

Total No. of Questions : 6]

SEAT No. :

P645

[Total No. of Pages : 3

**[4325]-101**  
**M.Sc. (Semester - I)**  
**PHYSICAL CHEMISTRY**  
**CH-110: Physical Chemistry-I**  
**(2008 Pattern)**

*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	=	$2.997 \times 10^{10} \text{ cm s}^{-1}$ $= 2.997 \times 10^8 \text{ m s}^{-1}$
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10. 1 amu		=	$1.673 \times 10^{-27} \text{ kg}$
11. Bohr magneton	$\beta_e$	=	$-9.274 \times 10^{-24} \text{ J T}^{-1}$
12. Nuclear magneton	$\beta_n$	=	$5.051 \times 10^{-27} \text{ J T}^{-1}$
13. Mass of an electron	$m_e$	=	$9.11 \times 10^{-31} \text{ kg}$

**P.T.O.**

## SECTION - I

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

- a) Explain Einstein's photoelectric effect. How does it support Planck's hypothesis of quantization of energy ?
- b) Write and explain the terms in the three dimensional time independent Schrodinger equation. Why is the time dependent Schrodinger equation not used by chemists ? How can this equation be expressed as an eigen value equation.
- c) Derive the work done in a reversible adiabatic expansion of an ideal gas.
- d) Why is entropy called the arrow of time ? Show that the entropy of a system and surroundings taken together remains constant in a reversible process but increases in an irreversible process.
- e) What is residual entropy ? Explain with the example of the  $N_2O$  molecule. Write the corollary of the third law of thermodynamics.

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

- a) Write the combined mathematical statement of first and second law of thermodynamics. What are the inadequacies of the first law ?
- b) Derive the Gibbs - Duhem equation. What are its applications ?
- c) Derive the Clayperon equation and give its applications.
- d) What are Azeotropes ? Explain the method for separating Azeotropes.
- e) What is chemical potential ? Obtain an expression for the free energy of mixing of ideal gases.

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

- a) Determine the wavelength when a pg particle travels a Gm in a ms.
- b) The hexatriene molecule ( $6\pi$  -electrons) absorbs light of 250 nm during the transition to the first excited level. What is the length of the molecule ?
- c) Calculate the osmotic pressure at  $25^\circ C$  for a solute concentration of 0.5 mol per litre in a body cell that is impermeable to the solute molecules.
- d) Evaluate  $\Delta G_{mix}$  and  $\Delta S_{mix}$  if the gases, 1 mole helium, 3 moles neon, 2 moles argon and 2.5 moles xenon are mixed at  $25^\circ C$ .

## SECTION - II

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

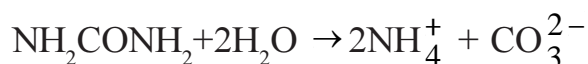
- a) What is enzyme catalysis ? Derive Michaelis - menton equation for enzyme catalyzed reactions.
- b) Compare transition state theory and collision theory for the rate of bimolecular reaction.
- c) Why do certain reactions end into explosion ? Explain their mechanism.
- d) Which are the techniques for studying kinetics of fast reactions ? Discuss any one of them.
- e) Distinguish between order and molecularity of a reaction. Write the general expression for order and half-life of a reaction.

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

- a) Derive Eyring equation for reaction rates.
- b) Write a note on potential energy surface.
- c) Derive the vibrational contribution to the molar entropy and Gibb's free energy of the system.
- d) Distinguish between Maxwell Boltzman and Bose-Einstein statistics.
- e) What are diffusion controlled limits ? Derive the equation for diffusion controlled reactions.

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

- a) Calculate the rotational contributions to entropy and free energy for oxygen gas at 25°C and 1 atmosphere pressure. The moment of inertia (I) of O<sub>2</sub> gas is 1.9373 x 10<sup>-46</sup> kg m<sup>2</sup>.
- b) Calculate the molar residual entropy of a crystal in which the molecules can adopt six orientations of equal energy at ok.
- c) The relaxation time for the fast reaction is 10 μs and the equilibrium constant is 1x10<sup>-3</sup>. Calculate the rate constants for the forward and backward reactions.
- d) The decomposition of urea in 0.1 m HCl occurs according to the reaction



The first order rate constant for this reaction at 71.2°C is 2.77 x 10<sup>-5</sup> min<sup>-1</sup> with the frequency factor 1.38 x 10<sup>13</sup> S<sup>-1</sup>. Calculate the entropy of activation at 71.2°C



Total No. of Questions : 6]

SEAT No. :

P648

[Total No. of Pages : 3

**[4325]-201**  
**M.Sc. (Semester - II)**  
**PHYSICAL CHEMISTRY**  
**CH-210: Physical Chemistry - II**  
**(2008 Pattern)**

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

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**P.T.O.**

## SECTION - I

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

- a) Predict the intensity distribution in the hyperfine lines of the ESR spectrum of  $\text{CD}_3$ .
- b) Explain in brief Width of spectra lines.
- c) What is Raman scattering ? Describe the quantum theory of Raman effect.
- d) Explain the principle of NMR spectroscopy and give its applications.
- e) Discuss the rotational vibrational spectrum of a diatomic molecule.

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

- a) Explain dissociation energy and dissociation product with respect to electronic spectrum.
- b) Explain the rule of mutual exclusion and its converse. Sketch and explain the polarizability ellipsoids of the various modes of vibration of  $\text{CO}_2$  molecule. Which of these are Raman active ?
- c) Write a note on stark effect.
- d) Discuss the applications of mössbauer spectroscopy.
- e) Explain rotational spectra of symmetric top molecule.

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

- a) The rotational spectra of CO has a spacing of  $3.84235 \text{ cm}^{-1}$ . Determine the bond length. (At.wt. : C = 12, O = 16)
- b) Compute the relative population of states of an electronic spin in magnetic field of 0.3T at 300K ( $g=2$ ).
- c) The fundamental vibrational frequency of  $^1\text{H}^{35}\text{Cl}$  molecule is  $86.63 \times 10^{12} \text{ Hz}$ . Calculate the zero point energy and force constant of HCl.
- d) Calculate the population of the first excited level if the ground state has 1000 molecules at 29K. ( $\Delta E=4.005 \times 10^{-23} \text{ J molecule}^{-1}$ )

## SECTION - II

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

- a) Explain different types of G.M. counters.
- b) How will you determine the steady state concentration of radicals?
- c) Describe the working of Fricke dosimeter. What precautions must be taken while using it ?
- d) Explain the terms i) tracks, ii) spurs, iii)  $\delta$ -rays and iv) stopping power.
- e) What is separation factor ? Explain electromagnetic method for separation of isotopes.

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

- a) What is natural nuclear reactor ? Discuss Oklo phenomenon and the Oklo reactor.
- b) How are uranium and plutonium recovered from spent fuels?
- c) Discuss India's three phase nuclear energy programme.
- d) What is diffusion phenomenon ? Discuss zone-diffusion technique to determine diffusion coefficient.
- e) How is  $^{14}\text{C}$  obtained naturally and artificially ? Give different steps involved in transformation of  $^{14}\text{C}$  from fossils into benzene.

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

- a) 10.0 ml KBr solution tagged with radioactive bromine was titrated with 0.01M  $\text{AgNO}_3$ . Addition of 2.5 ml of titrant followed by removal of AgBr precipitate decrease in activity from 12500 counts for 5 min to 6000 counts for 6 min. Calculate the amount of bromine in original solution. The detector gave background counts 100 for 10 min.  
[Given At.wts. of Ag=108, N=14, O=16, K=39 and Br=80]
- b) Potassium - 40 ( $t_{1/2} = 1.3 \times 10^9\text{y}$ ) constitutes 0.012% of the potassium in nature. Human body contains 0.35% potassium by weight. Calculate the radioactivity resulting from potassium-40 decay in a 70 kg man.
- c) When single atom of  $^{235}\text{U}$  undergoes fission energy obtained is 200 MeV. Calculate the power released during the fission of 1 kg  $^{235}\text{U}$  in 1 day.



Total No. of Questions : 5]

SEAT No. :

P651

[Total No. of Pages : 3

[4325]-301

M.Sc.(Semester - III)

PHYSICAL CHEMISTRY

CH-310: Quantum Chemistry and Solid State Chemistry

(2008 Pattern)

Time : 3 Hours]

[Max. Marks : 80

Instructions to the candidates :

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- 2) All questions are COMPULSORY.
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P.T.O.

## SECTION - I

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

- a) State and illustrate the conditions for the wave function to be acceptable.
- b) If  $\hat{A} = 3x^2$  and  $\hat{B} = \frac{d}{dx}$ , then show that  $\hat{A}\hat{B} \neq \hat{B}\hat{A}$ .
- c) A closed shell electronic configuration always gives rise to the  $^1S$  term. Explain.
- d) Give quantum mechanical definition of angular momentum. Explain its physical significance.
- e) Apply the variation method to the system of Helium atom to calculate its energy.
- f) Explain the following :
  - i) perturbation operator
  - ii) expansion theorem and
  - iii) non-degenerate states

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

- a) Set up the secular determinant and write the secular equation for benzene.
- b) Explain the mnemonic model of Frost and Musulin used to deduce HMO energies for annucleus.
- c) Compare perturbation method with the variation method on the basis of the principle, precision and convergence.
- d) Comment giving examples on the positive or negative nature of REPE value for a molecule.
- e) Write the secular equations for cyclo-butadiene and hence calculate the delocalization energy on the basis of Hückel's approximation.
- f) Explain why cyclooctatetraene is unstable but its dianion is stable and planar.

## SECTION - II

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

- a) Compare the resistivities of annealed and unannealed Cu-Au alloys.



- b) Discuss with a suitable example, how the forbidden band gap can be determined by studying optical properties of semiconductors.
- c) Discuss the mechanism of diffusion in solids.
- d) Give briefly the occurrence of elastic and plastic deformations in solids.
- e) Explain the mechanism of a photographic process.

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

- a) Discuss the factors that affect the progress of a Chemical change in solid-solid reactions.
- b) Explain the origin of colour centres in ionic crystals.
- c) The fast growing faces are eliminated whereas slow growing faces persist in a crystal - prove this statement on the basis of geometrical consideration.
- d) Write a note on Brillouin zones.
- e) Draw and describe the various  $\alpha$ -t plots for the decomposition of a single solid.

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

- a) The number of free electrons in a monovalent crystal is  $10^{19}$  per  $\text{cm}^3$  at 300K. Calculate the Fermi energy ( $E_0$ ) in eV.
- b) A certain alkali halide ( $A^+X^-$ ) with molecular weight 74.6 and NaCl structure has the interionic distance  $A^+ - X^-$  equal to 0.32 nm. Calculate the density of the salt for 0.1% Schottky defects.
- c) Calculate the Hall constant having carrier density for n-type of semiconductor as  $10^{16} \text{ cm}^{-3}$  and the charge of electron as  $4.803 \times 10^{-10}$  esu.



Total No. of Questions : 6]

SEAT No. :

**P651**

[Total No. of Pages : 3

**[4325]-302**

**M.Sc. (Semester - III)**

**PHYSICAL CHEMISTRY**

**CH - 311: Nuclear and Radiation Chemistry**

**(2008 Pattern)**

*Time : 3 Hours]*

*[Max. Marks : 80*

*Instructions to the candidates :*

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**P.T.O.**

## SECTION - I

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

- a) What is nuclear fission ? Give the charge distribution on the fission fragments.
- b) Explain the origin of prompt and delayed neutrons.
- c) Write the various types of nuclear reactions based on the nature of projectile and ejectile.
- d) Write a note on photonuclear reactions.
- e) Illustrate with example the significance of magic numbers.

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

- a) What are the different forms of potential ? Explain the square well potential.
- b) Draw a schematic diagram of nuclear reactor. Explain briefly the function of various parts of nuclear reactor.
- c) Give the classification of reactors on the basis of energy of neutron and fuel.
- d) Discuss the principle of particle induced X-ray emission technique. What are its advantages ?
- e) Discuss the compound nucleus theory of nuclear reactions.

