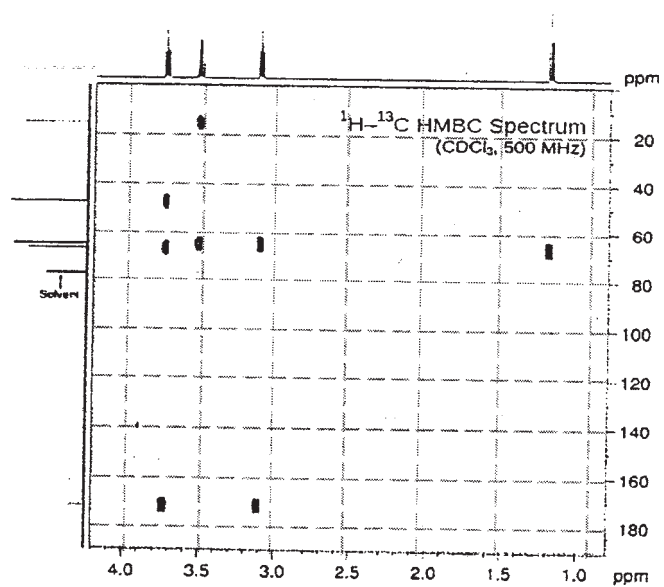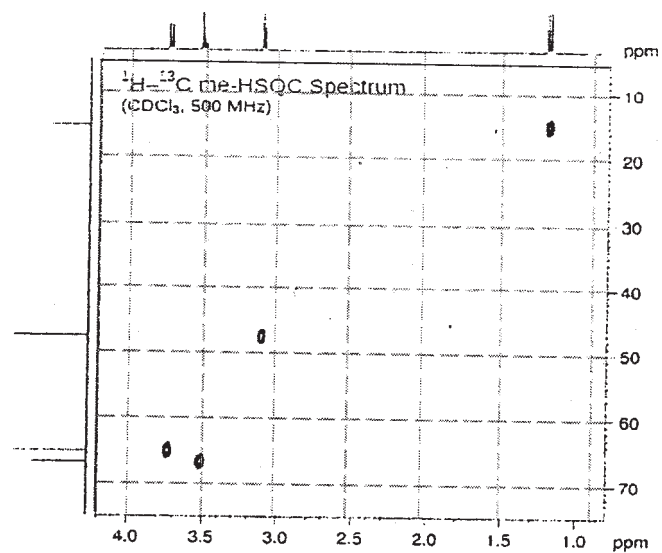
ORGANIC CHEMISTRY

CH - 352 : Organic Stereochemistry

(2008 Pattern) (Semester - III)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

    1)   *All questions are compulsory.*

    2)   *Figures to the right indicate full marks.*

    3)   *Answer to the two sections should be written in separate answer books.*

SECTION - I

Q1) Answer any four of the following: **[16]**

    a)   Draw the stable conformations of cis-syn-cis and cis-anti-cis perhydro-phenanthrenes. Calculate their energies and comment on their optical activities.

    b)   Comment on the anomalous behaviour observed in uv spectra of following compounds

        i)   Paracyclophanes (when n = 3, m = 4)

        ii)   Solvent sensitive absorption band in trans - 5 - cyclodecenone.

    c)   Yohimbin and corynanthine on saponification followed by hydrolysis gives the same acid - yohimbic acid, whereas esterification of yohimbic acid gives only yohimbin. Explain

    d)   How many conformations are possible for bicyclo [3.3.1] nonane. Draw all and comment on the most stable conformation giving reason.

    e)   Describe inoculation method for resolution of (±) sodium ammonium tartarate.

P.T.O.

Q2) Predict the product/s in any four of the following and explain the stereochemical principles involved. Justify. **[12]**

a) $\xrightarrow{HNO_2}$?

b) $+ H_2C=C=O \longrightarrow$? $\xrightarrow[ii) H_2 / Pt]{i) wolff\ kishner\ reduction}$?

c) $\xrightarrow{\Delta}$?

d) $\xrightarrow{H_3O^{\oplus}}$?

e) $\xrightarrow[ii)\ H_3O^+]{i)\ Ph\ mg\ Br}$? $\xrightarrow[Br_2]{NaOEt}$?
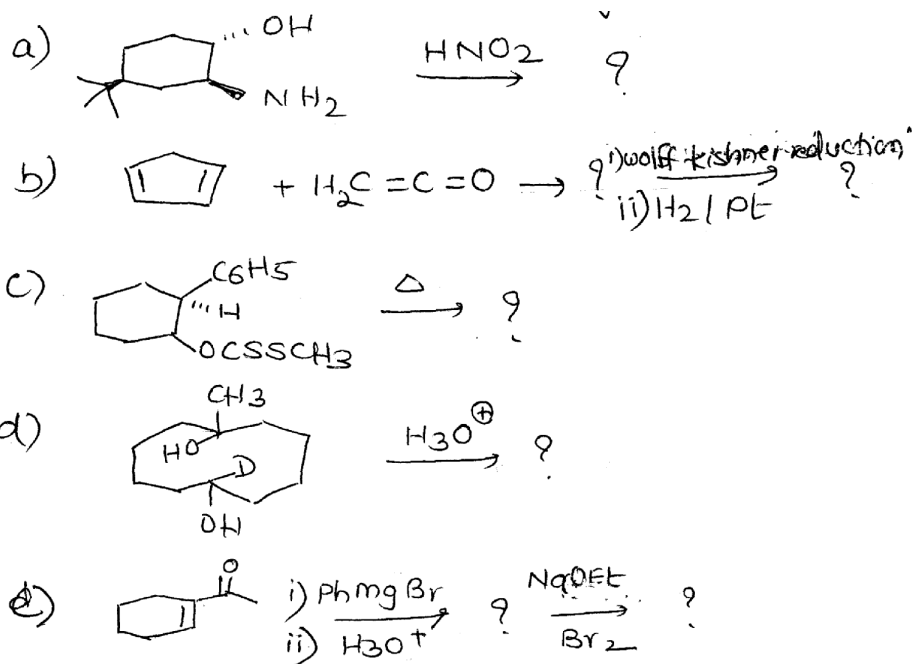
Q3) Attempt any three of the following. **[12]**

a) Write a short notes on T-strain.

b) Describe the role of chiral solvating reagents in resolution.

c) Write short notes on
   i) 2-alkyl ketone effect and
   ii) 3-alkyl ketone effect

d) Calculate energies for
   i) Cis-decalin
   ii) trans-decalin
   iii) 9-methyl-cis-decalin
   iv) 9-methyl-trans-decalin

SECTION - II

Q4) Answer any three of the following: **[12]**

a) On the basis of coupling constant explain the stereochemistry of lectone fusion into enhydrin.

b) Prove that Cinchonine and Cinchodine have different configuration at C_8.

c) Give the evidances to explain the stereochemistry of C_3 - vinyl group in quinine.

d) Predict the product and explain stereochemistry of the product. Justify your answer.
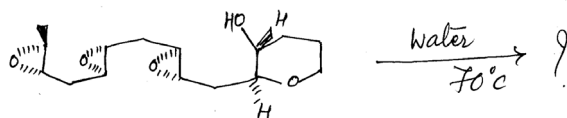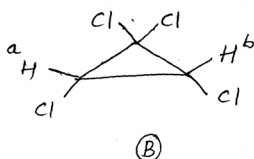

Q5) Attempt the following (any four) **[12]**

a) In the folloiwng molecules, A, B, indicates whether the hydrogens marked H^a, H^b are homotopic, enantriotopic or diasteriotopic.
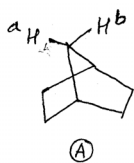
b) Write the products by hydride attack from Re and Si faces on compounds (I). Give the relation between two products.

(I)
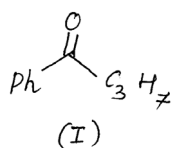
c) The isomeric coumarinic acid (I) show two isomer one of the isomer cyclise easily compair to others isomer. Explain with mechanism.
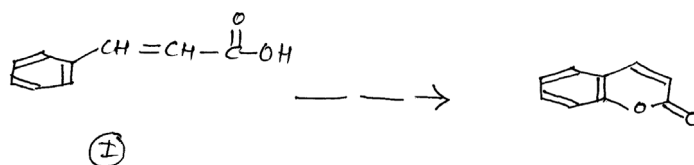
d) Explain the term optical purity. Calculate enantiomeric excess in following reactions.
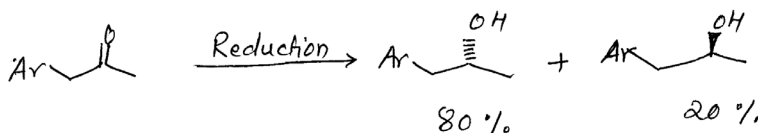
e) Indentify pro 'R' and pro 'S' hydrogen atoms in the following compounds.
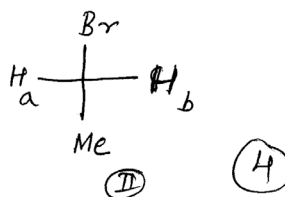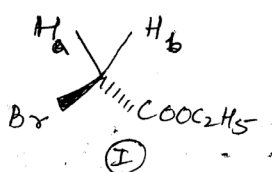
Q6) a) Predict the product/s and write stereo chemistry of the following reaction. (Any four) **[8]**

(i) [structure: cyclohexane with OH groups, ''''OH, —OH, OH] ——PhCHO/H⊕——→ ?

(ii) HO—C(=O)—C(=O)—Ar ——H₂ / [(S)-BINAP] Ru(OAc)₂——→ ?

(iii)
```
        COOH
         |
   HO — C — H          ——SOCl₂——→ ?
         |             |
       CH₂COOH         |—PCl₅—→ ?
```
S-(−) Malic acid.

(iv) [benzene ring with CH(Ph)—CH(Ph)—OH and CH₂NMe₂ substituents] ——① MeI ② Δ——→ ? + ?

(v) [cyclohexene with C(=O)—C₂H₅] ——① Ph Mg Br ② H⊕——→ ?
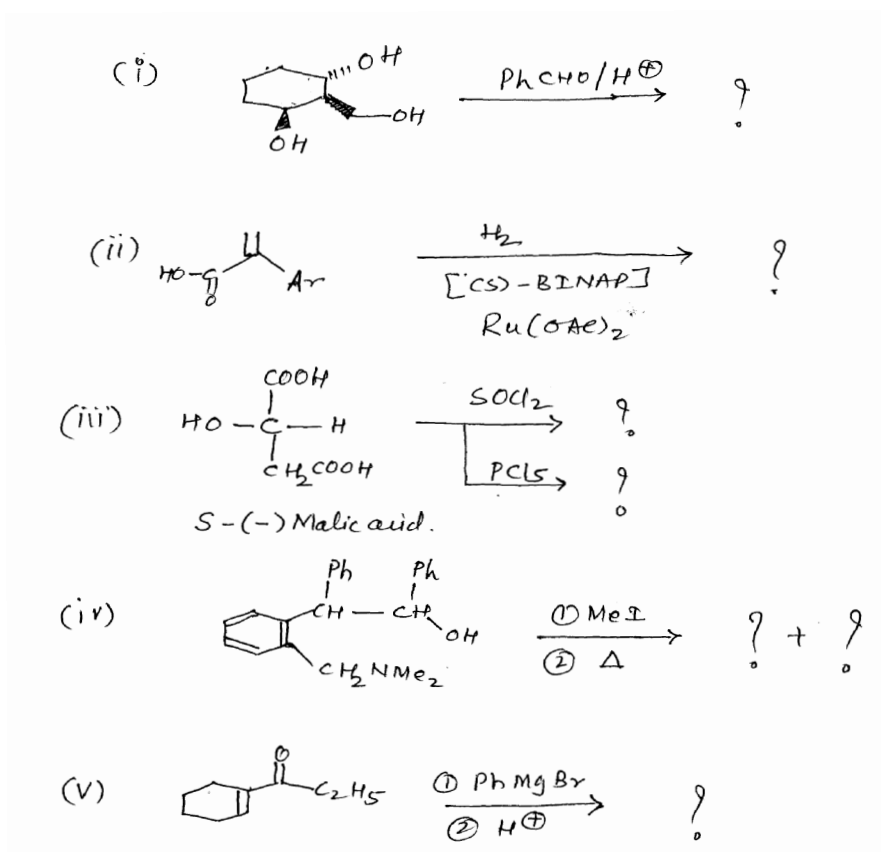
b) Suggest the reagent and write mechanism of the following reactions (any two) **[8]**
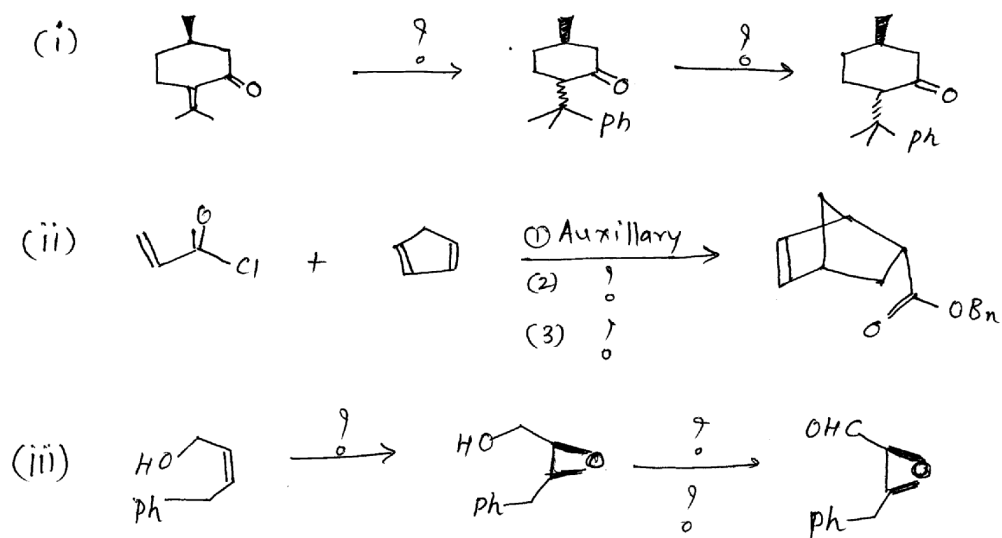
(i) [cyclohexanone with methylene group] ——?——→ [cyclohexanone with Ph substituent] ——?——→ [cyclohexanone with Ph substituent]

(ii) [acryloyl chloride] + [cyclopentadiene] ——① Auxillary ② ? ③ ?——→ [bicyclic structure with OBn ester]

(iii) HO—[cyclopentene]—Ph ——?——→ HO—[epoxide]—Ph ——?——→ OHC—[epoxide]—Ph

✗   ✗   ✗

M.Sc. - II (Organic Chemistry)

CH - 353 : FREE RADICALS, PHOTOCHEMISTRY AND PERICYCLIC REACTIONS AND THEIR APPLICATIONS

(2008 Pattern) (Semester - III)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

 1)   All questions are compulsory.

 2)   Figures to the right side indicate full marks.

 3)   Answers to the two sections should be written in separate answer books.

SECTION - I

Q1) a)   Write short notes on any two of the following: **[8]**

 i)   Photoisomerization of Benzene.

 ii)   Paterno-Biichi reaction.

 iii) Autoxidation.

 b)   Explain any two of the following: **[6]**

 i)   Blue colour is observed when the solution of cumene and tetramethyl-p-phenylene diamine is treated with oxygen.

 ii)   1, 3, 5-Trimethyl benzene on irradiation with UV-light gives 1, 2, 4-trimethyl benzene.

 iii) Photoreaction of z-methylacetophenone with maleic anhydride gave Diels-Alder product and not photoreduced diol.

Q2) Predict the product/s indicating mechanism in any four of the following: **[12]**

a)

b)

c)

d) 2 $\xrightarrow{h\nu}$?

e) $\xrightarrow[\text{vapour}]{h\nu}$?
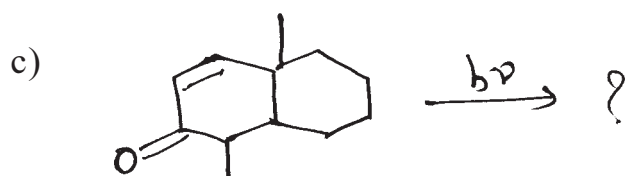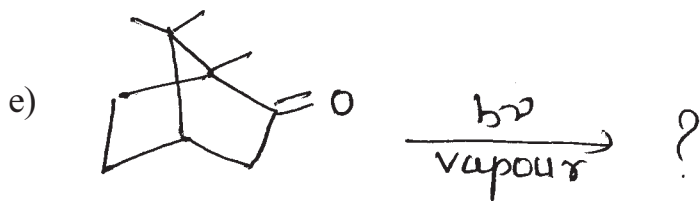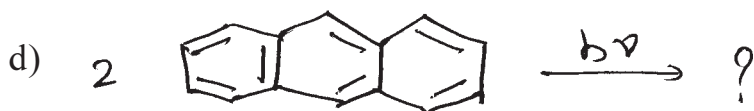
Q3) a) Propose the suitable mechanism for any five of the following: **[10]**

i) $Ph\overset{\overset{\displaystyle O}{||}}{C}H$ + $CH_3-C\equiv C-CH_3$ $\xrightarrow[-78°C]{h\nu}$

ii) $\xrightarrow{h\nu}{MeOH}$

iii) $\xrightarrow[AIBN, C_6H_6]{Bu_3SnH}$

iv) $\xrightarrow{h\nu}$

v) $\xrightarrow{h\nu}{t-BuOH}$ +

vi) $\xrightarrow{h\nu}$
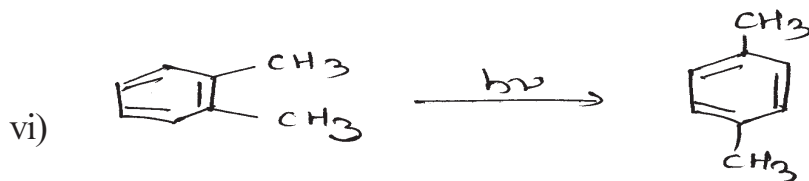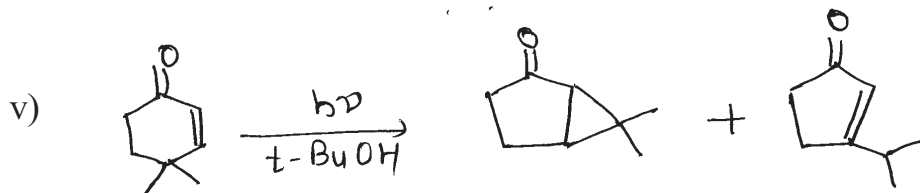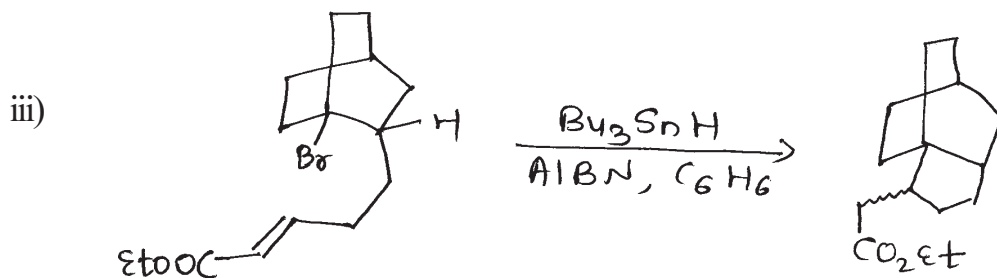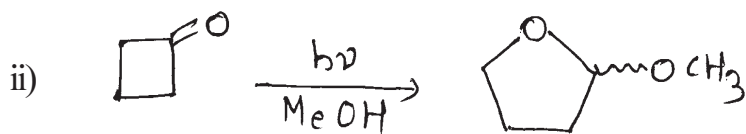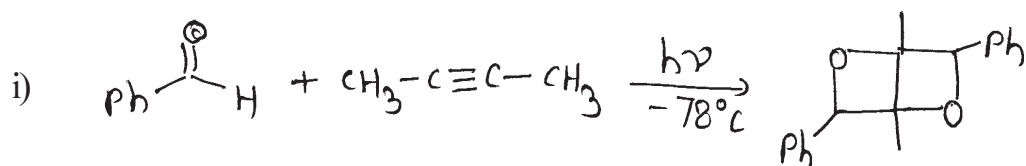
b) Explain the different physical processes occured when a molecule is excited photochemically with the help of Jablonski diagram. **[4]**

Q4) a) Construct the correlation diagram for Disrotatory conversion of 1, 3, 5-hexatriene to cyclohexadiene and predict the reaction is thermally or photochemically allowed. **[6]**

b) Predict the products in any four of the following. Explain their stereochemistry and mechanism. **[8]**

i)

ii)

iii)

iv)

v)
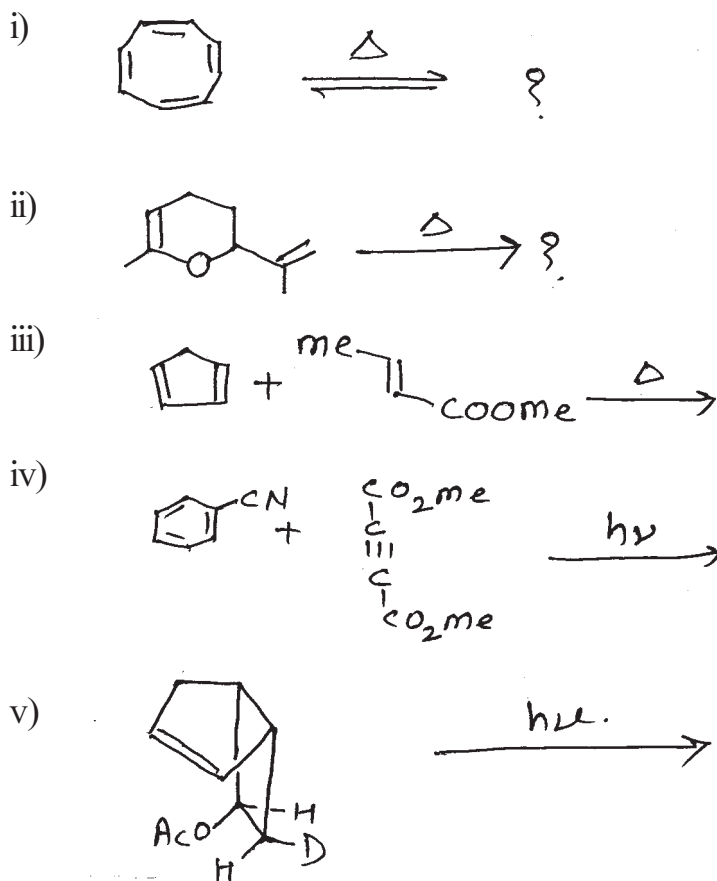
Q5) a) Using the Aromatic Transition concept predict whether the $\pi 4s + \pi 2s$ cycloaddition reaction is photochemically or thermally allowed. **[4]**

b) Explain the mechanism for any four of the following. **[8]**

i)

ii)

iii)

iv)

v)
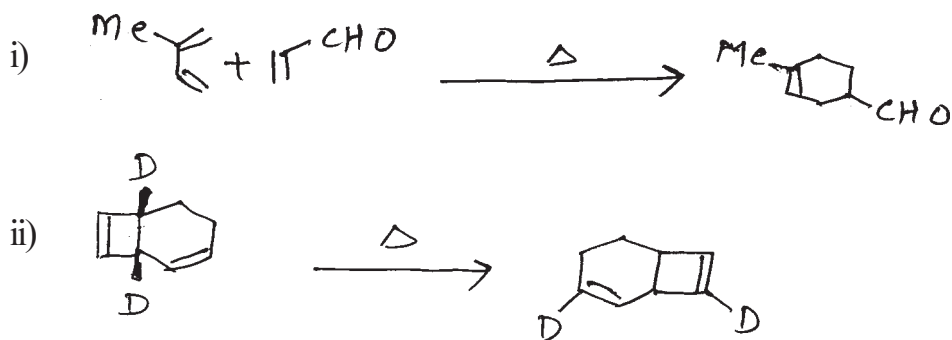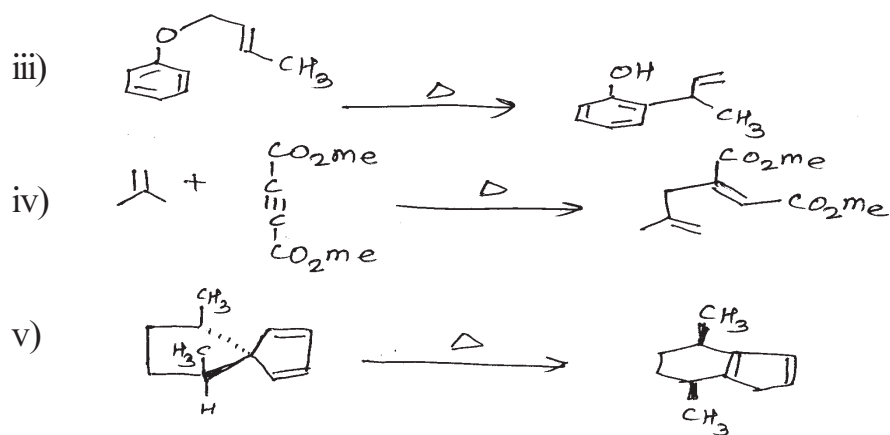
Q6) a) Complete the following synthetic sequence indicating all intermediates and reagents required. **[6]**
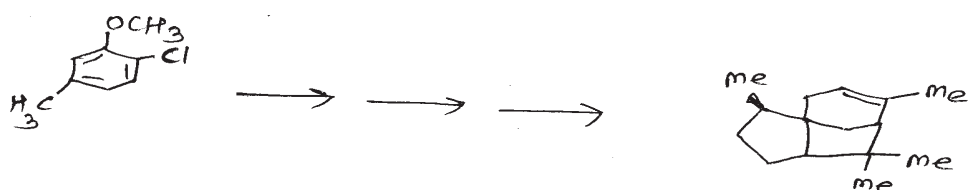
b) Complete any two of the following: **[8]**
   i) Explain the retrosynthetic analysis of Isocomene.
   ii) Explain the Black's hypothesis for the synthesis of Endiandric acid B and C.
   iii) Complete the following synthetic sequence.
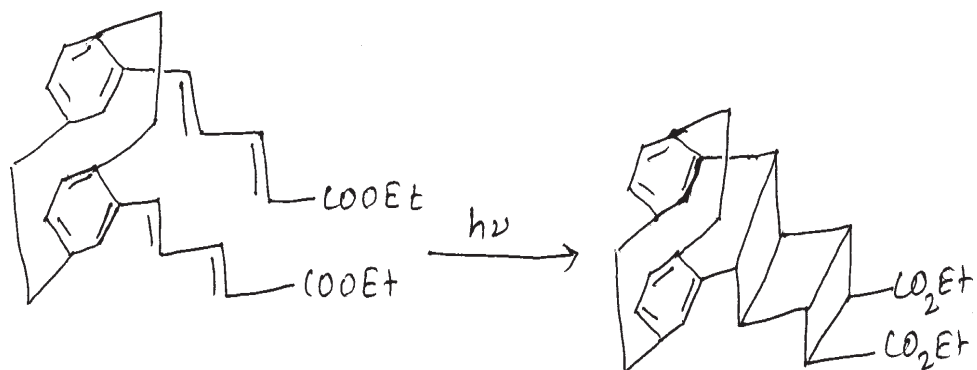
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M.Sc.-II

ANALYTICAL CHEMISTRY

CH – 390 : Electroanalytical and Current Analytical Methods in Industries

(2008 Pattern) (Semester - III)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) *All questions are compulsory and carry equal marks.*

2) *Neat diagrams must be drawn wherever necessary.*

3) *Use of logarithmic tables, non programmable calculator is allowed.*

4) *Answer to the two sections should be written in seperate answer book.*

SECTION - I

Q1) Answer any four of the following.   **[20]**

    a) State the principle of electrogravimetric analysis. Explain the importance of hydrogen over potential in the electrogravimetry determination of metal ions.

    b) What is coulometry? With example explain the technique primary coulometric titration.

    c) Write a note on cathodic stripping voltametry.

    d) Calculate the diffusion current of Cd^{2+} ion in solution having concentration 7.1mm, if the drop time for 10 drops was 34.7 sec. The mercury flowrate was 1.72 mg/sec.