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

- a) Calculate the excitation energy of the compound nucleus formed in the reaction  $^{24}\text{Mg}(\alpha, p)^{27}\text{Al}$ , the energy of  $\alpha = 2.75 \text{ MeV(Ls)}$ .

Given : Mass of  $^{24}\text{Mg} = 23.985045$ , mass of  $\alpha$ -particle = 4.00260, mass of  $^{28}\text{Si} = 27.97631 \text{ amu}$ .

- b) In the fission of  $^{239}_{94}\text{Pu}$ , the fragments have the mass numbers 100 and 138 whose stable isobars are  $^{100}_{42}\text{Mo}$  and  $^{138}_{56}\text{Ba}$ . What are the primary fragments ?
- c) Calculate the approximate critical dimensions of a  $^{239}\text{Pu}$  reactor to function in a steady state ( $k = 1.04$ ), in the case where the reactor is of a cubical shape.

Given : The migration area =  $0.032\text{m}^2$ .

## SECTION - II

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

- a) Discuss the working of Vande Graaff generator.
- b) What are the basic components of a particle accelerator ? Explain the function of each component.
- c) What is Szilard-Chalmer reaction ? Derive the expression  $E = \frac{536 E_s^2}{A}$ .
- d) What you understand by the term intrinsic and extrinsic semiconductor ? Explain the working of surface barrier detector.
- e) Explain with suitable example retention in organic compounds.

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

- a) Discuss the free radical theory of radiolysis of water.
- b) Explain the various stages of interaction of radiations with biological cells.
- c) Enlist various natural and man made sources of radiations. Describe the procedure for safe handling of these sources.
- d) Distinguish between somatic and genetic effects of radiations.
- e) What are the after effects of chernobyl nuclear accident ?

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

- a) Find out thickness of lead needed to decrease the activity of Co-60 source from 25,000 cpm to 4000 cpm. Given:  $e^{\mu} = 0.211$  b/e,  $Z$  of Pb = 82,  $A$  of Pb = 207, density of Pb =  $11.35 \text{ g cm}^{-3}$ .
- b) Find out dose due 200 mci CS-137 radiation source at a distance of 3 meters. Given : gamma energy = 0.67 MeV.
- c) A radiation worker is exposed to following doses of radiations in 6 months.  
1 mrad due to  $\alpha$ -particles  
1 mR due to  $\beta$  particles  
0.01 Gy due to  $\gamma$  rays.  
Find out his effective dose. Is it permissible ?



Total No. of Questions : 6]

SEAT No. :

P652

[Total No. of Pages : 4

[4325]-303

M.Sc.(Semester - III)

PHYSICAL CHEMISTRY

CH-312: Advanced Instrumental Methods of Analysis

(2008 Pattern)

Time : 3 Hours]

[Max. Marks : 80

Instructions to the candidates :

- 1) Answers to the two sections should be written in separate answer books.
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P.T.O.

## SECTION - I

**Q1)** Answer the following (any three) **[15]**

- a) Define and explain the terms isotopic abundance and excitation function.
- b) What are the advantages of NAA technique ?
- c) Explain the parameters which govern the sensitivity of the NAA technique.
- d) How are qualitative and quantitative analyses performed by x-ray absorption methods ?
- e) Describe EPXMA technique with a neat labelled diagram of an electron microprobe.

**Q2)** Answer the following (any three) **[15]**

- a) Draw a neat labelled diagram of an ESCA spectrometer and explain with reference to the samples used in it.
- b) Discuss the applications of the ESCA technique.
- c) Explain the cylindrical mirror analyzer used in ESCA with a neat labelled diagram.
- d) State the principle of mass spectrometry. Explain the terms molecular ion and base ion.
- e) What are the types of detectors used in mass spectrometry ? Explain the Faraday Cup detector with a neat labelled diagram.

**Q3)** Solve the following (any two) **[10]**

- a) 120 mg sample containing 0.021% gold was irradiated in a neutron flux of  $5 \times 10^8 \text{ ncm}^{-2}\text{s}^{-1}$  for 20 hrs. Find the activity of the sample after a cooling period of 5 hrs.

[Given :  $r = 100\%$ ,  $\sigma = 98.86 \text{ b}$ ,  $t_{1/2}$  of  $^{198}\text{Au} = 2.7\text{d}$ ].

- b) Aluminium is to be used as windows for a cell for x-ray absorption measurements with the Ag  $K\alpha$  line. The mass absorption coefficient for aluminium at this wavelength is  $2.724 \text{ cm}^2/\text{g}$ , its density is  $2.699 \text{ g/cm}^3$ . What maximum thickness of aluminium foil could be employed to fabricate the windows if no more than 3.5% of the radiation is to be absorbed by them ?
- c) In a particular time-of-flight mass spectrometer an ion with  $m/z$  178 required  $1.44 \mu\text{S}$  to strike the detector after emission from the source. Determine the time needed for an ion with  $m/z$  246 to strike the detector.

### SECTION - II

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

- a) Describe the sample introduction in an ICP technique.
- b) Discuss the applications of plasma emission spectroscopy.
- c) Explain the effect of structural rigidity on the luminescence of an analyte.
- d) Write a note on electro chemiluminescence.
- e) Discuss the factors which affect the results of thermogravimetric analysis.

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

- a) Draw a typical DTA curve. State its characteristics.
- b) With a neat labelled diagram of a cell, describe constant current coulometric analysis.
- c) Explain with examples the application of coulometry to perform redox titrations. What are the possible sources of error in such titrations.
- d) Describe the various excitation signals used in voltametry.
- e) Discuss the technique of cyclic voltametry as an analytical tool.

**Q6)** Solve any two of the following :

**[10]**

- a) A 100 ml solution of chloride is coulometrically titrated with silver ion using a current of 1.00 mA. Calculate the concentration of chloride if the end point is detected after 102 seconds.
- b) An electroactive species yielded a wave with a limiting current of 15.2  $\mu\text{A}$  at an rde which was rotated at 10.0 r/s. What limiting current would be expected at 30.0 r/s ?
- c) A 0.6025 g sample was dissolved and the  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  ions present were precipitated as  $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . The oxalates were then heated in a thermogravimetric apparatus leaving a residue of anhydrous oxalates that weighed 0.5713 g in the temperature range of 320°C to 400°C and the residue of carbonates that weighed 0.4673g in the temperature range 580°C to 620°C. Calculate the percentage of Ca and of Ba in the sample.  
[At. wts. : Ba = 137.34, Ca=40, C=12, O=16]





Total No. of Questions : 5]

SEAT No. :

P654

[Total No. of Pages : 3

[4325]-304

**M.Sc.(Semester - III)**  
**PHYSICAL CHEMISTRY**  
**CH-314: Polymer Chemistry**  
**(2008 Pattern) (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 tables/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	$\beta_e$	=	$-9.274 \times 10^{-24} \text{ J T}^{-1}$
12. Nuclear magneton	$\beta_n$	=	$5.051 \times 10^{-27} \text{ J T}^{-1}$
13. Mass of an electron	$m_e$	=	$9.11 \times 10^{-31} \text{ kg}$

**P.T.O.**

## SECTION - I

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

- a) Define the following terms:
- |                  |                                     |
|------------------|-------------------------------------|
| i) polymer       | ii) copolymer                       |
| iii) homopolymer | iv) heteropolymer and configuration |
- b) Describe the secondary bond forces of polymer.
- c) What is polymerization ? Discuss various steps involved in addition polymerization.
- d) Distinguish between thermosetting and thermoplastic polymers.
- e) Write a note on - 'Instantaneous composition of polymers'.

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

- a) Describe the kinetics of condensation polymer.
- b) Discuss the effect of degree of crystallinity on permeability, hardness and modulus of a polymer.
- c) Write a note on : Crystallinity in Nylon-6.
- d) 'It is almost impossible to obtain a 100% crystalline polymer' - Explain.
- e) Define the term 'glass transition temperature' (T<sub>g</sub>) and describe any one method of its determination.

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

- a) The extent of reaction for linear step reaction polymerization is 0.90. Calculate the number average degree of polymerization and the weight fraction of the chain having  $\bar{X}_n$  repeating units.
- b) Calculate instantaneous composition of polymer when one mole of Vinyl acetate is copolymerised with three mole of Vinyl Chloride the monomer reactivity ratios are 0.25 and 1.75 respectively.  
[At.wt. C=12, H=1, O=16, Cl=35.5]

- c) The relative viscosities of a fraction of polystyrene of  $\bar{M}_n = 275000$ , dissolved in tetralin at 293K were

% concentration	0.01	0.025	0.05	0.10	0.25
Relative viscosity( $\eta_r$ )	1.05	1.12	1.25	1.59	2.70

Calculate the constant  $\alpha$  and hence estimate relative viscosity of 0.1% solution of polystyrene with  $\bar{M}_n = 455000$  in the same solvent.

### SECTION - II

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

- a) Distinguish between condensation and addition polymers.
- b) Discuss the use of TGA technique in the analysis of polymer.
- c) Write a note on: Conduction mechanism of conducting polymer.
- d) Describe the principle of membrane osmometry.
- e) Why does the IR spectra of amorphous and crystalline polymer differ ? Describe the method of preparation of polymer sample for IR spectrum.
- f) Describe the process of calendering with suitable diagram.

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

- a) Derive the stress strain equation for simple stretching of an elastomer.
- b) Explain the method to determine molecular weight of polymer by viscosity measurement.
- c) What is molding ? Discuss the injection molding with a neat diagram.
- d) What are the techniques used for the production of reinforced plastics. Explain any one technique with neat diagram.
- e) Discuss the viscous flow phenomenon and its mechanism in polymers.
- f) Explain the terms: Tenacity, Crimp, Denier, moisture regain and fibre with reference to textile.



Total No. of Questions : 4]

SEAT No. :

P655

[Total No. of Pages : 3

[4325]-305

M.Sc.(Semester - III)

PHYSICAL CHEMISTRY

CH-315: Special Topics in Physical Chemistry

(2008 Pattern) (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.

**Physical - Chemical Constants**

1. Avogadro Number	N	=	$6.022 \times 10^{23} \text{ mol}^{-1}$
2. Boltzmann Constant	k	=	$1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1}$ $= 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1}$
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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	$\beta_e$	=	$-9.274 \times 10^{-24} \text{ J T}^{-1}$
12. Nuclear magneton	$\beta_n$	=	$5.051 \times 10^{-27} \text{ J T}^{-1}$
13. Mass of an electron	$m_e$	=	$9.11 \times 10^{-31} \text{ kg}$

P.T.O.

## SECTION - I

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

- a) Write proton condition for  $\text{Na}_3\text{PO}_4$  and  $\text{NaHSe}$ .
- b) The pH of 0.01 M solution of a salt of succinic acid is 5.6. Find the concentration of  $\text{C}_6\text{H}_6\text{O}_4$ ,  $\text{C}_4\text{H}_5\text{O}_4^-$  and  $\text{C}_4\text{H}_4\text{O}_4^{2-}$ . (Given :  $\text{pK}_{a_1}=4.19$ ,  $\text{pK}_{a_2} = 5.48$ ).
- c) Set up the mass balance on sodium and carbonate in 0.1 M  $\text{Na}_2\text{CO}_3$  and acetate in 0.1 M acetic acid.
- d) Calculate the pH and concentration of all ionic species for 0.02 M  $\text{CH}_3\text{COOH}$ . [Given :  $\text{K}_a = 1.85 \times 10^{-5}$ ].
- e) What are active and passive sensors ?
- f) Discuss the mechanism observed in chemiresistors.

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

- a) What is the influence of surrounding gas atmosphere on the properties of semiconductor porous ceramics ?
- b) Write a note on potentiometric sensors.
- c) Discuss adsorption isotherms used in sensors.
- d) Define the terms activity, selectivity and inhibitor as used in catalyst.
- e) Give the mechanism of the phenol-acetone condensation reaction to get bisphenol A.
- f) Explain the dependence of the observed rate constant for oximation of acetone on pH at 20°C.