        [Give : Diffusion coefficient of $Cd^{2+} = 6.7 \times 10^{-6}$ cm^2/sec]

    e) An electroactive species yielded a wave with a limiting current of 15.0μ A with rotating discelectrode rotating at rate of 10 r/s. What limiting current would be expected at a rate of 30 rotation/sec.

Q2) Attempt any four of the following.   **[20]**

    a) Explain the terms.

        i) Half wave potential

        ii) Diffusion current

    b) Write a short note on cyclic voltametry.

P.T.O.

c) Describe the advantages of pulse polarography over classical polarographic methods.

d) State and explain the principle of amperometric titration. Explain the nature of amperogram when analyte and reagent both are electroactive.

e) Standard addition technique was used for polarographic analysis of Cd^{2+} in sample. From the data given below calculate the concentration of Cd^{2+} in a sample.

Added concentration in MM	Diffusion current in μA
0.0	3.8
1.20	5.5
2.50	7.2
4.04	9.5
6.00	12.2
7.50	14.3

SECTION - II

Q3) Answer any four of the following. **[20]**

a) Describe the various steps involved in neutron activation analysis.

b) State the principle of differential thermal analysis. Discuss its working in detail.

c) Give the applications of turbidimetry and nephelometry.

d) To determine the concentration of penicilin present in a commercial preparation an isotopically labelled reference of pencillin is used with specific activity of 75,000 Bq. $9m^{-1}$. A 10mg of labelled penicillin is added to 500mg of sample. After mixing 1.5 mg of penicillin was recovered which showed activity of 10 Bq. Calculate the concentration of penicillin in commercial preperation.

e) A TG curve was obtained for 10.05 mg of a sample containing $CuSO_4$. $5H_2O$. When the monohydrate formation was complete at about 200°c, the loss in mass was 1.2 mg. Find the percentage of $CuSO_4$. $5H_2O$ in the sample.

(Given At. Wt of Cu = 63.55, S = 32, O = 16, H = 1)

Q4) Answer any four of the following.   **[20]**

    a)   State the principle of nephelometry. Describe the instrumental set up used for it.

    b)   Write a short note on direct isotope dilution analysis.

    c)   Explain the principle and applications of spectroelectro chemistry.

    d)   Explain the terms

        i)   Neutron flux

        ii)   Specific activity

        iii)   Radiometry

    e)   Calculate the percentage of $MgCo_3$ and $CaCo_3$ in 85 mg of limestone sample that exhibits thermogram showing weight of 75 mg at 500°C and 60 mg at 900°C.

       (Give At wt. Co = 40.08 mg = 24.31 C = 12 O = 16)

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M.Sc. - II
ANALYTICAL CHEMISTRY
CH - 391 : Environmental and Analysis of Industrial Materials.
(2008 Pattern) (Semester-III)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) *Answers to the two sections should be written in separate answer book.*
2) *All questions are compulsory and carry equal mark.*
3) *Neat diagram drawn wherever necessary.*
4) *Use of logarithmic table, non-programmable calculator are allowed.*

SECTION-I

Q1) Attempt any four of the following: **[20]**

a) Explain the term compound fertilizer? Explain the Na-tetraphenyl borate method used for determination of potassium from mixed fertilizers.

b) Give an analytical procedure for determination of lead from sample of lead glass.

c) Explain the general scheme of analysis of soap.

d) Describe the method of determination of moisture by Karl-Fischer titration from explosives.

e) 0.650 gm of nitrogen fertilizer was kjeldahlised and NH_3 produced was absorbed in 50 ml N/10 H_2SO_4. The excess of acid required 19 ml of N/10 NaOH solution for neutralization. Find the percentage of nitrogen in the fertilizer. (Given: At. Wts. N = 14.008)

Q2) Attempt any four of the following: **[20]**

a) What is pigment? Describe importance of pigment volume concentration in surface coating industries.

b) Describe the method to estimate anionic surfactants.

c) What are cosmetics? Give the procedure for estimation of calcium from cosmetics.

d) 10 ml of 0.01 M $ZnSO_4$ solution required 9.5 ml EDTA solution for complete reaction. 0.310 gm of sample containing magnesium was dissolved in 250 ml of acid. An aliquot of 25 ml of sample solution required 24 ml EDTA solution. Calculate percentage of magnesium in sample. (Given: At. Wt. Mg = 24).

P.T.O.

e) 2.0 gm sample of cosmetic was dissolved in acid and the solution was diluted to 100 ml. 25 ml aliquot of this solution was analysed for sulphate. It gave 0.150 gm $BaSO_4$ precipitate. Calculate percentage of sulphate and sulphur from given sample. (Given: At. Wts : Ba = 137, S = 32, O = 16).

SECTION-II

Q3) Attempt any four of the following: **[20]**

a) What is steel? Explain the analytical procedure for the estimation of nickel from steel.

b) Explain the analytical procedure for the determination of calcium from dolomite ore?

c) Define sludge. Explain different method of sludge disposal.

d) 0.52 gm of ilmenite ore was fused with potassium per sulphate and the mass was extracted with H_2SO_4 solution. After removal of insoluble matter, the filtrate was diluted to 100 ml. From aliquot of 50 ml, after removal of iron Ti - cupferron complex was precipitated. After ignition of precipitate 0.130 gm of titanium oxide was obtained. Calculate percentage of TiO_2 and Ti in the sample. (Given: Atomic wts: Ti = 47.88, O = 16, Cupferron = 155).

e) Explain the generation of CO_x and its hazardous effect on human health. How it is controlled.

Q4) Attempt any four of the following: **[20]**

a) Explain construction and working of cyclone separator.

b) Describe trickling filter process for waste water treatment.

c) Explain an analytical method for the estimation of Arsenic from waste water.

d) Explain safety rules used in industries.

e) In the determination of COD from waste water sample, 50 ml of it was reflux with 10 ml of 0.1 N $K_2Cr_2O_7$ solution and 20 ml cone. H_2SO_4 solution. The solution was titrated with FAS solution. The titration reading was 8.5 ml 10 ml aliquot of 0.1 N $K_2Cr_2O_7$ solution required 12.0 ml of the same FAS solution. Calculate Chemical Oxygen Demand (COD) of waste water sample.

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M.Sc. - II

ANALYTICAL CHEMISTRY

CH-392: Advanced Analytical Techniques

(2008 Pattern) (Semester - III)

Time : 3 Hours] *[Max. Marks : 80*

Instructions to the candidates:

1) *Answers to the two sections should be written in separate answer books.*

2) *All questions are compulsory and carry equal marks.*

3) *Neat diagrams must be drawn wherever necessary.*

4) *Use of logarithmic tables/non programmable calculator is allowed.*

5) *Use of graph paper is allowed.*

SECTION - I

Q1) Attempt <u>any four</u> of the following : **[20]**

a) State and explain Faraday's laws of electrolysis. Give its important application.

b) Explain the terms :

i) Transformer ii) Resistor

iii) Capacitors iv) Conductance

v) Inductors

c) Write a critical note on discrete sample analyzer.

d) Describe the role of microprocessor control in AAs.

e) Calculate the output voltage with turn ratio 15:1 when voltage of 230 V is applied to the primary coil.

Q2) Attempt <u>any four</u> of the following : **[20]**

a) Explain the difference between metallic conductor, insulator and semiconductors on the basis of band theory.

P.T.O.

b) What is meant by rectification? Describe the working of crystal diode as half wave rectifier.

c) Write short note on continuous flow analyzers.

d) How long must a 0.320 A current flow in order to plate 0.742g of copper from Cu (II) sulphate.

   [Given At. Wt. of Cu = 63.54g, F = 96487C]

e) 3 Capacitor are connected in series across 230V d.c. supply out of which two are with capacity 6 μf, 16 μf. and third one of unknown capacity. The total capacitance is 2 μf. Calculate value of unknown capacitor and voltage across each capacitor.

SECTION-II

Q3) Attempt <u>any four</u> of the following :   **[20]**

a) Explain the following terms with respect to AAS.

   i)   Spectral interference   ii) Chemical interference

   iii) Ionisation interference   iv) Releasing agent

   v)   protective agent

b) Explain the role of supercritical Fluid Chromatography as an analytical tool in pharmaceutical analysis.

c) Describe how the laser enhanced ionisation technique is useful for detection of various gases, liquids and solids.

d) Explain clinical application of the radioimmuno assay of insulin.

e) 10ml sample of blood was treated with trichloroacetic acid to precipitate proteins. After centrifugation the resulting solution was brought to P^H 3 and extracted with 2 ml portion of methyl isobutyl ketone containing the organic lead complexing agent. The extract was aspirated directly into an air acetylene flame and yields absorbance 0.266 at 283.3 nm. 5 ml aliquot of standard solution containing 0.2 ppm and 0.3 ppm of lead were treated in same way yielding absorbance 0.198 and 0.299. Calculate ppm of lead in blood sample.

Q4) Attempt <u>any four</u> of the following :   **[20]**

   a)   Write a note on Resonance ionization spectroscopy.

   b)   Explain Enzyme-linked immunosorbent assay with respect to principle aspects and applications.

   c)   Mention various mass analyser used in atomic mass spectrometer and discuss any one.

   d)   Discuss the working of Hallow cathode lamp.

   e)   A solution of sample of plant ash gave a meter reading 42. To the solution B and C containing the same quantity of unknown solution 45 and 85 mg/ml of added potassium gave meter reading of 70 and 98. Calculate the concentration of potassium in the sample.

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M.Sc. - II

ANALYTICAL CHEMISTRY

CH - 380 : Pharmaceutical Analysis

(2008 Pattern) (Semester - III) (Optional)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) Answers to the two sections should be written in separate answer books.

2) All questions are compulsory and carry equal marks.

3) Neat diagrams must be drawn wherever necessary.

4) Use of logarithmic table/non-programmable calculator is allowed.

SECTION - I

Q1) Attempt any four the following: **[20]**

a) Give a brief account of impurities associated with pharmaceutical manufacturing process.

b) What is limit test? Discuss the limit test for Arsenic.

c) Explain the dissolution test for tablets.

d) What is the principle of microbial assay? Give the method for two level factorial assay.

e) Describe biological assay for Tetanious antitoxin.

Q2) Attempt any four of the following: **[20]**

a) Explain the standardisation procedure of Karl-Fischer reagent.

b) Write a short note on 'Determination of ABO group of blood sample'.

c) Give a brief account of stability study of pharma product.

d) What is ash. Explain acid soluble ash and sulphated ash.

e) 100 ml saline was titrated with 02N $AgNO_3$ in presence of potassium chromate as an indicator. The burette reading was 40.0ml. Calculate the amount of sodium chloride present in 500 ml sample.

[Given Na = 23, Cl = 35.5, Ag = 108, N = 14 & O = 16]

Q3) Attempt any four of the following: [20]

a) Explain the role of binders and lubricants in the preparation of medicinal product.

b) Define aerosol. State advantages and disadvantages of aerosol.

c) Discuss about the precautions laid down for ophthalmic preparation.

d) What are injections and infusions! Distinguish between injection and infusion.

e) A 0.39 sample of paracetamol [$C_8H_9NO_2$] was dissolved in 30 ml 2N H_2SO_4. This solution was titrated with 0.1N ceric ammonium sulphate using ferroin sulphate as an indicator. This gave a burette reading 8.2 ml. Calculate percentage of paracetamol.

[At. wt. C = 12, H = 1, N = 14 & O = 16]

Q4) Attempt any four the following: [20]

a) Give an assay of salbutamol

b) Differentiate between solutions and suspensions with suitable examples.

c) Explain major steps involved in the development of new drug.

d) Write a note on types of powders used in pharma preparations.

e) 0.519 of sample containing calcium lactate [$C_9H_{10}O_6C_9SH_{20}$] was dissolved in 50ml of water and 2ml HCl. After dissolution the solution was neutralised with NaOH. This solution was fitrated with 0.05M EDTA using murexide and naphthol green indicator. The burette reading was 18.1 ml. Calculate the percentage of calcium lactate in given sample.

[Given C = 12, H = 1, O = 16 and Ca = 40.08]

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M.Sc. - II

ANALYTICAL CHEMISTRY

CH - 381 : Medicinal Chemistry

(2008 Pattern) (Semester - III) (Optional)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

  1)   Answers to the two sections should be written in separate answer books.

  2)   All questions are compulsory and carry equal marks.

  3)   Neat diagrams must be drawn wherever necessary.

SECTION - I

Q1) Attempt any four of the following: **[20]**

  a)   Discuss history and development of QSAR.

  b)   Write a short note on factors affecting bioactivity.

  c)   Explain the elementary treatment of drug receptor interactions with suitable examples.

  d)   Define the terms: soft drug, pro-drug, Resonance, Harmones, Inductive effects.

  e)   Explain chemical assay of drugs with suitable examples.

Q2) Attempt any four of the following: **[20]**

  a)   Discuss the term electronic ionization constant, steric and shelton activity.

  b)   Describe in short computer aided drug design.

  c)   Discuss in detail the free-Wilson analysis for evaluation of drugs.

  d)   Discuss important features of drug absorption, disposition and elimination.

  e)   Write a note on use of pharmacokinetics in drug development process.

SECTION - II

Q3) Attempt any four of the following: [20]

a) What is local antifective drugs? Discuss with suitable examples.

b) Write a short note on recent development in cancer chemotherapy.

c) What are sulphonamides? Explain the general mode of action.

d) Discuss the synthesis of any one cardiovascular agents.

e) Discuss the role of alkylating agents and antimetabolites in cancer treatment.

Q4) Attempt any four of the following: [20]

a) Give the process of synthesis of
   i) Quinidine   ii) Verapamil

b) Explain the mode of action of Quinolan antibacterial drug.

c) Define and explain the terms:
   i) Neuroleptic drug.
   ii) Drug inhibitor

d) Define antibiotics. Give the synthesis of any one anti-biotic drug.

e) What are sedatives and hypnotics? Give their classification.

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M.Sc.

PHYSICAL CHEMISTRY

CH - 410 : Molecular Structure and Spectroscopy

(2008 Pattern) (Semester - IV) (Old)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) *Answers to the TWO sections should be written in SEPARATE answer books.*
2) *ALL questions are COMPULSORY.*
3) *Figures to the RIGHT SIDE indicate FULL marks.*
4) *Use of logarithmic table/calculator is ALLOWED.*
5) *Neat diagrams must be drawn WHEREVER necessary.*

Physico - Chemical Constants

1.	Avogadro Number	N =	6.022×10^{23} mol^{-1}
2.	Boltzmann Constant	k =	1.38×10^{-16} erg K^{-1} molecule^{-1}
		=	1.38×10^{-23} J K^{-1} molecule^{-1}
3.	Planck Constant	h =	6.626×10^{-27} erg s
		=	6.626×10^{-34} J s
4.	Electronic Charge	e =	4.803×10^{-10} esu
		=	1.602×10^{-19} C
5.	1 eV	=	23.06 k cal mol^{-1}
		=	1.602×10^{-12} erg
		=	1.602×10^{-19} J
		=	8065.5 cm^{-1}
6.	Gas Constant	R =	8.314×10^7 erg K^{-1} mol^{-1}
		=	8.314 J K^{-1} mol^{-1}
		=	1.987 cal K^{-1} mol^{-1}
7.	Faraday Constant	F =	96487 C equiv^{-1}
8.	Speed of light	c =	2.997×10^{10} cm s^{-1}
		=	2.997×10^8 m s^{-1}
9.	1 cal	=	4.184×10^7 erg
		=	4.184 J
10.	1 amu	=	1.673×10^{-27} kg
11.	Bohr magneton	β_e =	-9.274×10^{-24} J T^{-1}
12.	Nuclear magneton	β_n =	5.051×10^{-27} J T^{-1}
13.	Mass of an electron	m_e =	9.11×10^{-31} kg

P.T.O.

SECTION - I

Q1) Attempt <u>any three</u> of the following: **[15]**

    a)   Explain the terms with reference to NMR Spectroscopy.

         i)   Coupling constant

         ii)   Spin-spin interactions

         iii)   Deshielding

         iv)   Spin decoupling

    b)   Describe classical and quantum mechanical approaches to NMR in brief?

    c)   What is the need of reference for recording high resolution NMR? Explain the advantages of TMS.

    d)   Write a note on ^{13}C NMR spectroscopy.

    e)   Discuss the applications of NAR spectroscopy.

Q2) Answer <u>any three</u> of the following: **[15]**

    a)   Explain the terms zerofield splitting, Kramer's degeneracy and Hyperfine coupling constant related to ESR spectroscopy.

    b)   What are the general rules governing the number of lines observed in ESR spectroscopy? Give suitable examples.

    c)   With the help of suitable diagram of PAS, explain the technique for PAS.

    d)   Explain the Mc Connel equation and discuss its applications in ESR.

    e)   How many ESR lines are expected in ESR spectra of an anthracene anion? Explain.

Q3) Solve <u>any two</u> of the following: **[10]**

    a)   Calculate the transitional frequency of a free electron placed in magnetic field strength of 1.4 KG.

    b)   Calculate the frequency required to excite a proton from $m_1 = \frac{1}{2}$ to $m_1 = -\frac{1}{2}$

         [Given: $g_N = 5.585$, Magnetic field applied $= 1.8T$].

    c)   The g-value of benzene radical anion Whose ESR spectrum is studied in a spectrometer operating at 9450 MHz is 2.0023. Calculate the magnetic field in which resonance occurs.

SECTION - II

Q4) Attempt <u>any three</u> of the following: **[15]**

a) How is Fourier synthesis used to determine a unit cell?

b) Compare the single crystal and powder diffraction X-ray methods of analysis.

c) What are the limitations of electron diffraction technique? Explain.

d) How are X-rays produced and detected? What is the principle of X-ray diffraction?

e) State the phase problem and outline the techniques used to overcome it.

Q5) Attempt <u>any three</u> of the following: **[15]**

a) Derive the equation for atomic susceptibility.

b) Give the characteristic properties of diamagnetic, paramagnetic, ferromagnetic and antiferromagnetic substances.

c) State the principle and working of Faraday method used for measurement of magnetic susceptibility.

d) What is spin only magnetic moment? Find these for a metal complex with four unpaired electrons.

e) Explain the principle of neutron diffraction. Describe the components of a neutron spectrometer with the help of a diagram.

Q6) Solve <u>any two</u> of the following: **[10]**

a) The gram susceptibility of $Ni(en)_3S_2O_3$ is 11.03×10^{-6} CGS units at 290 K. Find the susceptibility at 390 K.

b) Calculate the magnetic susceptibility of molecules having 3 and 6 unpaired electrons at 27°C.

c) X-ray diffraction studies of sodium chloride crystal gave the unit cell dimension as 564 pm. Find the number of units in the unit cell.

[Given : Density of sodium chloride 2.165 g cm^{-3}. Atomic Weight of Na=23, Cl=35.5]

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M.Sc.
PHYSICAL CHEMISTRY
CH - 411 : Surface Chemistry and Electro-Chemistry
(2008 Pattern) (Old) (Semester-IV)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1)   Answer to the TWO sections should be written in SEPARATE answer books.

2)   All questions are COMPULSORY.

3)   Figures to the RIGHT SIDE indicate full marks.

4)   Use of logarithmic tables, calculator is ALLOWED.

5)   Neat diagrams must be drawn WHEREVER necessary.

Physico-Chemical Constants

1)	Avogadro Number	$N = 6.022 \times 10^{23}$ mol^{-1}
2)	Boltzmann Constant	$k = 1.38 \times 10^{-16}$ erg K^{-1} molecule^{-1}
		$= 1.38 \times 10^{-23}$ JK^{-1} molecule^{-1}
3)	Planck Constant	$h = 6.626 \times 10^{-27}$ erg s
		$= 6.626 \times 10^{-34}$ Js
4)	Electronic Charge	$e = 4.803 \times 10^{-10}$ esu
		$= 1.602 \times 10^{-19}$ C
5)	1 eV	$= 23.06$k cal mol^{-1}
		$= 1.602 \times 10^{-12}$ erg
		$= 1.602 \times 10^{-19}$ J
		$= 8065.5$ cm^{-1}
6)	Gas Constant	$R = 8.314 \times 10^{7}$ ergK^{-1}mol^{-1}
		$= 8.314$ JK^{-1}mol^{-1}
		$= 1.987$ cal K^{-1}mol^{-1}
7)	Faraday Constant	$F = 96487$ C equiv^{-1}
8)	Speed of light	$c = 2.997 \times 10^{10}$ cm s^{-1}
		$= 2.997 \times 10^{8}$ cm s^{-1}
9)	1 cal	$= 4.184 \times 10^{7}$ erg
		$= 4.184$ J
10)	1 amu	$= 1.673 \times 10^{-27}$ kg
11)	Bohr magneton	$\beta_e = -9.274 \times 10^{-24}$ J T^{-1}
12)	Nuclear magneton	$\beta_n = 5.051 \times 10^{-27}$ J T^{-1}
13)	Mass of an electron	$m_e = 9.11 \times 10^{-31}$ kg

P.T.O.

Q1) Answer any **three** of the following : **[15]**

    a)   Derive Gibbs equation for adsorption.

    b)   What is detergency? Describe the properties of detergents.

    c)   Discuss thermodynamics of physical adsorption.

    d)   How is chemisorption explained on the basis of localised bond theory?

    e)   Describe the Polanyi theory for multilayer adsorption.

Q2) Answer any **three** of the following : **[15]**

    a)   Give comparison between B.E.T. and Harkins-Jura equations.

    b)   Describe the modellers method for determination of pore size distribution.

    c)   What is capillary condensation? How is it useful to explain adsorption hysteresis?

    d)   What is catalyst deactivation? Explain the factors responsible for deactivation.

    e)   Explain the disposal of radioactive waste by using zeolites.

Q3) Solve any **two** of the following : **[10]**

    a)   The surface tensions of dilute solutions of phenol in water at 30°C were:

wt % phenol	0.024	0.047	0.118	0.471
γ, dynes cm^{-1}	72.6	72.2	71.3	66.5

        Calculate Γ from the Gibbs isotherm for a 0.1% solution.

    b)   The pressures of nitrogen required to cause the adsorption of $1.0 cm^3 g^{-1}$ of gas on carbon black are 24 Pa at 77.5k and 290 Pa at 90.1K. Calculate the enthalpy of adsorption using the clausins-clapeyron equation.

    c)   A monomolecular film containing $8.2 \times 10^{-4} g$ protein per m^2 gave the surface tension lowering of 0.036 dyne cm^{-1} at 300k. Calculate the molecular weight of the protein.

SECTION - II

Q4) Answer any **three** of the following : **[15]**

    a)   Write Bernal-Fowler equation for heat of solvation, explain the terms involved in it.

    b)   Show that maximum value of charge on spherical cell is at $\gamma = x^{-1}$.

    c)   Discuss the postulates of Dehye-Huckel theory and derive an expression for charge density.

    d)   Describe Helmholtz model of electrical double layer.

    e)   Derive Fick's law for steady state diffusion.

Q5) Attempt any **three** of the following : **[15]**

    a)   Discuss briefly the local cell theory of corrosion.

    b)   What are secondary cell? Describe one secondary cell.

    c)   Enlist the desirable trends in order to maximize the energy density and power output in a cell.

    d)   Write Butler-Volmer equation and explain the exchange current density.

    e)   Explain the ways of transport of ions.

Q6) Solve any **two** of the following : **[10]**

    a)   Calculate the constants A and B in D. H. equation for solvent with dielectric constant 2.6 at 20°C.

    b)   Calculate the thickness of ionic atmosphere at 25°C in 0.01M solution of KBr. The dielectric constant of water is 78.54.

    c)   If the mobility of the silver ion in aqueous solution at 25°C is 6.5×10^{-4} $cm^2 s^{-1} v^{-1}$. Calculate the diffusion coefficient and equivalent conductivity of the silver ion.