## SECTION - II

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

- a) Write a note on scanning tunneling microscope.
- b) What are intelligent gels ? Explain their functioning and applications.
- c) Explain the technique of Lithography.
- d) Write a note on the uses of nanomaterials.
- e) Explain the applications of biomimatics.
- f) Explain how a smart sensor can test freshness of fish.

**[4325]-305**

**2**

**Q4)** Attempt any four of the following :

**[20]**

- a) Describe the phase diagram of the water system.
- b) Describe the anomalous properties of nanoparticles.
- c) Write a note on carbon nanotubes.
- d) Describe the principle of preparing tunable smart materials.
- e) Write a note on rubber like ceramics.
- f) Describe the chemical methods of preparing nano particles.



Total No. of Questions : 4]

P655

[Total No. of Pages : 3

[4325]-305

M.Sc.(Semester - III)

PHYSICAL CHEMISTRY

CH-316: Environmental Chemistry

(2004 Pattern) (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

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11. Bohr magneton	$\beta_e$	=	$-9.274 \times 10^{-24} \text{ J T}^{-1}$
12. Nuclear magneton	$\beta_n$	=	$5.051 \times 10^{-27} \text{ J T}^{-1}$
13. Mass of an electron	$m_e$	=	$9.11 \times 10^{-31} \text{ kg}$

P.T.O.

## SECTION - I

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

- a) What are the effects of MIC on human health ?
- b) Explain the following terms with suitable examples.
  - i) Occupier
  - ii) Aerosol
  - iii) Pollutant
  - iv) BOD
  - v) Trade effluent
- c) Write a note on biochemical effect of DDT.
- d) Give the classification of air pollutants and discuss the sources of oxides of carbon.
- e) Sketch and label the structure of atmosphere. Explain stratosphere and troposphere zones of the atmosphere.
- f) Distinguish between classical smog and photochemical smog.

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

- a) What do you mean by acidic rain ? Explain the role of air pollutants in acidic rain.
- b) Explain role of petroleum hydrocarbons in pollution.
- c) Discuss the main objectives of water sampling.
- d) Explain the nature and composition of ground water and sea water.
- e) What are surfactants ? Discuss in brief anionic surfactants.
- f) Write a note on organic pollutants.

## SECTION - II

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

- a) Discuss the impact of noise pollution on human health.
- b) Describe the 'cooling tower' to prevent thermal pollution.
- c) What are the sources of thermal pollution ? Discuss any one in detail.



- d) Explain the mechanism of polymer degradation by photosensitizer additives.
- e) How do the modern agricultural practices pollute the soil ?
- f) What are soil indicator plants ? Discuss these in detail.

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

- a) Describe how alkalinity in water is determined.
- b) What are the sources of cadmium pollution? Explain the effects of cadmium poisoning.
- c) What are carcinogen ? Explain in detail.
- d) Explain with examples, the enzyme inhibition by toxic chemicals in human beings.
- e) Discuss the detrimental effects of urban waste products on soil.
- f) Write a note on pollution hazards due to lead.



Total No. of Questions : 4]

SEAT No. :

**P656**

**[4325]-306**

[Total No. of Pages : 2

**M. Sc. - II Semester-III**

**INORGANIC CHEMISTRY**

**CH - 326 : Organometallic Compounds of Transition**

**Metals and Homogeneous Catalysis**

**(2008 Pattern)**

*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 : Mn=25, Fe=26, Co=27, Ni=28, Zr=40, Rh=45, Pd=46*

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

- a) For the following molecules, give the formal oxidation state of the metal, d-electron count, total valence electrons (TVE) and the number of M-M bonds if any.
  - i)  $[\text{CpCo}(\text{CO})_2(\mu\text{-CO})]$  ;      ii)  $(\text{Cyclo } \text{C}_4\text{H}_4) \text{PdCl}_2$
  - iii)  $[\text{Cp.Mn}(\text{CO})_3]$       iv)  $(\text{C}_x^3\text{-allyl})_2 \text{Ni}$
  - iv)  $\text{Cp}_2\text{ZrCl}_2$
- b) For the following polynuclear complexes, indicate the total number of electrons, determine the number of M-M bonds present and predict a structure.
  - i)  $\mu\text{-Co}[\text{C}_x^4\text{-C}_4\text{H}_4] \text{Fe}(\text{CO})_2$
  - ii)  $\mu\text{-Co}-\mu\text{-CRR}'\text{-}[\text{Cp}^*\text{Rh}]_2$
- c) Give an account of the chemistry structure and bonding of the TT-allyl complexes of transition metals.
- d) Explain the typical reactions of  $[(\text{x}^6\text{-C}_6\text{H}_6)_2 \text{Cr}]$
- e) Describe the systematic classification of  $n^5$  cyclopentadienyl T.M. derivatives along with their preparative methods.

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

- a) Explain - "Ni-C bondlength in nickelocene is longer than the Fe-C bondlength in Ferrocene".

**P.T.O.**

- b) What is catalysis ? Why do T.M's acts as catalyst ? Give two examples of homogeneous catalyst.
- c) Discuss in detail production of aldehyde by wacker process.
- d) Propose a structure of  $(C_5H_5)_3 Ni_3(CO)_2$  based on IR data. Does each Ni atom obey the  $18\bar{e}$  rule?
- e) What hapticities are possible for the following ligands:
  - i)  $C_2H_4$  ; ii) Cyclopentadienyl, iii)  $C_6H_6$  ; iv) Butadiene ;
  - v) Cyclo octatetraene.

**Q3)** Attempt any FOUR of the following. **[20]**

- a) Explain the catalytic role of Alkyl Molybdate (VI) compound in epoxidation reactions.
- b) Explain the role of OMC's as protecting agent.
- c) Discuss briefly OMC of group IV in medicine.
- d) Predict the product and state which reactions are cyclometallation, elimination reaction, oxidative addition and which are insertion reactions.
  - i)  $Cp (CO)_3 Re + Br_2 \rightarrow ?$
  - ii)  $Cp (CO)_2 Fe - CH_3 + PPh_3 \rightarrow ?$
  - iii)  $CO_2 (CO)_8 + C_2F_4 \rightarrow ?$
  - iv)  $Mn[(COC_6H_4Me-P) (CO)_5] \xrightarrow{h\nu} ?$
  - v)  $[(\eta^5-C_5H_5)_2 MoH_2] + [Mn(CO)_5 CH_3] \rightarrow ?$
- e) Discuss in brief industrial applications of Heck reaction.

**Q4)** Write short notes on any FOUR **[20]**

- a) Tertiaryphosphine complexes of TM's.
- b) Pinnacol compounds.
- c) Environmental aspects of OMC's
- d) Non-Rigid molecules in different coordination geometries.
- e) Wilkinson's Catalyst.

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Total No. of Questions : 4]

SEAT No. :

**P657**

**[4325]-307**

[Total No. of Pages : 2

**M. Sc. - II Semester-III**

**INORGANIC CHEMISTRY**

**CH - 330 : Coordination Chemistry, Magnetism and Reaction Mechanism  
(2008 Pattern)**

*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 and calculator is allowed.*

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

- a) Explain the Magnetic properties in dimeric Cu(II) acetate monohydrate.
- b) Explain why Fe<sub>2</sub>(CO)<sub>9</sub> is diamagnetic ?
- c) Explain the terms
  - i) Magnetic domain
  - ii) Ferrimagnetism
- d) Discuss the Factors that affect the crystal field stabilization energy in T.M. complexes.
- e) Differentiate between magnetically dilute system and magnetically concentrated system.

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

- a) Give the nomenclature for the following molecules.
  - i) Rh(acac)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>,
  - ii) [Co(en)<sub>2</sub>(Ox)]Cl.
  - iii) K<sub>3</sub>[Fe(Ox)<sub>3</sub>]; 3H<sub>2</sub>O,
  - iv) Li [Co(N(CH<sub>3</sub>)<sub>4</sub>)<sub>2</sub>]
  - v) [Co(NH<sub>3</sub>)<sub>4</sub>(ONO)]Cl<sub>2</sub>
- b) Predict the type of magnetic exchange which occurs via the 90° exchange pathway in the system d<sup>1</sup> - d<sup>1</sup>, d<sup>2</sup> - d<sup>2</sup>, d<sup>3</sup> - d<sup>3</sup>, d<sup>8</sup> - d<sup>8</sup> and d<sup>9</sup> - d<sup>9</sup>.
- c) The extent of exchange interaction in the Cu<sub>2</sub>O<sub>2</sub> ring system is greater than that in Cr<sub>2</sub>O<sub>2</sub> ring system. Explain.
- d) Explain the solute-solute interaction.
- e) The magnetic moment of a certain octahedral Co(II) complex is 4.0 μ<sub>B</sub>. What is its d-electron configuration. Draw the simplified crystal field diagram of octahedral system.

**P.T.O.**

**Q3)** Attempt any FOUR of the following. **[20]**

- a) What is conjugate base dissociation mechanism ?
- b) Discuss in brief isomerisation of octahedral complexes.
- c) Discuss the mechanism of electron transfer reaction with reference to the inner-sphere reaction.
- d) Which isomer can you obtain from the following synthetic pathways ? Give precise explanation and correct structure of the product.
  - i)  $[\text{PtCl}_4]^{-2} \xrightarrow{+\text{NH}_3} ? \xrightarrow{+\text{NO}_2^-} ?$
  - ii)  $[\text{Pt}(\text{PR}_3)_4]^{+2} \xrightarrow{+\text{Cl}^-} ? \xrightarrow{+\text{Cl}^-} ?$
- e) Explain in brief Anation reactions.

**Q4)** Attempt any FOUR of the following. **[20]**

- a) Discuss in brief Reductive elimination reactions.
- b) What is mixed order substitution reactions ? Explain with suitable examples.
- c) Write a note on-Raci misation of tris-chelate complexes.
- d) “Kinetically inert complexes are Hermodynamically unstable and vice-versa”. Justify this statement with suitable examples.
- e) Complete the reactions:
  - i)  $[\text{Co}(\text{NH}_3)_6]^{+3} + \text{H}_3\text{O}^* \rightarrow ? + ?$
  - ii)  $[\text{Fe}(\text{CN})_6]^{-4} + [\text{Fe}(\text{CN})_6]^{-3} \rightarrow ? + ?$
  - iii)  $(\text{CH}_3)_3\text{B} + \text{N}(\text{CH}_3)_3 \rightleftharpoons ?$
  - iv)  $\text{BF}_3 + \text{F}^- \rightarrow ?$
  - v)  $\text{C}_2(\text{CO})_6 + \text{Py} \rightarrow ? + ?$

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Total No. of Questions : 4]

SEAT No. :

P658

[4325]-308

[Total No. of Pages : 2

M. Sc. - II Semester-III  
INORGANIC CHEMISTRY

CH - 331 : Structural Methods in Inorganic Chemistry

Time : 3 Hours]

[Max. Marks : 80

Instructions to the candidates:

- 1) All questions are compulsory.
- 2) All questions carry equal marks.
- 3) Use of log-table and calculator is allowed.

Q1) Attempt the following (any four) [20]

- a) Explain the principle underlying DSC.
- b) Sketch the Fluorine nmr of  $\text{BrF}_5$  and comment on the structure of the molecule.
- c) Predict the ESR spectro of:
  - i) Catecholate anion.



given :  $I_{\text{H}} = 1/2$  ;  $I_{\text{N}} = 1$

- d) How is Mössbauer Spectroscopy useful to characterise oxidation states of tin in organotin compounds.
- e) Sketch the energy level diagram and transitions for a quadrupole nucleus with  $I = 5/2$  and  $\eta \neq 0$ .