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M.Sc - II

PHYSICAL CHEMISTRY

CH - 414 : Biophysical Chemistry and Related Techniques

(Old) (2008 Pattern) (Semester - IV) (Optional)

Time : 3 Hours] *[Max. Marks : 80*

Instructions to the candidates:

1) *Answers to the TWO sections should be written in SEPARATE answer books.*
2) *ALL questions are COMPULSORY.*
3) *Figures to the RIGHT SIDE indicate FULL marks.*
4) *Use of logarithmic table/calculator is ALLOWED.*
5) *Neat diagrams must be drawn WHEREVER necessary.*

Physico - Chemical Constants

1.	Avogadro Number	N	=	6.022×10^{23} mol^{-1}
2.	Boltzmann Constant	k	=	1.38×10^{-16} erg K^{-1} molecule^{-1}
			=	1.38×10^{-23} J K^{-1} molecule^{-1}
3.	Planck Constant	h	=	6.626×10^{-27} erg s
			=	6.626×10^{-34} J s
4.	Electronic Charge	e	=	4.803×10^{-10} esu
			=	1.602×10^{-19} C
5.	1 eV		=	23.06 k cal mol^{-1}
			=	1.602×10^{-12} erg
			=	1.602×10^{-19} J
			=	8065.5 cm^{-1}
6.	Gas Constant	R	=	8.314×10^{7} erg K^{-1} mol^{-1}
			=	8.314 J K^{-1} mol^{-1}
			=	1.987 cal K^{-1} mol^{-1}
7.	Faraday Constant	F	=	96487 C equiv^{-1}
8.	Speed of light	c	=	2.997×10^{10} cm s^{-1}
			=	2.997×10^{8} m s^{-1}
9.	1 cal		=	4.184×10^{7} erg
			=	4.184 J
10.	1 amu		=	1.673×10^{-27} kg
11.	Bohr magneton	β_e	=	-9.274×10^{-24} J T^{-1}
12.	Nuclear magneton	β_n	=	5.051×10^{-27} J T^{-1}
13.	Mass of an electron	m_e	=	9.11×10^{-31} kg

P.T.O.

SECTION - I

Q1) Attempt any four of the following: **[20]**

    a)   Calculate R_{rms} for a polymer with 300 monomer units and total length 400 nm.

    b)   Compare animal and plant cell structures

    c)   Discuss the role of ATP in energy transfer

    d)   What are flickering clusters?

    e)   How is Henderson's equation used in buffer preparation?

    f)   Explain what is reverse osmosis.

Q2) Attempt any four of the following   **[20]**

    a)   Give applications of Donnan equilibrium

    b)   Deduce the relation $\overline{R} = l \times \sqrt{\dfrac{8N}{3\pi}}$

    c)   Explain the significance of nucleic acids in cell biology

    d)   What are smooth muscles and their functions?

    e)   Discuss the role of directionality in H bond.

    f)   How is pH of blood maintained constant?

SECTION - II

Q3) Answer any four of the following: **[20]**

    a)   Discuss briefly the composition of a cell membrane

    b)   Explain the thermodynamic treatment of membrane transport.

c) Define the terms:

    i) neuron   ii) nerve   iii) membrane lipids
    iv) membrane proteins and   v) carrier proteins

d) Draw and explain the graph showing various events of action potential.

e) Discuss sedimentation equilibrium method to determine the molecular weight of biopolymers.

f) Differentiate between micelles and biolayers with respect to their structure and function.

Q4)   Answer any four of the following   **[20]**

a) Explain the role of optical rotary dispersion forces involved in structural stability.

b) Briefly discuss any two methods for determination of the size of biopolymers.

c) Explain the light scattering method for determination of the molecular weight of biopolymers.

d) Discuss the factors affecting enzyme activity.

e) Discuss viscosity method to determine the molecular weight of a biopolymer.

f) Write a note on helix-cell transitions.

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[5323]-54

M.Sc. - II

PHYSICAL CHEMISTRY

CH - 415 : Special Topics in Nuclear Radiation Chemistry

(2008 Pattern) (Semester - IV) (Old)

Time : 3 Hours] *[Max. Marks : 80*

Instructions to the candidates:

1) *Answers to the TWO sections should be written in SEPARATE answer books.*
2) *ALL questions are COMPULSORY.*
3) *Figures to the RIGHT SIDE indicate FULL marks.*
4) *Use of logarithmic tables/calculator is ALLOWED.*
5) *Neat diagrams must be drawn WHEREVER necessary.*

Physico - Chemical Constants

1.	Avogadro Number	N	=	6.022×10^{23} mol^{-1}
2.	Boltzmann Constant	k	=	1.38×10^{-16} erg K^{-1} molecule^{-1}
			=	1.38×10^{-23} J K^{-1} molecule^{-1}
3.	Planck Constant	h	=	6.626×10^{-27} erg s
			=	6.626×10^{-34} J s
4.	Electronic Charge	e	=	4.803×10^{-10} esu
			=	1.602×10^{-19} C
5.	1 eV		=	23.06 k cal mol^{-1}
			=	1.602×10^{-12} erg
			=	1.602×10^{-19} J
			=	8065.5 cm^{-1}
6.	Gas Constant	R	=	8.314×10^{7} erg K^{-1} mol^{-1}
			=	8.314 J K^{-1} mol^{-1}
			=	1.987 cal K^{-1} mol^{-1}
7.	Faraday Constant	F	=	96487 C equiv^{-1}
8.	Speed of light	c	=	2.997×10^{10} cm s^{-1}
			=	2.997×10^{8} m s^{-1}
9.	1 cal		=	4.184×10^{7} erg
			=	4.184 J
10.	1 amu		=	1.673×10^{-27} kg
11.	Bohr magneton	β_e	=	-9.274×10^{-24} J T^{-1}
12.	Nuclear magneton	β_n	=	5.051×10^{-27} J T^{-1}
13.	Mass of an electron	m_e	=	9.11×10^{-31} kg

SECTION - I

Q1) Answer any three of the following: **[15]**

   a)   Discuss the general principles for using radio pharmaceuticals in diagnosis and therapy.

   b)   Describe the method of separation of uranium isotopes.

   c)   Which ionizing sources are used for food preservation and sterlization? Write the various closes given and their effects on food items.

   d)   Describe the method for waste disposal of radio active gases.

   e)   Give an account of heavier element burning.

Q2) Answer any three of the following: **[15]**

   a)   Explain the terms planck era, GUT era. What are their characteristics?

   b)   Discuss the principle and procedure of positron emission tomography technique.

   c)   Discuss the solar neutrino problem.

   d)   Write short note on pre-mordial nucleosynthesis.

   e)   Draw and explain cosmic and abundance curve.

Q3) Attempt any two of the following: **[10]**

   a)   Write down the reactions in C-N-O bicycle.

   b)   99Mo with an activity of 24,000 cpm is loaded on alumina column. Find out the activity of $99mt_c$ when extracted after 8 hrs with an efficiency of 70%. Given t1/2 of $99m_o$ = 66.6h and $99mt_c$=6.0h.

   c)   Fin out dose due to 200 mci C_o - 60 at a distance of 3 meters. Given : gamma energy of C_o-60 is 2.5 Mev.

SECTION - II

Q4) Attempt any four of the following: [20]

    a)   Discuss effect of solute concentration on molecular yield in radiolysis of water.

    b)   Discuss a method to measure bean energy.

    c)   Write reactions involved in the radiolysis of methanol.

    d)   How are soft radiation emitters prepared?

    e)   10cc KCL was titrated with 10mm $AgNo_3$. After 1.5 cc addition, activity attenuated from 500 cpm to 250 cpm. Find molarity of Kcl.

Q5) Attempt any four of the following: [20]

    a)   How are radioactive nuclides for tracer use, prepared?

    b)   How is a radio chemical species purified after isolation? mention the problems encountered.

    c)   Explain neutralization radiomatric titration with a neat diagram.

    d)   What is radical scavenging? Give examples.

    e)   How are counters chosen to measure activity?

    f)   Give advantages of radimetric titrations in which β particles are absorbed.

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[5323]-55

M.Sc. - II

INORGANIC CHEMISTRY

CH - 430 : Inorganic Solids and Heterogeneous Catalysis

(2008 Pattern) (Semester-IV)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

  1)   All questions are compulsory.
  2)   All questions carry equal marks.
  3)   Neat diagrams should be drawn wherever necessary.

Q1) Attempt any four of the following: **[20]**

  a)   Find out the framework electrons in $Ir_4(CO)_{12}$ and predict the structure.

  b)   List out the various methods of preparation of hetereogenous catalyst and explain any one of them in detail.

  c)   Explain catalytic hydrogeneration of alkenes by using Pd as catalyst.

  d)   Discuss the use of nanomaterials as catalyst in organic synthesis.

  e)   What are the phosphazenes? How they are prepared? Write their structures.

Q2) Attempt any four of the following: **[20]**

  a)   What are silicones? Give general method of preparation and mentions the use.

  b)   Explain the use of powder XRD technique for determining the structure of zeolites.

  c)   Give an account of heteropolyanians of Mo and W.

  d)   Which types of reactions are catalyzed by semiconducting oxides? Explain in detail any one reaction catalyzed by these oxides.

  e)   What is chemical reactor? Name different chemical reactors and explain any one in detail.

Q3) Attempt any four of the following: [20]

   a) What is meant by phase transfer catalyst? Describe a reaction catalyzed by this type of catalyst.

   b) Give an account of temperature programmed techniques for characterization of heterogeneous catalysts.

   c) Pyrolysis has a considerable effect on the nuclearity of polynuclear carbonyls.

   d) Discuss in detail the basic principle and steps involved in heterogeneous catalysis.

   e) What are inorganic polymers? Give a method of classification of inorganic polymers.

Q4) Write short notes on: (any four) [20]

   a) Clay as a catalyst.

   b) Phosphazenes.

   c) MCM-41 as a catalyst.

   d) Fischer - Tropsch synthesis.

   e) Zeolite as hydrocracking catalyst.

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[5323]-56

M.Sc. - II (Inorganic Chemistry)
CH - 431 : MATERIAL SCIENCE
(2008 Pattern) (Semester - IV)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:
　　1)　All questions are compulsory.
　　2)　Neat diagrams must be drawn wherever necessary.
　　3)　Figures to the right indicate full marks.
　　4)　Use of logarithmic table and calculator is allowed.

Q1) Attempt any **FOUR** of the following :   **[20]**

　　a)　What is diffusion? Explain the types of diffusion mechanism in solids.

　　b)　Derive the expression $X = \dfrac{C}{T - \theta}$.

　　c)　Describe the different layers in the cross section of a tree stem with function of each layer.

　　d)　Explain the types of superconductors.

　　e)　What are Biomaterials? How they are classified?

Q2) Attempt any **FOUR** of the following :   **[20]**

　　a)　What is Portland cement? What are different types of Portland cement?

　　b)　What are nanomaterials? Name the various methods for synthesis of nanomaterials. Why these methods are important?

　　c)　What are the different types of magnetism?

　　d)　What is concrete? How it is prepared? Explain proportion of concrete mixture.

　　e)　What is Luminescence? Explain different types of Luminescences.

Q3) Solve any **FOUR** of the following : [20]

a) Saturation magnetisation of FCC Iron is $1700kA/m^2$. Calculate the net magnetic moment per Iron atom in crystal. Given lattice parameter of FCC Iron is $2.87°A$.

b) Calculate the energy gap in Silicon given that it is transparent to radiation of wavelength greater than $11000°A$.

c) Mobility of electrons and holes in sample of intrinsic Ge at room temperature are $3600cm^3/Vsec$ and $1700cm^3/Vsec$. respectively. If electron and hole densities are equal to $2.5\times10^3/cm^3$. Calculate the conductivity.

d) In an n-type semiconductor the fermilevel lies 0.3eV below the conduction band at room temperature. If the temperature is increased at $330°k$. Find the position of fermilevel. [Room temp. $= 300°K$].

e) In 'Si' energy gap is 0.75 eV. What is wavelength at which start absorption of light?

Q4) Write a short note on any **FOUR** : [20]

a) Working of n-p junction

b) Ferroelectrical materials

c) Glass transition temperature

d) Photoconductivity

e) Macrodefect free cement

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[5323] - 57

M.Sc. -II

INORGANIC CHEMISTRY

CH-445: Inorganic Applications in Industry, Biotechnology and Environmental Chemistry

(2008 Pattern) (Semester - IV)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) *Attempt any two sections from the following.*

2) *Both sections should be written in the same answer book.*

3) *All questions are compulsory.*

4) *Figures to the right indicate full marks.*

5) *Neat diagrams must be drawn wherever necessary.*

6) *Use of logarithmic table/calculator is allowed.*

SECTION - I

Applications of Inorganic Materials

Q1) Attempt any <u>three</u> of the following: **[15]**

    a)   What are Formazans? How are they classified as ligands? Give atleast two examples of each and draw the structure of metal complexes they form.

    b)   Explain the production and properties of glass fibers for reinforcing plastic resin.

    c)   Give in detail production of Portland cement.

    d)   Explain the microstructure of soft wood.

Q2) Attempt any <u>three</u> of the following: **[15]**

    a)   What do you understand by N_α-N_β isomerism in metal complexes of azo compounds? Explain with respect to Nickel and Copper complexes.

b) Give two examples and draw structure of

    i)   Metalized dyes,

    ii)   Additional reagents,

    iii) Medially metalized azodyes.

c) Explain the production and properties of glass fibers.

d) Discuss the different processes available for electro deposition of zinc.

Q3) Write notes on (any Two):   **[10]**

a) Yellow pigment.

b) Alloy plating.

c) Natural earth colour pigment.

SECTION-II
Environmental Chemistry

Q4) Attempt any Three of the following: **[15]**

a) What does primary and secondary treatment in a sewage treatment plant removes from the waste stream?

b) Draw a schematic diagram of an alkaline fuel cell (AFC). Write the reaction that occur at the cathode and anode. Show overall reaction. What is the electrolyte used in the AFC?

c) What is the main source of cadmium pollution in the environment? List four industrial uses of cadmium. What is galvanised iron? Are smokers more at risk for cadmium poisoning.

d) Will geothermal energy level be a major source of energy world wide? Explain.