Q2) Answer any four : [20]

- a) Explain the significance of 'G' in ESR.
- b) Explain the principle of photo electron spectroscopy.
- c) Explain Zeeman effect on Mössbauer spectrum of  $^{57}\text{Fe}$  compound with one example.
- d) Explain with suitable examples the effect of (i) Heating rate (ii) Furnace atmosphere (iii) Sample weight on TG curves.
- e) The utilized reflecting plane of a LiF analysing crystal has d value of  $2.014\text{\AA}$ . Calculate the wave length of the second order diffracted line which has a value of  $50.1^\circ$

P.T.O.

**Q3)** Attempt the following (any four) **[20]**

a) The TG plot of 2.89 mg of sample containing  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  shows a single step at on set temperature  $\sim 378^\circ\text{k}$  corresponding to formation of  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ . The mass loss in the step was 0.59 mg. Determine the percentage of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in the sample.

given At.Wts: Mg = 24.312; S = 32.064; H=1.008; O=15.999

b) Compounds of some elements are used in NMR as shift agents. Which are these elements ? Explain the use of shift agents in NMR.

c) With the help of ray diagram explain the principle of TEM.

d) How can we determine rate constants of different redox reactions using cycle voltametry.

e) "NMR is an excellent tool to study Metal phosphine compounds" Justify the statement.

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

a) Photo electron spectroscopy.

b) Braggs Law.

c) Differential Thermal Analysis.

d) Applications of ESR.

e) Isomer shifts in Mössbauer spec

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Total No. of Questions : 4]

SEAT No. :

**P659**

**[4325]-309**

[Total No. of Pages : 2

**M. Sc. - II Semester-III**

**INORGANIC CHEMISTRY**

**CH - 332 : Bio-Inorganic Chemistry :**

**Inorganic Elements in the Chemistry of Life**

*Time : 3 Hours]*

*[Max. Marks : 80*

*Instructions to the candidates:*

- 1) *All questions are compulsory.*
- 2) *All questions carry equal marks.*

**Q1)** Answer any four **[20]**

- a) Give structural features and functions of metallobiomolecules having copper as metal center.
- b) Which metalloenzymes are responsible for removal of  $H_2O_2$  ? Discuss their active site structure and function.
- c) How metal - DNA interactions are followed using different spectroscopic techniques ?
- d) Compare between therapeutic and diagnostic applications of radiopharmaceuticals.
- e) Why gadolinium complexes are preferred as MRI contrast agents ?

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

- a) What are the important structural features of Vit.  $B_{12}$  ? Explain its biochemical importance.
- b) What are hydrogenases ? Explain mechanism of reactions catalyzed by hydrogenases.
- c) Discuss and illustrate the principle of magnetic resonance imaging used in clinical diagnosis.
- d) Distinguish between the oxidative and hydrolytic mechanisms of DNA cleavage with suitable examples.
- e) Explain in detail the structural role of zinc with suitable examples.

**P.T.O.**



**Q3) A) Attempt any five: [15]**

- a) What kind of ionizing radiations are useful in radiopharmaceutical applications ?
- b) Name at least two diseases each caused due to deficiency of cobalt and copper.
- c) Draw and explain the structure of hemocyanin.
- d) Give reactions of Cis-DDP (cisplatin) in aqueous, biological and other media.
- e) Draw the structure of chlorophyll and discuss its role in photosynthesis.
- f) Explain 1, 2-shift reaction catalyzed by Vit B<sub>12</sub> coenzymes.

**B) Fill in the blanks :**

- g) Cytochrome-c oxidase has \_\_\_\_\_ at its active site.
- h) Pernicious anaemia is caused by \_\_\_\_\_.
- i) Urease has \_\_\_\_\_ at its active site.
- j) The cleavage of DNA caused by OH is called as \_\_\_\_\_.
- k) The trivalent ion of \_\_\_\_\_ used as MRI contrast agent interferes with Fe<sup>3+</sup>.

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

- a) Azurin and plastocyanin.
- b) Metal complexes as spectroscopic probes of DNA.
- c) Urease.
- d) Analog and digital imaging used in radiology.
- e) MRI.

\*\*\*

Total No. of Questions : 6]

SEAT No. :

**P660**

**[4325]-310**

[Total No. of Pages : 3

**M. Sc. - II**

**ORGANIC CHEMISTRY**

**CH - 350 : Organic Reaction Mechanism**

*Time : 3 Hours]*

*[Max. Marks : 80*

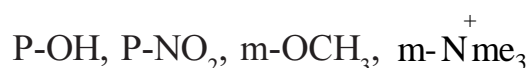
*Instructions to the candidates:*

- 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)** Attempt any four of the following. **[12]**

- a) Explain the evidences to support NGP.
- b) Butane 2, 3-dione exists exclusively in keto form, where as 1,2 -cyclopentane dione is 100% enolised. Explain.
- c) The ionisation constants of 3 and 4 cyano benzoic acids at 30<sup>0</sup>C are  $2.51 \times 10^{-4}$  and  $2.82 \times 10^{-4}$  respectively. Benzoic acid has ionisation constant  $k_a$  of  $6.76 \times 10^{-5}$  at 30<sup>0</sup>C. Calculate  $\sigma_m$  and  $\sigma_{m,p}$  for the cyano substituent.
- d) Predict the sign of Hammett ( $\sigma$ ) sigma constant for following substituents giving reasons.



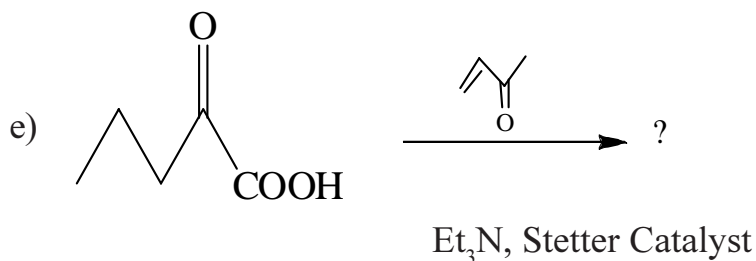
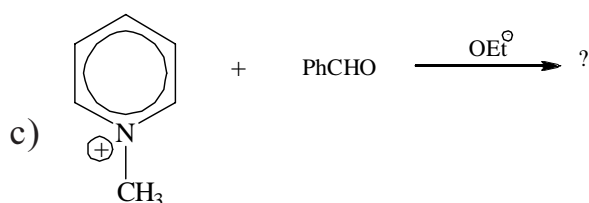
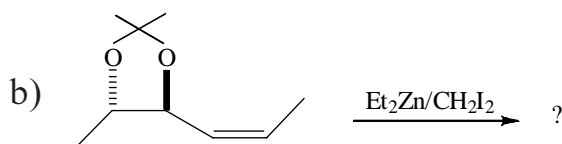
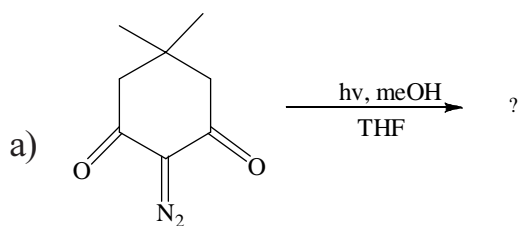
- e) Explain the importance of non-linear Hammett Plots.

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

- a) Trapping of intermediates.
- b) Perkin reaction.
- c) Transannular rearrangement.
- d) Stevens rearrangement.

**P.T.O.**

**Q3)** Predict the products with mechanism for any four of the following. [16]



### SECTION - II

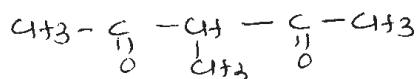
**Q4)** Explain any four of the following. [12]

a) Thiamine Pyrophosphate is a natural acyl ion equivalent.

b) Explain the observed enol contents of the following.

1, 3 - cyclohexane dione 95%

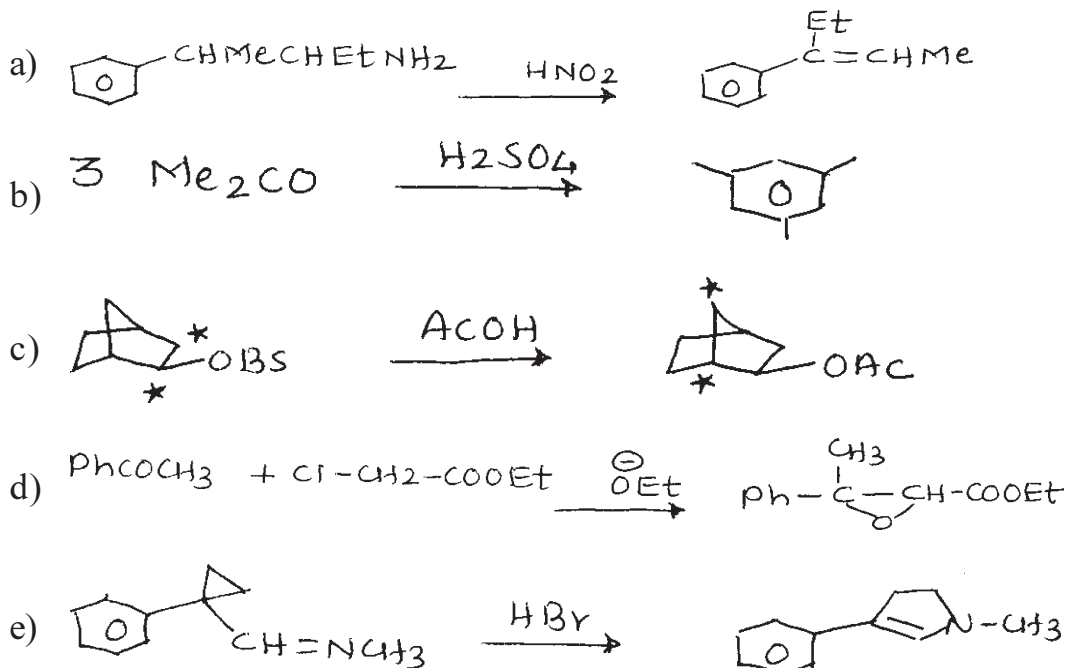
1, 2 - cyclopentane dione 99%

 33%

c) Ethyl methyl ketone with benzaldehyde in presence of base and acid gives two different products.

- d) Ethanolysis of  $\text{Ph}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OTs}$  proceeds with total inversion, whereas formolysis proceeds with retention of configuration.
- e) Explain any rearrangement which proceeds through carbene intermediate.

**Q5)** Suggest mechanisms for any four of the following. **[16]**



**Q6)** Answer any four of the following. **[12]**

- Give the mechanism of formation of ATP from ADP using phosphoenolpyruvate.
- Write a note on halogenation of unsymmetrical ketones in acidic and basic medium.
- Explain the use of isotopes in determining mechanism of organic reactions.
- The acetolysis of both 4-methoxy-1-pentyl brosylate and 5-methoxy-2-pentyl brosylate give the same mixture of products. Explain.
- Explain the factors that serve to stabilize carbanion.

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Total No. of Questions : 6]

SEAT No. :

**P646**

[Total No. of Pages : 7

**[4325] - 102**  
**M.Sc. (Part - I) (Semester - I)**  
**INORGANIC CHEMISTRY**  
**CH - 130: Inorganic Chemistry - I**  
**(2008 Pattern)**

*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) Neat and labelled diagrams must be drawn whenever necessary.*
- 4) Figures to the right indicate full marks.*

**Q1)** Attempt any three of the following:

**[15]**

- a) Develop stereographic projections for the following molecules. Justify your answer.
  - i)  $B_3N_3H_6$
  - ii)  $\text{trans } [Co (NH_3)_4Cl_2]^+$
- b) Using similarity transformation and group multiplication table given for  $C_{2v}$  point group, divide symmetry operations into appropriate classes. Given: Group multiplication table.
- c) Classify any two of the following molecules into appropriate point group. Justify it.
  - i)  $InCl_5^{2-}$
  - ii)  $PCl_5$
  - iii)  $AsH_3$

**P.T.O.**

- d) Give the properties of irreducible representations for  $C_{4v}$  point group label the irreducible representations with appropriate Mülliken symbols. Given: character table for  $C_{4v}$ .

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

- a) Sketch and explain the following symmetry elements in  $BF_5$  molecule and classify it into appropriate point group.
- i) Proper axis of symmetry.
  - ii) Improper axis of rotation.
- b) Discuss the symmetry criterion for a molecule to be optically active. Predict the optical activity for the following compounds.
- i)  $[Rh H (CO) (PR_3)_2]$
  - ii)  $[Co (en)_2 Cl_2]^+$
- c) Find out normalized SALC using projection operator of  $E_g$  irreducible representation which operates on  $\sigma_f$  orbital in  $[Cu(NH_3)_4]^{++}$  ion.

Given:

$D_{4h}$	E	$2C_4$	$C_2$	$2.C_2'$	$2.C_2''$	i	$2.S_4$	$\sigma_h$	$2\sigma_v$	$2.\sigma_d$
$E_g$	2	0	-2	0	0	2	0	-2	0	0

- d) For a  $[Ni(CN)_5]^{2-}$  molecule. Find reducible representation for which sigma bonds form the basis and find out which of the orbitals from the Ni atom will be offered for sigma bonding. Given: Character table for  $C_{4v}$  point group.

Q3) Answer the following:

[10]

- a) Select the proper answer from the given alternatives.
- i) A tetrahedral  $AB_4$  molecule belongs to  $T_d$  point group. The symmetry operations are  $E, 8C_3, 3C_2, 6S_4, 6\sigma_d$ . The trace for the reducible representation when symmetry operations of  $T_d$  applied to  $AB_4$  is,
- a) 4 2 0 0 1                                      b) 4 1 0 0 2  
c) 5 1 2 0 1                                      d) 5 1 0 0 2
- ii) The centre of inversion is well explained in,
- a) Trans, 1, 2 dichloro, dibromo ethane.  
b) Cis 1, 2, dichloro, dibromo ethane.  
c) Cis 1, 2, dichloro ethane.  
d) Cis 1, 2, dibromo ethane.
- iii) The  $SnF_4$  molecule belongs to following point group.
- a)  $C_{4v}$     b)  $T_d$   
c)  $D_{4h}$     d)  $D_{4d}$
- iv)  $D_{5h}$  point group is for the molecule
- a)  $SnCl_2$     b)  $IF_7$   
c)  $IF_5$     d)  $PCl_5$
- v) The improper axis of rotation is present in.
- a)  $BF_5$   
b)  $SO_2$   
c) Pyridine  
d)  $NF_3$
- b) What are Weiss indices? Explain with suitable examples. Draw (3 2 1) and (0 0 1) planes in cubic system.

Character table for  $C_{4v}$  point group

$C_{4v}$	E	$2C_4(z)$	$C_2$	$2\sigma_v$	$2\sigma_d$	Linear, rotations	quadratic
$A_1$	1	1	1	1	1	z	$x^2+y^2, z^2$
$A_2$	1	1	1	-1	-1	$R_z$	
$B_1$	1	-1	1	1	-1		$x^2-y^2$
$B_2$	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y) ( $R_x, R_y$ )	(xz, yz)

1-Group Multiplication Table for  $C_{2v}$

$C_2 V$	E	$C_2$	$\sigma V_1$	$\sigma V_2$
E	E	$C_2$	$\sigma V_1$	$\sigma V_2$
$C_2$	$C_2$	E	$\sigma V_2$	$\sigma V_1$
$\sigma V_1$	$\sigma V_1$	$\sigma V_2$	E	$C_2$
$\sigma V_2$	$\sigma V_2$	$\sigma V_1$	$C_2$	E



## SECTION - II

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

- a) Explain the reactions of dihydrogen.
- b) Explain in detail nitrides of boron.
- c) Give an account of extended silicon-oxygen compounds.
- d) With example explain the different oxidation states of nitrogen.
- e) Give an account of interhalogen compounds.

**Q5)** Write notes on any three of the following: **[15]**

- a) Extraction of alkali metals by using crown ethers.
- b) Metal fullerene compounds.
- c) Uses of noble gases.
- d) Synthesis and properties of saline carbides.
- e) Sulphur oxoanions.

**Q6)** a) Draw any five structures: **[5]**

- i)  $\text{XeF}_4$
- ii)  $\text{B}_5\text{H}_9$
- iii)  $\text{Si}_3\text{O}_9^{-6}$
- iv)  $\text{Li}_4(\text{CH}_3)_4$
- v)  $\text{IF}_5$
- vi)  $[\text{Cl}_2\text{PN}]_3$

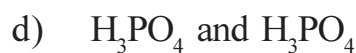
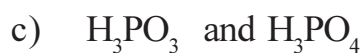
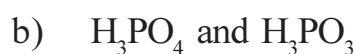
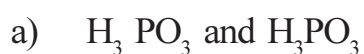
b) Attempt any five of the following:

[5]

i) Fullerene  $C_{60}$  reacts with K to give a compound which acts as a superconductor at 18 K. The compound is -----



ii)  $PCl_3$  and  $PCl_5$  undergo hydrolysis to produce respectively:



iii) The correct statement for  $(CH_3)_3 N$  and  $(SiH_3)_3 N$  are -----

i)  $(CH_3)_3 N$  and  $(SiH_3)_3 N$  both are planar.

ii)  $(CH_3)_3 N$  is planar and  $(SiH_3)_3 N$  is pyramidal.

iii)  $(CH_3)_3 N$  is Pyramidal and  $(SiH_3)_3 N$  is planar.

iv)  $(SiH_3)_3 N$  is Weaker base than  $(CH_3)_3 N$ .

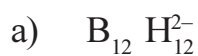
a) (ii), (iii) & (iv)

b) (iii), (iv)

c) (ii), (iv)

d) (i), (iii), (iv)

iv)  $B_{10} C_2 H_{12}$  is isoelectronic with -----



- v) Alkali metals in liquid ammonia are blue in colour because -----
- a) They contain alkali metal cations.
  - b) The free electron is trapped in solvent cage.
  - c) An ion pair is formed.
  - d) An amide ion is formed.
- vi) Which one of the following is the correct set of number of lone pair of electrons in  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  respectively?
- a) 0, 1, 2
  - b) 1, 2, 3
  - c) 3, 2, 1
  - d) 2, 1, 0

+++++++

Total No. of Questions : 6 ]

SEAT No. :

P650

[Total No. of Pages :4

[4325] - 203

M.Sc. - I ( Semester - II)

ORGANIC CHEMISTRY

CH - 250 : Synthetic Organic Chemistry and Spectroscopy  
(2008 Pattern)

Time :3 Hours]

[Max. Marks :80

Instructions to the candidates:

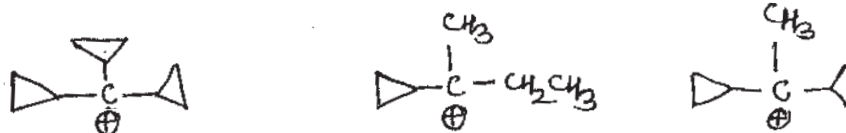
- 1) All questions are compulsory.
- 2) Figures to the right indicate full marks.
- 3) Answers to the two sections to be written in separate answer books.

SECTION - I

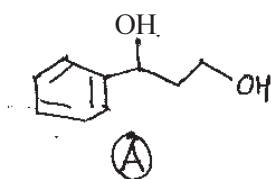
Q1) Explain any four of the following :

[16]

- a) Outline the details of Reformatsky reaction .
- b) Give two methods for preparation of acetanilide from acetophenone.
- c) Arrange the following cations as per their stability order and justify your answer.



- d) Cis - 4 hydroxy cyclohexane carboxylic acid undergoes lactonization on heating where as the trans isomer does not.
- e) What are the products of oxidation of compound (A) on treatment with
  - i)  $\text{MnO}_2$  / Acetone / R.T.
  - ii)  $\text{KMnO}_4 / \text{OH}^\ominus$



P.T.O.

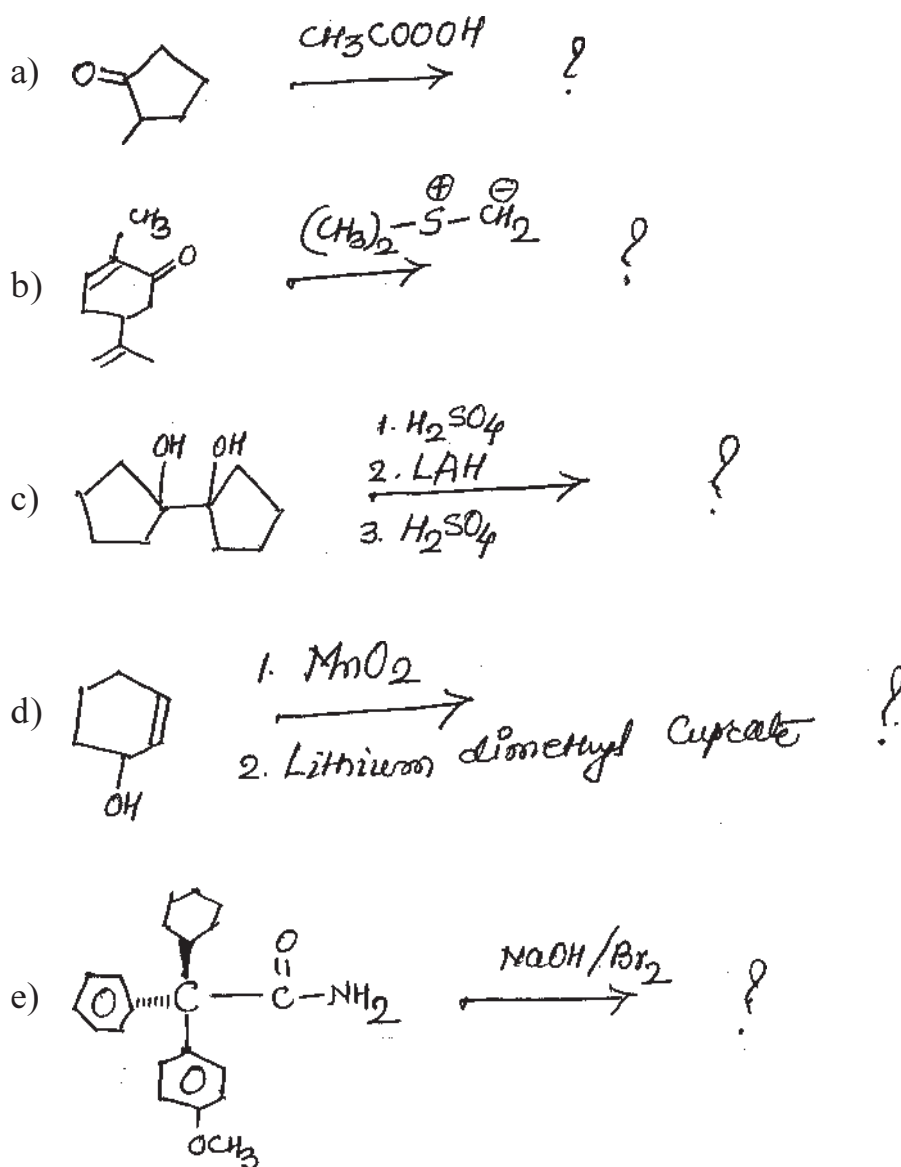
Q2) Write short notes on any three of the following :

[12]

- Organo copper reagents in organic synthesis.
- Jone's reagent.
- Wolf rearrangement.
- Generation and fate of carbenes.