[5323]-57   **2**

Q5) Attempt any Three of the following: **[15]**

a) List four forms of biomass. What is the energy yield obtained from burning biomass? List the advantages and disadvantages of using biomass as a source of energy.

b) Determine p^E for waste water that contains 5×10^{-4}M S^{-2}. Does this waste water favour oxidation or reduction? $S + 2\bar{e} \rightarrow S^{-2}, PE^{\circ} = -8.47$.

c) What is meant by point and non-point sources of pollutions? Give an example of each.

d) Draw a schematic diagram of a Phosphoric Acid Fuel Cell (PAFC). What reactions are occuring at the cathode and anode? Show overall reaction.

Q6) Write short notes (any Two): **[10]**

a) Tidal power and wind power.

b) Primary and secondary sludge.

c) Reverse osmosis.

SECTION-III
Biotechnology

Q7) Attempt any Three of the following: **[15]**

a) Which principles of genetics are used in biotechnology?

b) "Biotechnology is a branch which has developed by the contribution of various branches of science". Comment.

c) What is renin? Describe an experiment to demonstrate the effect of different factors on the action of renin on milk.

d) Why are living cells called miniature factories.

[5323]-57

Q8) Attempt any Three of the following: [15]

a) Explain the cycle of methane production using anaerobic bacteria.

b) How are variations induced in plants? Explain one method in detail.

c) What is recombinant DNA technology? What are its advantages and limitations?

d) State and explain main stages involved in making cheese.

Q9) Write short notes - any Two: [10]

a) DNA mapping.

b) Tissue culture.

c) Antibiotics.

EEE

M.Sc.
ORGANIC CHEMISTRY
CH - 450 : Chemistry of Natural Products
(2008 Pattern) (Semester-IV)

Time : 3 Hours]   *[Max. Marks : 80*
Instructions to the candidates:
  1) *All questions are compulsory.*
  2) *Figures to the right indicate full marks.*
  3) *Answers to the two sections should be written in separate answer books.*

SECTION-I

Q1) Outline the steps in <u>any four</u> of the following synthetic sequences. Indicate the reagents used and discuss the mechanism and stereochemistry involved.**[16]**

a)

b)

c)

d)

e)
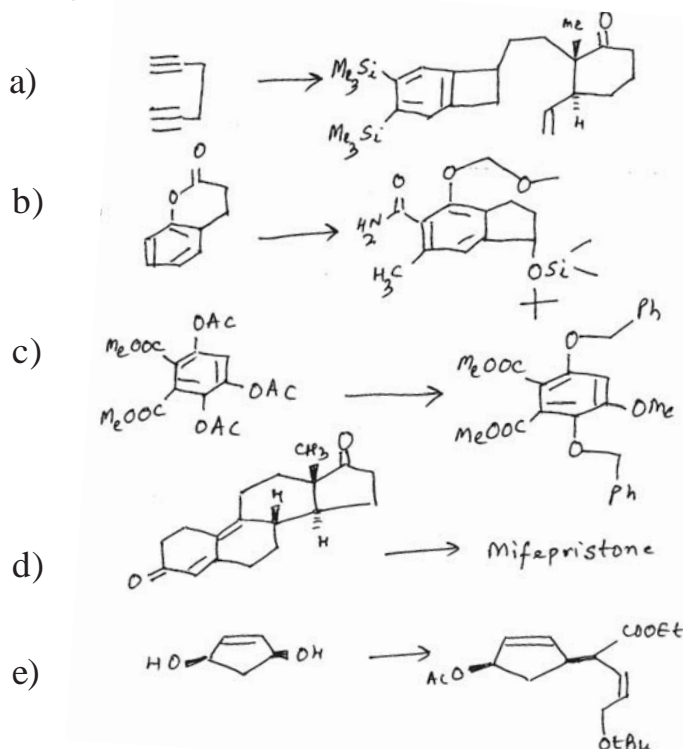
Q2) Answer any three of the following: **[12]**

   a)   Give chemical and physical evidence to prove the presence of
       i)   Lactone ring and
       ii) Tertiary - OH group in camptothecin

   b)   Give evidences to establish the relative stereochemistry of the four possible isomers of deoxypodophyllotoxin.

c) A stereoisomer of hardwickiic acid (A) has the following structure.
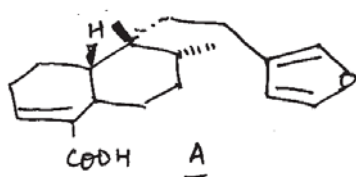
How will you prove the presence of C-9 methyl and the stereochemistry of the same.

d) How will you prove the presence of pyrolloquinoline in hydroxy camptothecin.

Q3) a) Complete the following sequence using appropriate reagents provided. Explain the steps. **[6]**

i)   aq. KOH, DMSO

ii) KI_3, $NaHCO_3$, H_2O, O'C

iii) MCPBA/$NaHCO_3$

iv)
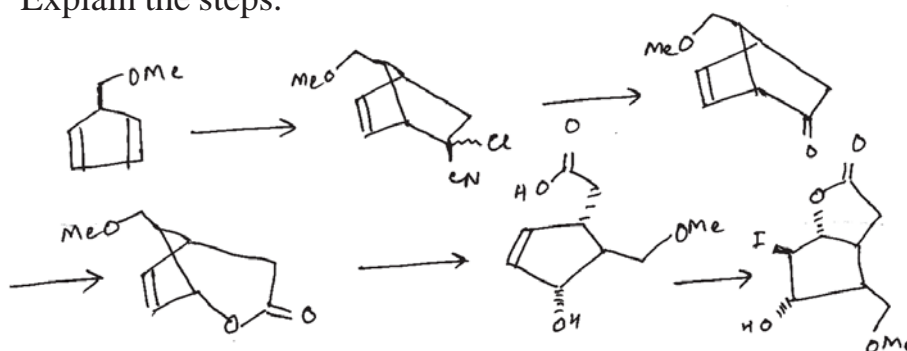
v)   NaOH, H_2O, O'C, CO_2

b) Nuciferal (A) was synthesized from (B) via a series of slips. **[6]**
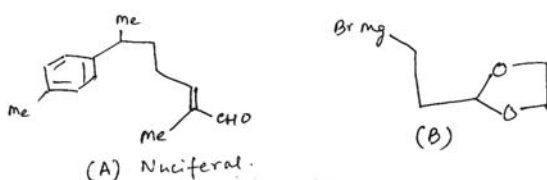
i)   Suggest the synthesis of (B) from simple starting compounds.

ii) Suggest the retrosynthesis of Nuciferal from (B).

iii) Explain the steps involved in conversion of (B) into Nuciferal.

SECTION-II

Q4) a) Discuss the importance of Wagner-Meerwin rearrangements in biogenesis with suitable examples. **[4]**

**b)** Suggest biogenetic scheme for <u>any three</u> of the following: **[12]**

i) GPP ⟶

ii) 2Z, 6E - FPP ⟶

iii) ⟶

iv) ⟶
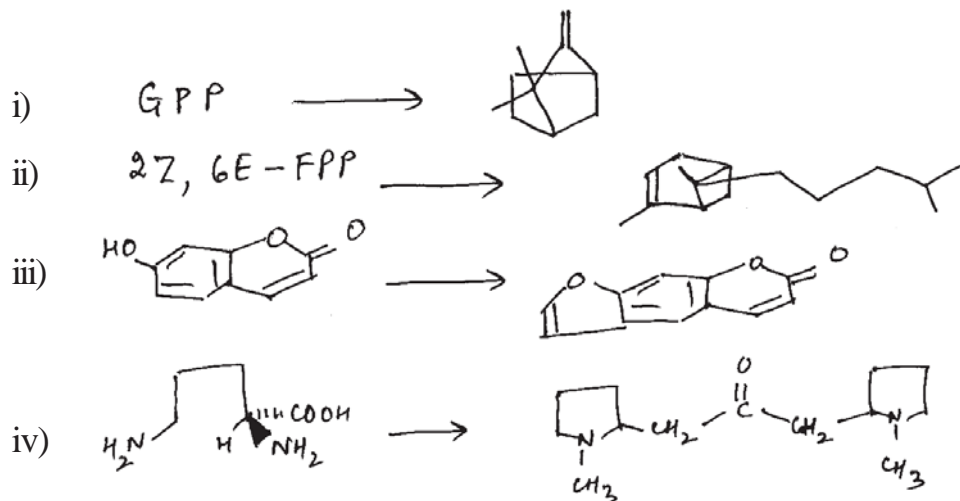
Q5) Attempt <u>any two</u> of the following: **[12]**

a) Explain all the steps involved in the biogenesis of squalene from two farnesyl pyrophosphate molecules.

b) Suggest the steps involved in the following biogenetic scheme.
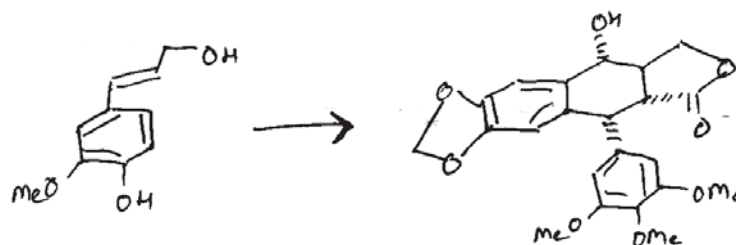
c) Give the steps involved in the following conversion:

$H_2N \cdot (CH_2)_3 \cdot CH \, NH_2 \, COOH \longrightarrow$
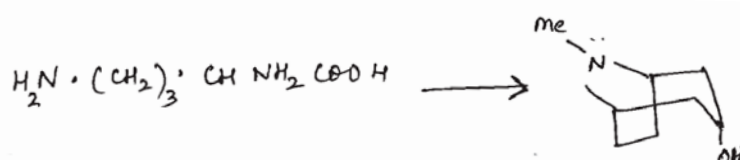
Indicate the position of label in each step and in the final product.

Q6) Write all steps in <u>any two</u> of the following biogenetic conversion: **[12]**

a) Erythrose - 4 - phosphate → Shikimic acid.
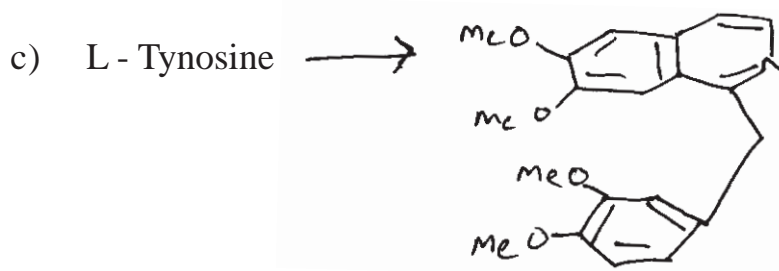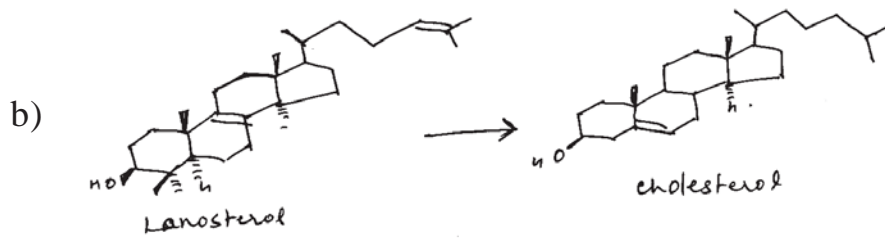
b)

Lanosterol → cholesterol

c) L - Tynosine ⟶

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M.Sc. - II

ORGANIC CHEMISTRY

CH - 451 : Synthetic Methods in Organic Chemistry

(2008 Pattern) (Semester - IV)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

   1)   *All questions are compulsory.*

   2)   *Figures to the right indicate full marks.*

   3)   *Answers to the two sections should be written in separate answer books.*

SECTION-I

Q1) Explain any **four** of the following :   **[12]**

   a)   Synthesis of 1, 2-dicarbonyl compounds involve umpolung of reactivity.

   b)   Role of isopinocamphenyl borane in organic synthesis.

   c)   Use of triphenyl phosphine to convert alcohols to alkyl halides.

   d)   Use of organosulphur compounds in organic synthesis.

   e)   Use of the following synthons in organic synthesis

      i) $\overset{\ominus}{C}OOH$

      ii)

      iii) $CH_3-\overset{\ominus}{C}H-NH_2$
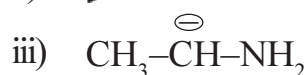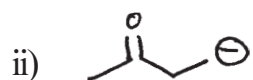
Q2) Complete any **four** of the following transformations and justify your answer.