Q3) Predict the products and suggest the mechanism for any four of the following :

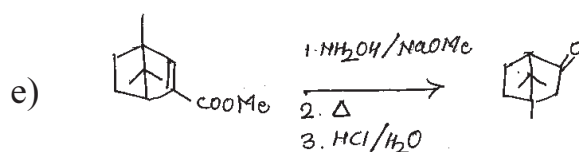
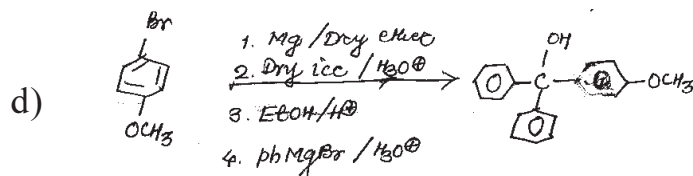
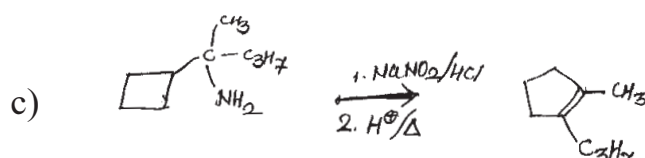
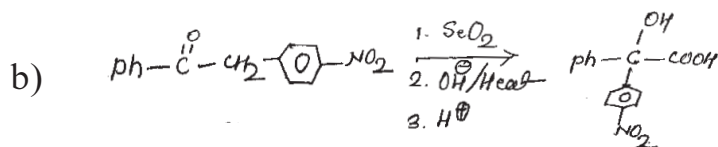
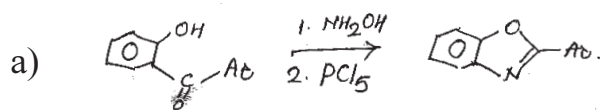
[12]



## SECTION - II

**Q4)** Suggest mechanism for any four of the following :

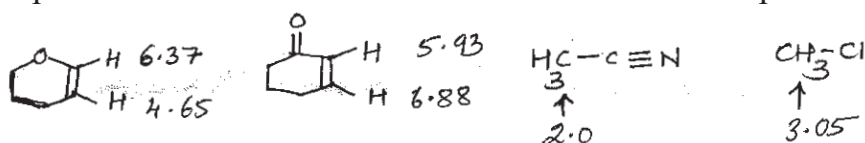
[12]



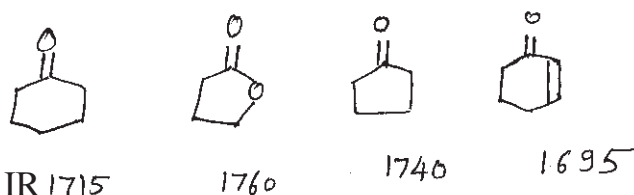
**Q5)** Attempt any four of the following :

[16]

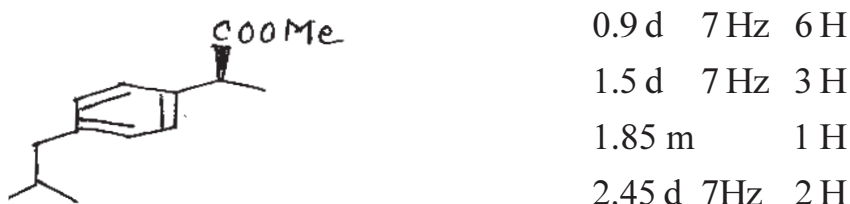
a) Explain the chemical shift observe for the indicated protons.



b) Explain IR absorption frequencies for the following.



c) Assign the chemical shift for the following.

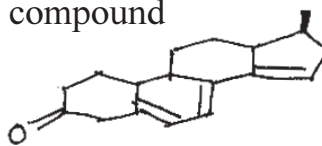
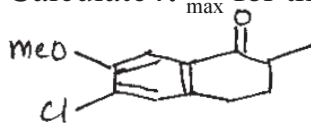


3.6s 3 H

7.1d 8Hz 2 H

7.3d 8Hz 2 H

d) Calculate  $\lambda_{\max}$  for the following compound



e) Explain any two of the following.

i) Bathochromic shift.

ii) Diamagnetic Anisotropy.

iii)  $\alpha$  - haloketo rule.

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

a) M.F :  $C_8H_8O_2$ .

UV : 250, 260, 265 nm ( $\epsilon$  220, 250, 200).

IR : Very broad band between 2700 – 3300, 1700, 1600 (w). 1500, 920  $cm^{-1}$ .

$H^1NMR$  : 3.5 (12mm, s).

7.2 (30 mm, s).

12.3 (6 mm, s).

b)  $C_8H_{10}O_2$

IR : 3939, 1599, 1497, 1173  $cm^{-1}$ .

$H^1NMR$  : 2.35 (t,  $J=6$  Hz, 10 mm Ex).

3.97 (q,  $J=6$  Hz, 20 mm).

4.08 (t,  $J=6$  Hz, 20 mm).

6.93 (d,  $J=8$  Hz, 20mm).

6.97 (t,  $J=8$  Hz, 10mm).

7.27 (t,  $J=8$  Hz, 20 mm).

c) MF :  $C_4H_5O_2N$

UV : Featureless above 210 nm,

IR : 2250; 1750  $cm^{-1}$

NMR : 3.5 (10 mm, s)

3.8 (15 mm, s)

d) MF :  $C_7H_{14}O$

$H^1NMR$  : 0.9 (t, 6 H)

1.6 (Sext. 4 H)

2.4 (t, 4 H)



[4325]-412

M.Sc. - II

ANALYTICAL CHEMISTRY  
CH-490: Analytical Spectroscopy  
(Semester - IV)

[Max. Marks : 80

Time : 3 Hours]

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 - IQ1) Attempt any four of the following : [20]

- a) Explain the following terms used in instrumental analysis.
  - i) Dispersive power
  - ii) Resolving power
  - iii) Period
- b) Enlist the electromagnetic spectral regions that are useful for chemical analysis with electromagnetic radiation spectrum.
- c) Draw schematic diagram and explain working of single beam spectrophotometer..
- d) Calculate molar absorptivity for the complex formed between bisulphite (III) and thiores having  $3.7 \times 10^{-2}$  M concentration of complex, gave transmittance of 78.3% in a 1.0 cm path length at 470 nm.
- e) A certain photomultiplier tube has ten dynodes and each dynode emits an average of 4.2 electrons for impinging electrons. Calculate the amplification factor of a photomultiplier tube.

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

- a) Enlist the diffraction methods of crystal analysis. Describe Bragg's method for crystal analysis. How the reflection for different order are noted by this technique.
- b) Explain the origin of chemical shift in ESCA lines. Describe the use of chemical shift in quantitative analysis.

R.T.O.



- (c) Explain the principle of chemiluminescence. Describe its analytical applications.
- (d) Describe X-ray absorptive method for crystal analysis.
- (e) Calculate the electron binding energy of Nitrogen in nitrate ion from the incident x-ray photon that was used to create the inner-shell vacancy had a wavelength of 0.922 nm. The work function of spectrometer was 7.2 eV and the kinetic energy of measured electron was 889.4 eV.
- [Given: Planck's constant =  $6.625 \times 10^{-34}$  J s,  $C = 2.998 \times 10^8$  M<sup>2</sup>s<sup>-1</sup>]

## SECTION - II

- Q3) [20]** Attempt any four of the following :
- (a) Distinguish between proton magnetic resonance spectra and non-protonic resonance spectra.
- (b) What is meant by Larmor precession? Explain the principle of NMR spectroscopy based on classical theory.
- (c) What is meant by relaxation? Explain spin-spin and spin-lattice relaxation.
- (d) A proton appears at a quartet at  $\delta = 4.2\delta$ ,  $J = 6$  Hz on a 300 MHz instrument. indicates the line position in Hz of each line and give its relative intensities.
- (e) Calculate the chemical shift in PPM of a particular nucleus in a 60 MHz instrument if the reference nucleus absorbs at a magnetic flux density that is 0.063 G which greater than nucleus.
- [Given: For <sup>1</sup>H nucleus 14000 G required to cause absorption at 60 MHz].
- Q4) [20]** Attempt any four of the following :
- (a) Describe with suitable example application the applications of ESR spectroscopy in a qualitative and quantitative analysis.
- (b) Draw a schematic diagram of SEM, label its components. Describe how the image of a surface of solid sample is obtained using a finely Focused beam of electrons.
- (c) Explain the following terms :
- i) ELDOR
  - ii) ENDOR
- (d) Distinguish between NMR and ESR spectroscopy with reference to its principle, sources, reference compounds, applied magnetic fields and detectors.

e) if a resonance was observed for an unpaired electron at a magnetic flux density 0.33 T and a frequency of 9.2 GHz, calculate g-factor for unpaired electron.

[Given: Planck's constant =  $h = 6.625 \times 10^{-34} \text{ J s}$   
 Bohr Magnetron =  $\mu_B = 9.285 \times 10^{-24} \text{ J T}^{-1}$ ].





Total No. of Questions : 6]

SEAT No. :

P647

[Total No. of Pages : 4

[4325] - 103

M.Sc. - I (Semester - I)

ORGANIC CHEMISTRY

CH - 150 : Organic Reaction Mechanism and Stereo Chemistry  
(2008 Pattern)

Time : 3 Hours]

[Max. Marks : 80

Instructions to the candidates :

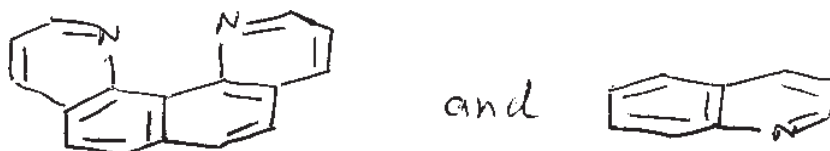
- 1) All questions are compulsory.
- 2) Figures to the right indicate full marks.
- 3) Answers to the two sections should be written in separate answer books.

SECTION - I

Q1) Attempt any four of the following :

[16]

- a) Which of the following compound is stronger base? Why?



- b) Methyl cinnamate undergoes electrophilic substitution mainly at meta position. Explain.
- c) Solvolysis of  $\text{PhCH}_2\text{CH}_2\text{OBS}$  is faster than  $n\text{-propylbrosylate}$ . Explain.
- d) Reaction of  $n\text{-propyl bromide}$  with toluene in presence of  $\text{AlBr}_3$  gives 4-methyl cumene. Explain.
- e) Menthyl chloride on treatment with  $\text{NaOEt}$  gives only one product whereas neo-menthyl chloride gives two different products. Explain.

P.T.O.