                                                       [12]

   a)

   b)

   c)

   d)

e)
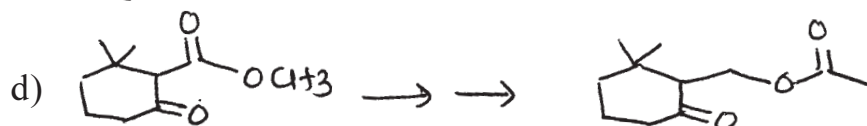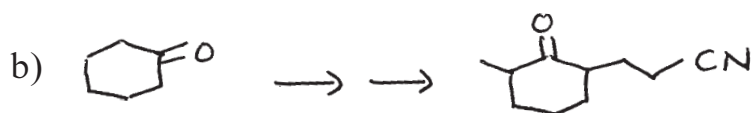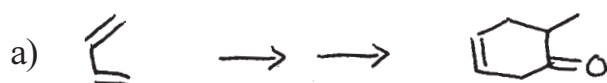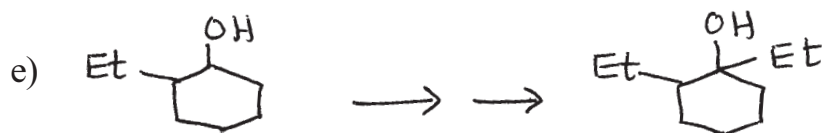
Q3) a) Discuss the use of any **two** of the following reagents. **[4]**

    i) Fe [CO]$_5$

    ii) [Ph$_3$P]$_3$ RhCl

    iii) 9-BBN
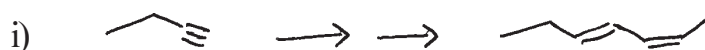
b) Explain any **four** of the following : **[12]**

    i) Pauson-khand reaction with suitable example.

    ii) α-alkylation of the carbonyl compounds involving enamine approach.

    iii) Use of organotin reagents in organic synthesis.

    iv) Role of enol-silyl ethers in organic synthesis.
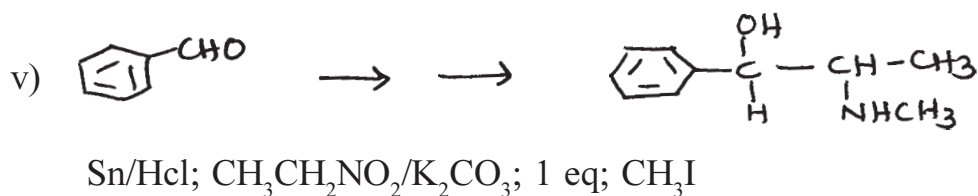
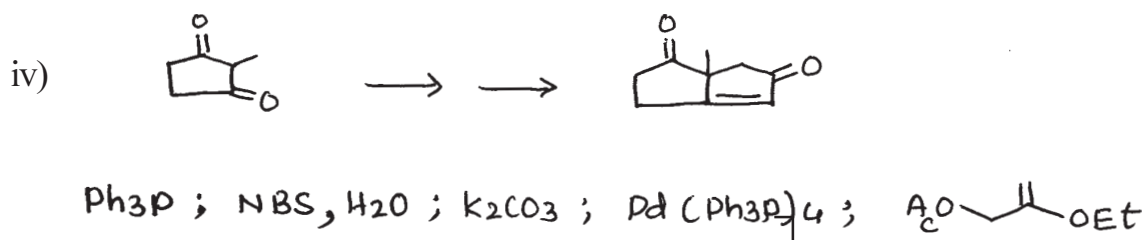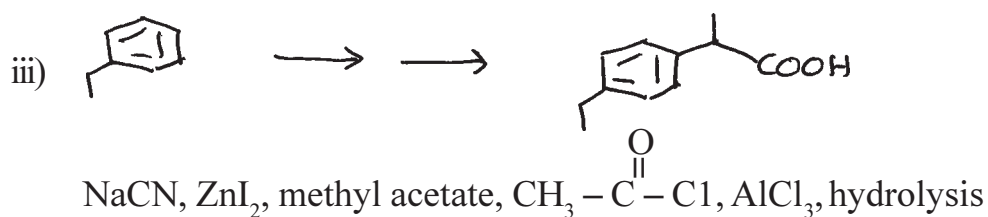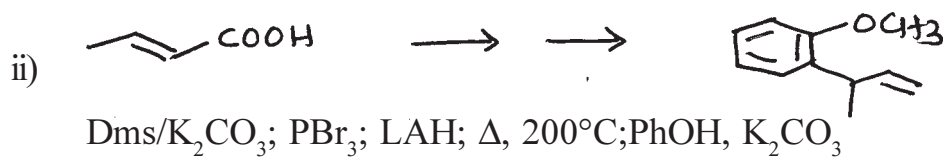   v) Urethane protection of NH$_2$ group in peptide synthesis.

SECTION-II

Q4) Write short notes on any **four** of the following : **[12]**

a) Solid phase peptide synthesis

b) oxo process

c) Suzuki coupling

d) Negishi coupling

e) Reppe reaction

Q5) Write the reagents and conditions in proper order to achieve the following conversions. Write the structures of the intermediates (any four) : **[12]**

i)

ii) → →

Dms/K$_2$CO$_3$; PBr$_3$; LAH; Δ, 200°C;PhOH, K$_2$CO$_3$

iii) → →

NaCN, ZnI$_2$, methyl acetate, CH$_3$ – C̈ – Cl, AlCl$_3$, hydrolysis

iv) → →

Ph3P ; NBS, H2O ; K2CO3 ; Pd (Ph3P)4 ;

v) → →

Sn/Hcl; CH$_3$CH$_2$NO$_2$/K$_2$CO$_3$; 1 eq; CH$_3$I

Q6) Using retrosynthetic analysis, suggest a suitable method for the synthesis of any four of the following compounds. **[16]**

i)

ii)

iii)

iv)

v)
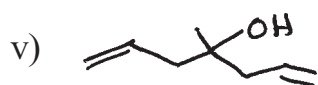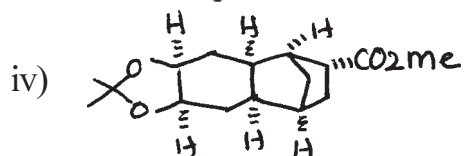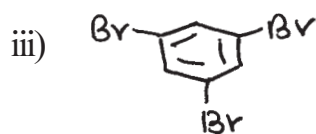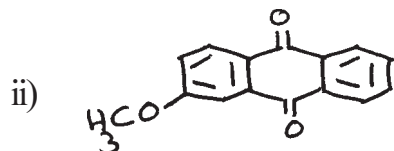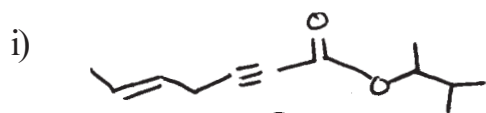
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M.Sc.

ORGANIC CHEMISTRY

CH-452: Heterocyclic Chemistry, Chiron Approach and Medicinal Chemistry

(2008 Pattern) (Semester - IV)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

  1)   All questions are compulsory .

  2)   Figures to the right indicate full marks.

  3)   Answer to the two sections should be written in separate answer book.

SECTION-I

Q1) a)   Explain the following (Any -3):   **[6]**

  i)   Imidazole is much stronger base than pyrazole.

  ii)   Pyridine - N-oxide readily under goes electrophilic substitution at the 4 - position.

  iii) Indole reacts with chloroform in alkali to give 3- chloroquinoline as one of the product.

  iv)   Electrophilic substitution in 4- phenyl pyridine occurs in the benzene ring.
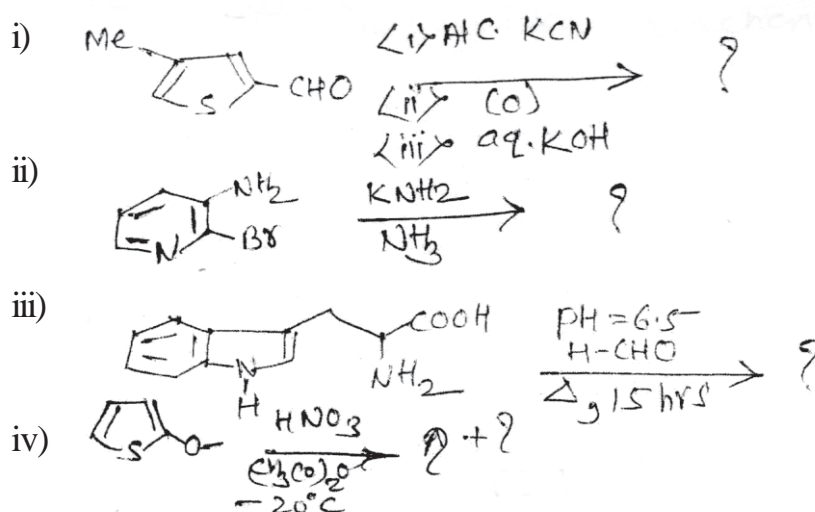
  b)   Attempt (Any - 2):   **[4]**

  i)   4 - chloro -3 nitrophyridine hydrolyses readily.

  ii)   Thiophene is resistant to ring opening than furan & pyrrole.

  iii) Benzofuran is more stable than furan towards acid.

  c)   Give applications of supramolecular chemistry.   **[2]**

P.T.O.

Q2) a) Predict the product and also give suitable mechanism (Any - 3) **[6]**

i)

Me—〔S〕—CHO
⟨i⟩ AlC KCN
⟨ii⟩ (O)
⟨iii⟩ aq.KOH
→ ?

ii)

NH_2, Br on pyridine ring
$\dfrac{KNH_2}{NH_3}$ → ?

iii)

indole structure with $COOH$, NH_2
$\dfrac{pH = 6.5}{H-CHO}$ $\xrightarrow{\Delta, 15\,hrs}$?

iv)

〔S〕—O—
$\dfrac{HNO_3}{(CH_3CO)_2O}$ $-20°C$ → ? + ?

b) Give reactions of following reagents with quinotine **[4]**

i) LAH, Et$_2$O.

ii) KNH$_2$, NH$_3$(liq.)' – 60°C.

iii) 30% oleum, 90°C.

iv) TSCl, kCN, CH$_2$Cl$_2$, H$_2$O, R.T.

c) Explain use of thiourea in the synthesis of thiozole. **[2]**

Q3) a) Write note on Any -2: **[6]**

i) The Hinsberg Thiophene Synthesis.

ii) First Benary furan synthesis.

iii) Hantzsch pyridine, synthesis.

b) Complete the following reaction sequence (Any - 2): **[4]**

i)

〔S〕—NH$_2$ $\xrightarrow[5°C]{NaNO_2, HCl}$ Ⓐ $\xrightarrow[\text{in NaOH}]{\beta\text{-naphthol}}$ Ⓑ

ii)

$\xrightarrow{Ⓐ}$ ... $\xrightarrow{Pd, C}$ Ⓑ

iii)

$\xrightarrow{Li, Hg}$ Ⓐ $\rightarrow$ Ⓑ
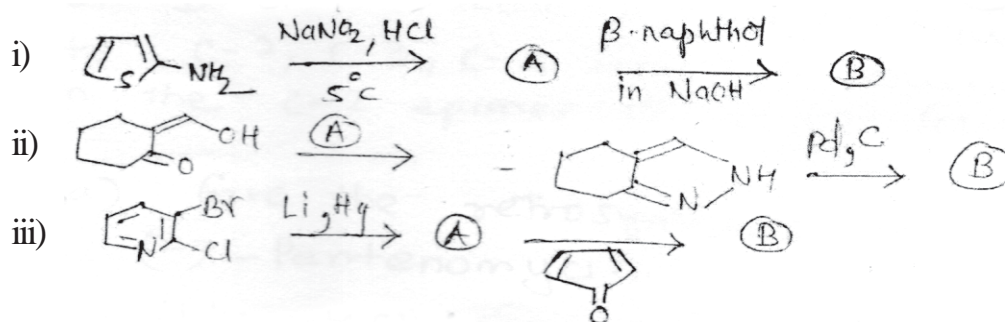
c) i) Write note on: Reissert Indole synthesis **[2]**

ii) Solve any - 2: **[4]**

1) Quinoline is used as a solvent in decarboxylation reactions - Explain.

2) Why isooxazole is less basic than oxazole.

3) Why pyrixidines readily under go. diels - Alder reaction.

SECTION-II

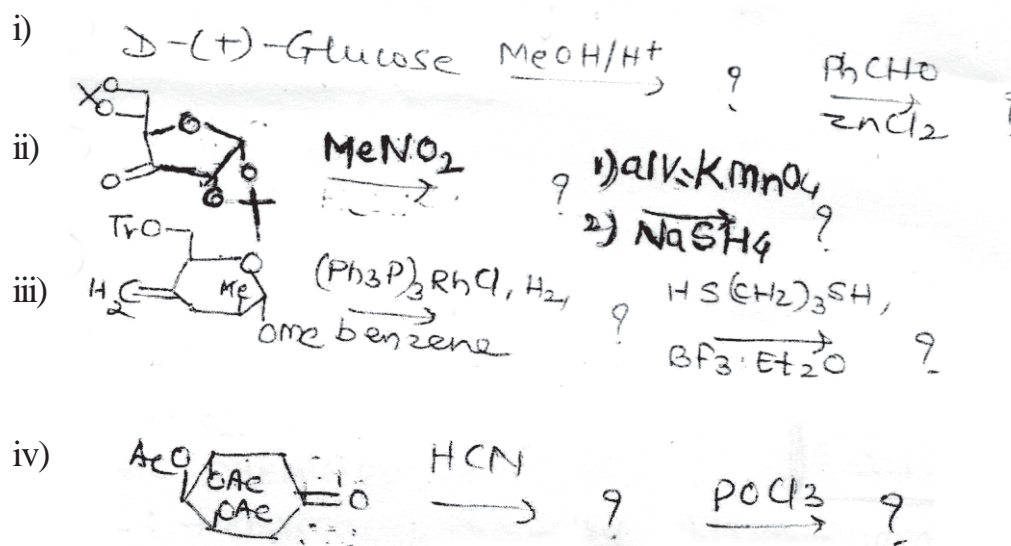*Q4)* Answer any three of the following:

a) "Fructose gives red precipitate in Febilings test" Explain.

b) "Glucosse on complete acetylation given (two isomeric) pentracetates which donot react with either phenye hydrazine or Tollen's reagent" . Explain.

c) Write a short note on "anomeric effect".

d) What are epimers? Write the open chain structure for C-2 epimer of D-(+) - Glucose Assign configurations to C - 2, C - 3, C - 4 and C - 5 carbon atom in the C - 2 epimer of D - (+) - Glucose. **[12]**

Q5) a) Give the retrosynthesis for (–) - pentenomycin. **[4]**

b) How will you convert D - mannitor into (s) - propanediol? **[2]**

c) What is the role of "rule of fire" in chiron approach? **[4]**

d) Predict the products for any three of the following. **[6]**

i)

D-(+)-Glucose $\xrightarrow{MeOH/H^+}$? $\xrightarrow[ZnCl_2]{PhCHO}$?

ii)

$\xrightarrow{MeNO_2}$? $\xrightarrow[2)\ NaBH_4]{1)\ alk.KmnO_4}$?

iii)

$\xrightarrow[ome\ benzene]{(Ph_3P)_3RhCl,\ H_2}$? $\xrightarrow[BF_3\cdot Et_2O]{HS(CH_2)_3SH,}$?

iv)

$\xrightarrow{HCN}$? $\xrightarrow{POCl_3}$?