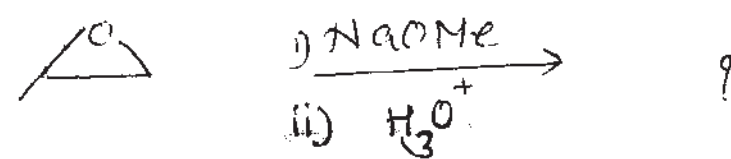
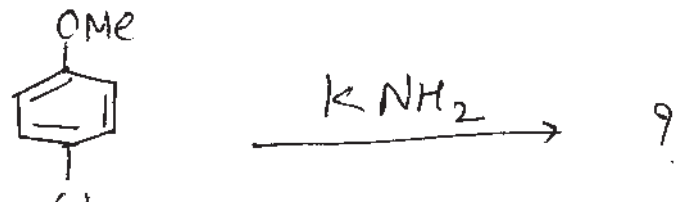
Q2) Write short notes on any three of the following :

[12]

- Crown ether
- Jacobsen reaction
- Factors affecting strength of Acids.
- SET mechanism

Q3) Predict the products with mechanism (any three)

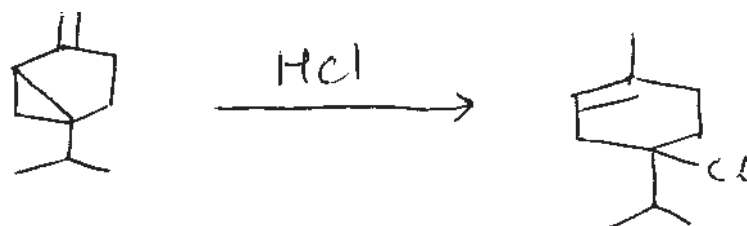
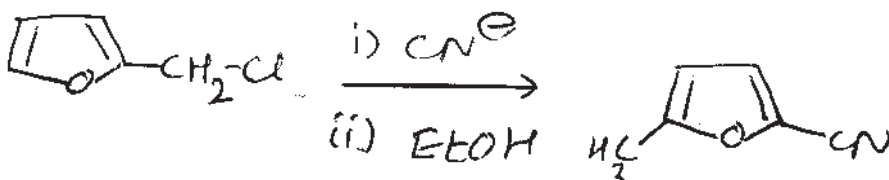
[12]

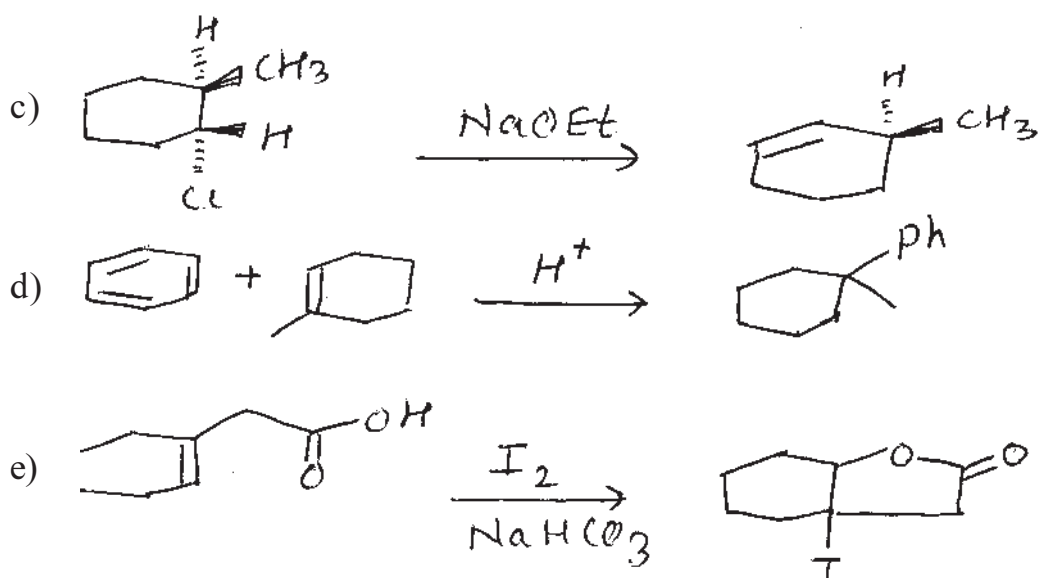
-  Anthracene  $\xrightarrow{\text{NO}_2\text{BF}_4}$  ?
- meso-2, 3-dibromobutane  $\xrightarrow{\text{I}^-}$  ?
-  Propylene oxide  $\xrightarrow{\text{i) NaOMe}}$   $\xrightarrow{\text{ii) H}_3\text{O}^+}$  ?
-  4-methoxychlorobenzene  $\xrightarrow{\text{KNH}_2}$  ?

### SECTION - II

Q4) Suggest mechanism for any four of the following :

[12]

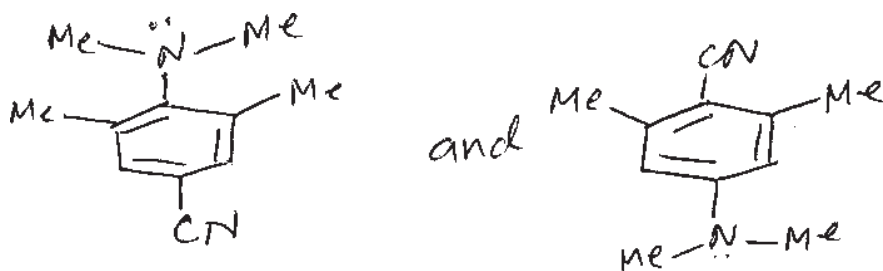
-  1,2-dimethylcyclohexane  $\xrightarrow{\text{HCl}}$  1-chloro-2,2-dimethylcyclohexane
-  2-(chloromethyl)furan  $\xrightarrow{\text{i) CN}^-}$   $\xrightarrow{\text{ii) EtOH}}$  2-cyano-2-methylfuran



Q5) Attempt any four of the following :

[12]

a) Which of the following is stronger base? Explain.



b) Give a brief account on metallocene with special reference to ferrocene.

c) Draw the resonance structures of :

- i) Phenanthrene
- ii) m-nitro anisole

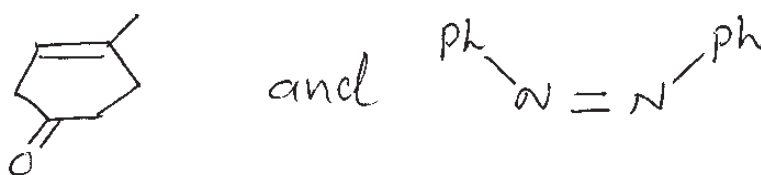
d) The proportion of gauche conformation of 2-hydroxy ethanethiol is more than expected. Explain.

e) 1-methyl cyclohexane on treatment with HBr/H<sub>2</sub>O<sub>2</sub> gives 2-bromo-1-methyl cyclohexane. Whereas with HCl/H<sub>2</sub>O<sub>2</sub> gives 1-chloro-1-methyl cyclohexane Explain.

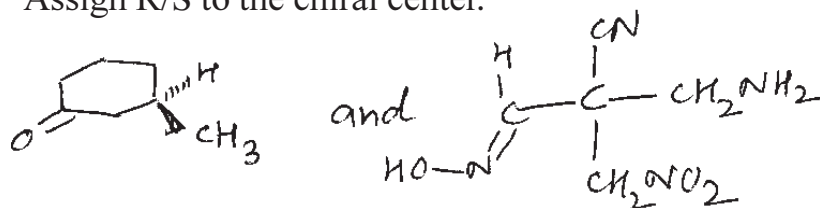
Q6) Attempt any eight of the following :

[16]

a) Assign E/Z to the following compounds

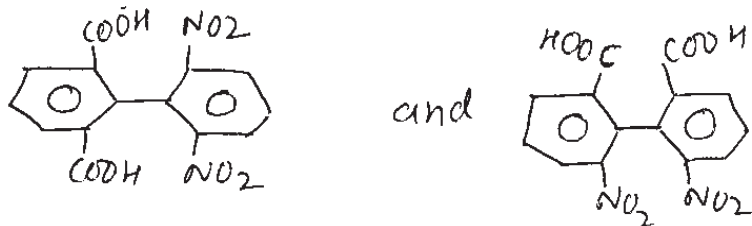


b) Assign R/S to the chiral center.

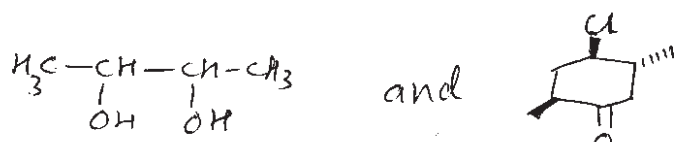


c) Pyrrole is stronger acid than pyrrolidine. Explain.

d) Which of the following is optically active? Justify.



e) Identify chiral carbons and find total no. of stereo-isomers in the following compounds.



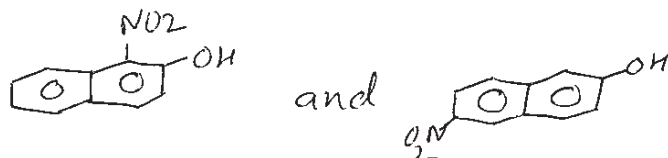
f) Assign Re/Si faces to the following.



g) Identify aromatic, antiaromatic and nonaromatic amongst the following:



h) Which of the following compound is more acidic? Justify.



i) Chlorobenzene can not be hydrolysed by using  $S_N1$  or  $S_N2$  conditions. Explain.

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Total No. of Questions : 6]

SEAT No. :

P649

[Total No. of Pages : 7

[4325] - 202  
M.Sc. -I (Semester - II)  
INORGANIC CHEMISTRY  
CH - 230 : Inorganic Chemistry - II  
(2008 Pattern)

*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) *Neat diagrams must be drawn wherever necessary.*
- 4) *Figures to the right indicate full marks.*
- 5) *Use of log tables and calculators is allowed.*
- 6) *Atomic number [ $T_i = 22$ ,  $M_n = 25$ ,  $C_o = 27$ ,  $N_i = 28$   $C_u = 29$ ]*

**SECTION - I**

**Q1)** Attempt any three of the following :

**[15]**

- a) Work out possible number of micro states for the following systems.
  - i)  $s^1 d^1$
  - ii)  $2(p^2 f^4)$
  - iii)  $f^7$
  - iv)  $d^7$
  - v)  $3p^1 4p^1$
- b) Determine the ground state term for any two metal ions in the following complexes.
  - i)  $[\text{Co}(\text{NH}_3)_6]^{2+}$
  - ii)  $[\text{Ni}(\text{en})_3]^{2+}$
  - iii)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

**P.T.O.**



- c) Determine the spin multiplicities of states arising from  $+2g^2$  configuration, when infinitely strong octahedral field is relaxed to strong field using Bethe's method of descending symmetry, correlation table and direct product table.
- d) Classify the following transitions in the octahedral complex as orbitally allowed, vibronically allowed and forbidden transitions. Justify your answer.
- i)  $E_g \rightarrow E_g$                       ii)  $A_{2u} \rightarrow T_{2g}$                       iii)  $A_{2g} \rightarrow T_{2g}$
- e) The tetrahedral complex  $[\text{CoCl}_2(\text{aniline})_2]$  exhibits three d-d bands, the lowest energy band appearing at  $6500 \text{ cm}^{-1}$  ( $\gamma_1$ ) predict the energy of the  $\gamma_2$  and  $\gamma_3$  bands. ( $B = 880 \text{ cm}^{-1}$ ).

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

- a) Give the splitting of  $5_D$  R. S. term in weak cubic field using character table for pure rotational point group (0).
- b) Explain the concept of hole equivalency and mention at least two examples.
- c) Explain the following :
- i) The electronic spectrum of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  complex exhibits a shoulder on the main band.
- ii) Peaks for forbidden transitions are more sharp than those for allowed transitions.
- d) How would you account for the magnetic moments listed against each of the following complexes.
- i)  $\text{Na}_4[\text{Co}(\text{NO}_2)_6]$   $\mu = 1.88 \text{ BM}$ .
- ii)  $\text{Cs}[\text{Ti}(\text{SO}_4)_2]$   $\mu = 1.84 \text{ BM}$ .

- e) For complex  $[\text{CoCl}_4]^{2-}$  ion spin orbital coupling constant is  $-190 \text{ cm}^{-1}$ . The  $\gamma_1$  transition is observed at  $2940 \text{ cm}^{-1}$ . Calculate effective magnetic moment of  $\text{Co}^{2+}$  ion in the complex.

**Q3) Write short note on (any two) :** **[10]**

- a) Tanabe - Sugano diagrams.
- b) Quenching of orbital angular momentum.
- c) Chemiluminescence.

### **SECTION - II**

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

- a) Give an account of model compounds and spontaneous self assembly.
- b) Give account of Principles of coordination chemistry utilised in bioinorganic chemistry w.r.t. Irving- Williams series.
- c) Give the classification of metalloproteins.
- d) Give an account of metal Proteins involved in electron transfer reactions.
- e) What are the possible pathways of absorption of metal by cell.

**Q5) Write short notes - (any three) :** **[15]**

- a) Metals in medicine.
- b) Dioxygen transport.
- c) Acetylcholine receptor.

- d) Detoxification of mercury.
- e) Amino acids as ligands.