Q6) Answer any three of the following: [12]

a) What are the characteristics of an ideal drug?

b) What is green chemistry? Explain any four principles involved in green chemistry.

c) Describe the concept of atom economy and percentage yield.

d) Describe the processes involved in elimination of a drug.

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M.Sc. - II

ANALYTICAL CHEMISTRY

CH - 481 : Bioanalytical and Forensic Science

(2008 Pattern) (Semester - IV)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) Answers to the two sections should be written in separate answer books.

2) All questions are compulsory and carry equal marks.

3) Neat diagrams must be drawn whrever necessary.

4) Use of logarithmic table/non-programmable calculator is allowed.

SECTION - I

Q1) Attempt any four of the following   **[20]**

a)   Give a method for estimation of lactic acid from milk.

b)   Explain in brief "Coloring Matters".

c)   Explain with suitable examples "microneutrients".

d)   Describe the method for estimation of caffeine from coffee.

e)   Calculate the percentage of tannin in 4.50 gm of tea sample. If it requires 14.0 ml of 0.2M KM_nO_4.

       (Given : Mol. wt. of tannin acid = 208.)

P.T.O.

Q2) Attempt any four of the following: **[20]**

a) Explain the procedure for estimation of glucose.

b) Give the procedure for estimation of vitamin-C.

c) Define saponification value of oil. Describe the method for estimation of saponification value of oil.

d) Outline the analytical procedure for estimation of iodine from iodited salt.

e) A sample of butter weighing 2.5 gm was dissolved in chloroform and treated with KI solution and titrated against 0.01N $Na_2S_2O_3$. It require 8.4 ml titrant. Calculate peroxide value of sample.

SECTION - II

Q3) Attempt any four of the following. **[20]**

a) Discuss the principle of isolation and determination of amphetamine from urine samples.

b) Outline the procedure for determination of benzodiazepine.

c) Discuss the isolation and determination of amphetamine form urine sample.

d) How are duitable goods transferred from one warehouse to another bonded warehouse?

e) Normal specimen of blood urine produces red colour change in diphenyl thiozone solution.

   i) Concentration of known barbiturate = 4.6 mg

   ii) Peak area of drug in sample = 11.8 min

   iii) Peak area of internal standard = 8.4 min

   iv) Peak area of known drug sample = 5.6 min

   v) Peak area of internal standard reference barbiturate solution = 15.8 min

   Calculate the percentage of bartiturate in sample.

Q4) Attempt any four of the following. [20]

    a) Define the term

        i) Duitable goods

        ii) Alcohol

        iii) Coca-leaf

        iv) Manufacture

    b) Write a note on "Ayurvedic preparations".

    c) Discuss the process for obtaining rectified spirit from non-bonded laboratory.

    d) Give the rules related to export medicinal and toilet preparation containing alcohol.

    e) State the narcotic drugs and Psychotropic substances rules 1985 related to cultivation of opium poppy and production of opium poppy straw.

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M.Sc.-II

ANALYTICAL CHEMISTRY

CH-490 : Analytical Spectroscopy

(2008 Pattern) (Semester-IV)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) *Answer to the two sections should be written in separate answer books.*
2) *All questions are compulsory and carry equal marks.*
3) *Neat diagrams must be drawn wherver necessary.*
4) *Use of logarithmic table/non-programmable calculator is allowed.*

SECTION-I

Q1) Attempt any **four** of the following :   **[20]**

a) Enlist the electromagnetic spectral regions that are useful for chemical analysis with electromagnetic radiation spectrum.

b) Explain the terms :
   i) Molar absorptivity
   ii) Radiant power

c) Give principle of ESCA with schematic diagram explain essential components of ESCA instrument.

d) Calculate the mass absorptive coefficient of an alloy which consists of 60% Zn, 32% Fe and 8% Cu. The mass absorptive coefficient for pure elements are 840, 570 and 740 cm^2/gm respectively for Zn, Fe and Cu.

e) Calculate the molar extinction coefficient of 1.30×10^{-4} M solution, which shows 45% transmittance in a 0.9 cm cell.

Q2) Attempt any **four** of the following :   **[20]**

a) What is meant by x-ray fluorescence? With schematic diagram explain energy dispersive x-ray fluorometer.

b) Explain the principle of chemiluminescence? Mention their types. Give an account of chemiluminescence titrations.

c) Draw and explain the energy level diagram of x-ray induced electron emission.

d) Write a short note on electro-chemiluminescence.

e) Calculate 1S electron binding energy of nitrogen in tetra methyl ammonium ion from the incident x-ray photon that was used to create the inner shell vacancy had a wavelength of 1.90Å. The work function of spectrometer was 7.2 eV and the kinetic energy of measured electron was 802.1 eV. (Given : $h = 6.626 \times 10^{-34}$ J.s, $C = 3 \times 10^8$ m/s)

SECTION-II

Q3) Attempt any four of the following : [20]

a) Write note on ^{31}P and ^{19}F in the field of biochemistry.

b) Explain the following term :
   i) Coupling constant in NMR spectroscopy.
   ii) Solvent used in NMR spectroscopy.

c) Write note on nuclear Overhauser effect.

d) Calculate energy of radiation that is required for excitation in each of the following two allowed transitions for a ^{14}N nucleus if applied field has flux density of 10,000 G. [For N, $\mu = 0.40357$, $m_I = 1$, $\beta = 5.0505 \times 10^{-31}$ J/G, $I = 1$].

e) Determine the ratio of the number of ^{19}F nuclei in the upper energetic level to lower energetic level at 25°C in a magnetic field with flux density of 15,000 G [$\mu = 2.6272$, $I = \frac{1}{2}$, $\beta = 5.0505 \times 10^{-31}$ J/G, $k = 1.381 \times 10^{-23}$ J/k].

Q4) Attempt any **four** of the following : [20]

a) Explain the following term in ESR.
   i) g-factor
   ii) hyperfine splitting

b) Write note on magic T.

c) Explain principle of ESR. Explain Instrumentation used in ESR.

d) With suitable example give any two applications of ESR.

e) If a resonance was observed for an unpaired electron at a magnetic flux density of 0.33T and frequency of 9.5 GHz. Calculate 'g' factor for unpaired electron.
   (Given : $h = 6.626 \times 10^{-34}$ Js, Be $= 9.285 \times 10^{-24}$ J/T).

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M.Sc. - II

ANALYTICAL CHEMISTRY

CH-491: Polymer Technology

(2008 Pattern) (Old Course) (Semester - IV)

Time : 3 Hours]   *[Max. Marks : 80*

Instructions to the candidates:

1) *All questions are compulsory and carry equal marks.*

2) *Answer to the two sections should be written in separate answer book.*

3) *Neat diagrams must be drawn wherever necessary.*

SECTION-I

Q1) Attempt <u>any four</u> of the following: **[20]**

    a)   Derive kinetic rate equation for chain polymerization.

    b)   Write a note on photodegradation of polymers.

    c)   Explain the mechanism of anionic polymerization.

    d)   Give the method of preparation and uses of

        i)   Teflon

        ii)   Polystyrene

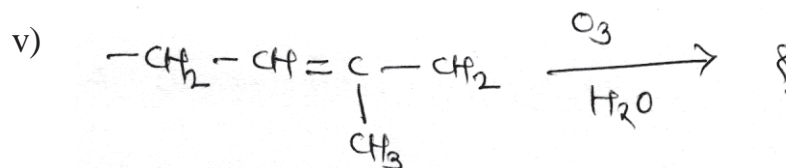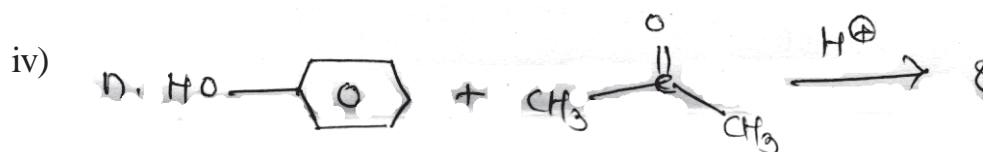   e)   Classify the polymers on the basis of their origin and structure of main chain.
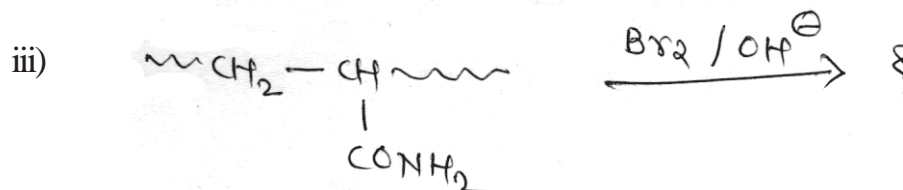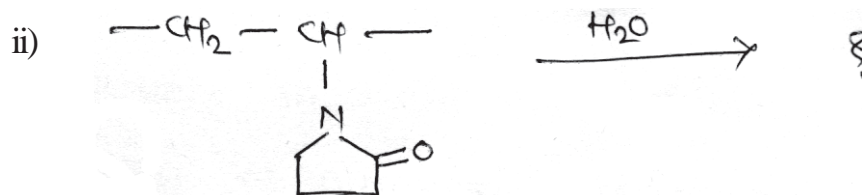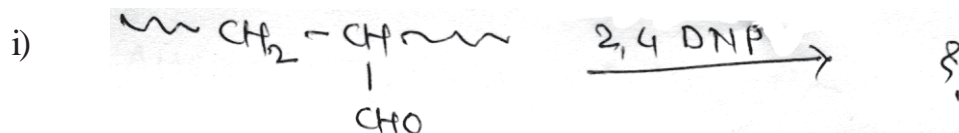
Q2) Attempt <u>any four</u> of the following: **[20]**

    a)   Write a note on cure-reactions.

    b)   Explain reactivity ratio and copolymerization behaviour.

    c)   Give salient features of emulsion polymerization.

    d)   Explain ring-opening polymerization.

e) Predict the products.

i)

$$\text{~~CH}_2-\text{CH~~} \quad \xrightarrow{\text{2,4 DNP}} \quad ?$$
with CHO group below CH

ii)

$$-\text{CH}_2-\text{CH}- \quad \xrightarrow{H_2O} \quad ?$$
with N-containing ring (pyrrolidone) below CH

iii)

$$\text{~~CH}_2-\text{CH~~} \quad \xrightarrow{Br_2/OH^\ominus} \quad ?$$
with CONH$_2$ group below CH

iv)

$$D. \; HO-\underset{O}{\bigcirc} \; + \; \text{CH}_3-\overset{O}{\overset{\|}{C}}-\text{CH}_3 \quad \xrightarrow{H^\oplus} \quad ?$$

v)

$$-\text{CH}_2-\text{CH}=\text{C}-\text{CH}_2 \quad \xrightarrow[H_2O]{O_3} \quad ?$$
with CH$_3$ below C

SECTION-II

Q3) Attempt <u>any four</u> of the following: **[20]**

a) Explain the term fibre-spinning. Explain importance of post treatment of fibres.

b) Write a note on injection - moulding.

c) What is ageing? Mention the reaction encountered in ageing and explain any one method used for ageing.

d) Explain softening temperature and flammability of the polymers.

e) A carbonyl terminated and hydroxyl terminated polybutadiene dissolve in mixture of ethanol and toluene, it was titrated with 0.1242 N KOH. The burette reading was 5.1. Calculate the average weight of polymer.

(Given: Weight of sample = 0.075 gm)

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Q4) Attempt <u>any</u> <u>four</u> of the following: **[20]**

a) Describe with a neat diagram, the dry spinning process.

b) Describe in detail the cryscopic method for the determination of number average molecular weight of polymers.

c) Describe in detail the blow-moulding.

d) Explain the term compounding. What are the ingradients used in compounding process? Give the role of each ingradient.

e) A suspension containing equal masses of particles of molecular weight 20,000 and 40,000 respectively. Calculate the number average and weight average molecular weight.

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