**Q6)** Draw structure of the following (any five) :

**[10]**

- a)  $[2\text{Fe} - 2\text{S}]^{+2}$
- b) Tyrosine
- c) Aquocobalmin
- d) Deoxy hemoglobin
- e) Siderophore
- f) Flavin

Character Table for O rotational group

O	E	6C <sub>4</sub>	3C <sub>2</sub> (=C <sub>4</sub> <sup>2</sup> )	8C <sub>3</sub>	6C <sub>2</sub>	
A <sub>1</sub>	1	1	1	1	1	$x^2 + y^2 + z^2$
A <sub>2</sub>	1	-1	1	1	-1	
E	2	0	2	-1	0	
T <sub>1</sub>	3	1	-1	0	-1	$(R_x, R_y, R_z); (x, y, z)$
T <sub>2</sub>	3	-1	-1	0	1	

Correlation Table for the Group O<sub>h</sub>

O <sub>h</sub>	O	T <sub>d</sub>	D <sub>4h</sub>	D <sub>2d</sub>	C <sub>4v</sub>	C <sub>2v</sub>	D <sub>2d</sub>	D <sub>2</sub>	C <sub>2h</sub>
A <sub>1g</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1g</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1g</sub>	A <sub>1</sub>	A <sub>g</sub>
A <sub>2g</sub>	A <sub>2</sub>	A <sub>2</sub>	B <sub>1g</sub>	B <sub>1</sub>	B <sub>1</sub>	A <sub>2</sub>	A <sub>2g</sub>	A <sub>2</sub>	B <sub>g</sub>
E <sub>g</sub>	E	E	A <sub>1g</sub> +B <sub>1g</sub>	A <sub>1</sub> +B <sub>1</sub>	A <sub>1</sub> +B <sub>1</sub>	A <sub>1</sub> +A <sub>2</sub>	E <sub>g</sub>	E	A <sub>g</sub> +B <sub>g</sub>
T <sub>1g</sub>	T <sub>1</sub>	T <sub>1</sub>	A <sub>2g</sub> +E <sub>g</sub>	A <sub>2</sub> +E	A <sub>2</sub> +E	A <sub>1</sub> +B <sub>1</sub> +B <sub>2</sub>	A <sub>2g</sub> +E <sub>g</sub>	A <sub>2</sub> +E	A <sub>g</sub> +2B <sub>g</sub>
T <sub>2g</sub>	T <sub>2</sub>	T <sub>2</sub>	B <sub>2g</sub> +E <sub>g</sub>	B <sub>2</sub> +E	B <sub>2</sub> +E	A <sub>1</sub> +B <sub>1</sub> +B <sub>2</sub>	A <sub>2g</sub> +E <sub>g</sub>	A <sub>2</sub> +E	2A <sub>g</sub> +B <sub>g</sub>
A <sub>1u</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>1u</sub>	B <sub>1</sub>	A <sub>2</sub>	A <sub>1</sub>	A <sub>1u</sub>	A <sub>1</sub>	A <sub>u</sub>
A <sub>2u</sub>	A <sub>2</sub>	A <sub>1</sub>	B <sub>1u</sub>	A <sub>1</sub>	B <sub>2</sub>	A <sub>1</sub>	A <sub>2u</sub>	A <sub>2</sub>	B <sub>u</sub>
E <sub>u</sub>	E	E	A <sub>1u</sub> +B <sub>1u</sub>	A <sub>1</sub> +B <sub>1</sub>	A <sub>2</sub> +B <sub>2</sub>	A <sub>1</sub> +A <sub>2</sub>	E <sub>u</sub>	E	A <sub>u</sub> +B <sub>u</sub>
T <sub>1u</sub>	T <sub>1</sub>	T <sub>2</sub>	A <sub>2u</sub> +E <sub>u</sub>	B <sub>2</sub> +E	A <sub>1</sub> +E	A <sub>1</sub> +B <sub>1</sub> +B <sub>2</sub>	A <sub>2u</sub> +E <sub>u</sub>	A <sub>2</sub> +E	A <sub>u</sub> +2B <sub>u</sub>
T <sub>2u</sub>	T <sub>2</sub>	T <sub>1</sub>	B <sub>2u</sub> +E <sub>u</sub>	A <sub>2</sub> +E	B <sub>1</sub> +E	A <sub>2</sub> +B <sub>1</sub> +B <sub>2</sub>	A <sub>2u</sub> +E <sub>u</sub>	A <sub>2</sub> +E	2A <sub>u</sub> +B <sub>u</sub>

## DIRECT PRODUCTS

1. Groups of the form  $G \times I$  or  $G \times \sigma_1$  :  
 The  $g, u$  or  $'$  additions to the IR symbols in these groups satisfy  
 $g \times g = u \times u = g, g \times u = u, ' \times ' = ' \times ' = ' \times ' = ' .$
2. Products of the form  $A \times A, B \times B, A \times B$  :  
 For all groups :  
 Letter symbols :  $A \times A = A, B \times B = B, A \times B = B.$   
 Subscripts :  $1 \times 1 = 1, 2 \times 2 = 1, 1 \times 2 = 2$   
 except for the H representations of  $D_2$  and  $D_{2h}$  where  
 $B \times B = B$  and  $1 \times 2 = 3, 2 \times 3 = 1, 3 \times 1 = 2.$
3. Products of the form  $A \times E, B \times E$  :  
 (a) For all groups :  $A \times E_1 = E_1$  irrespective of the suffix on A.  
 (b) For all groups except  $D_{4h}, D_{6h}, S_8$  :  
 $B \times E_1 = E_1, B \times E_2 = E_1$   
 Irrespective of the suffix on B. (If the group has only one E representative  
 put  $E_1 = E_2 = E.$ )  
 (c) For  $D_{4h}$  :  
 $B \times E_1 = E_2, B \times E_2 = E_3, B \times E_3 = E_1, B \times E_4 = E_2, B \times E_5 = E_1$   
 irrespective of the suffix on B.  
 (d) For  $D_{6h}, S_8$  :  
 $B \times E_1 = E_2, B \times E_2 = E_3, B \times E_3 = E_1$   
 irrespective of the suffix on B.
4. Products of the form  $E \times E$  :  
 (For groups which have A, B or E symbols without suffixes put  $A_1 = A_2 = A,$   
 etc. in the equations below )  
 (a) For  $O_h, O, T_d, D_{2h}, D_{6h}, C_{4v}, C_{2v}, C_{3v}, S_6, D_{3d}, D_{3h}, D_3, C_{3v}, C_{2v}, C_3$  :  
 $E_1 \times E_1 = E_2 \times E_2 = A_1 + A_2 + E_2; E_1 \times E_2 = E_1 + E_2 + E_1$   
 (b) For  $D_{2h}, D_4, C_{2v}, C_{2h}, C_2, S_2, D_{2d}$  :  
 $E \times E = A_1 + A_2 + B_1 + B_2$   
 (c) For  $D_{4h}$  :  
 $E_1 \times E_1 = E_2 \times E_2 = A_1 + A_2 + E_2$   
 $E_3 \times E_3 = E_4 \times E_4 = A_1 + A_2 + E_4$   
 $E_5 \times E_5 = A_1 + A_2 + B_1 + B_2$   
 $E_1 \times E_2 = E_3 \times E_3 = E_1 + E_2, E_1 \times E_3 = E_2 \times E_2 = E_2 + E_4$   
 $E_1 \times E_4 = E_2 \times E_3 = E_2 + E_3, E_2 \times E_3 = E_3 \times E_4 = E_1 + E_2$   
 $E_1 \times E_5 = B_1 + B_2 + E_3, E_2 \times E_4 = B_1 + B_2 + E_3$

(d)  $D_{5d}, D_{3h}, D_3, C_{5v}, C_{3h}, C_5$ :

$$E_1 \times E_1 = A_1 + A_2 + E_2, E_2 \times E_2 = A_1 + A_2 + E_1,$$

$$E_1 \times E_2 = E_1 + E_2.$$

(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. Products involving the T (or F) representations of  $O_h, O$  and  $T_d$

$$A_1 \times T_1 = T_1, A_1 \times T_2 = T_2, A_2 \times T_1 = T_2, A_2 \times T_2 = T_1,$$

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

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

$$T_1 \times T_2 = A_2 + E + T_1 + T_2.$$

6. The complete results 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	$A_1 + A_2 + E$	$T_1 + T_2$	$T_1 + T_2$
$T_1$	$T_1$	$T_2$	$T_1 + T_2$	$A_1 + E + T_1 + T_2$	$A_2 + E + T_1 + T_2$
$T_2$	$T_2$	$T_1$	$T_1 + T_2$	$A_2 + E + T_1 + T_2$	$A_1 + E + T_1 + T_2$

⌘ ⌘ ⌘

[4325]-311

M.Sc. - II (Semester - III)  
ORGANIC CHEMISTRYCH-321 : Spectroscopic Methods in Structure Determination  
(2008 Pattern)

[Max. Marks : 80

Time : 3 Hours]

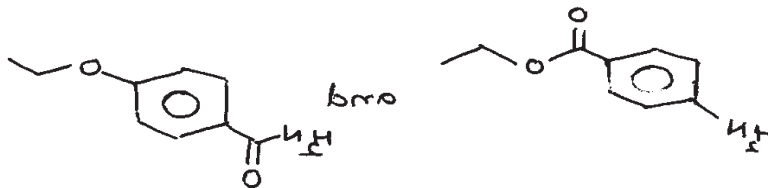
Instructions to the candidates :

- 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) a) Answer any Four of the following : [8]

i) Differentiate the following pair by mass.



ii) Mass spectrometry can be used to determine the number of chlorine and bromine atoms in organic compounds. Explain.

iii) DEPT is preferred over off-resonance in CMR. Explain.

iv) Differentiate the following pair by CMR.



v) Geminal could be used to determine the ring size in small rings. Explain.

b) Predict the structure

M.F. :  $C_{10}H_{16}O_4$

IR :  $1722\text{ cm}^{-1}$

CMR:  $12(p, str), 20(p, str), 60(t, str), 122(s, w), 122(s, w), 122(s, w)$

PMR:  $1.3(t, \Delta H, \theta H) 2.0(s, \theta H) 4.3(p, \Delta H, \Delta H)$

c) Predict the structure

M.F. :  $C_7H_{16}O_4$

IR :  $1110\text{ cm}^{-1}$

CMR:  $32, 21 (str.), 100$

DEPT 135:  $32(down), 21\text{ and }100(up)$

PMR :  $1.8(t, \Delta H, \Delta H) 3.3(s, 12H) 4.2(t, \Delta H, \Delta H)$

b) Deduce the structure

M.F. :  $C_2H_6O_2$

IR :  $1796\text{ cm}^{-1}$

CMR:  $12(p) 34(t) 98(d) 123(s) 178(s)$

a) Deduce the structure

M.F. :  $C_8H_9NO_2$

IR :  $1672, 1512, 1360\text{ cm}^{-1}$

CMR:  $20(p, str), 36(d) 124(d) 122(d) 146(s) 126(s) 196(s)$

PMR:  $7.6(d, \Delta H, \Delta H) 7.9(d, \Delta H, \Delta H) 1.4(d, \Delta H, \Delta H) 3.4(septet, \Delta H, \Delta H)$

Q2) Answer any four of the following : [16]

b) Calculate the chemical shift in ppm of an AB quartet whose line positions in hertz (Hz) are  $300, 292, 282$  in a  $100\text{ MHz NMR}$ . [4]



e) Deduce the structure from the given data

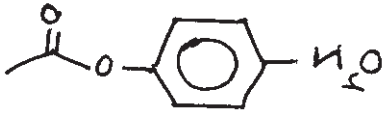
M.F.:  $C_2H_{10}O_3$   
 IR:  $1713\text{ cm}^{-1}$   
 CMR:  $161.9, 32.72, 17.9$   
 DEPT  $135^\circ$ :  $16.19, 32.72$  up  
                    $17.9$  absent  
 PMR:  $4.1(d, 2H, \Delta, 1H, 2.2\text{ to }8.0(\text{broad signal}, 2H, \text{exch.}))$   
            $0.92(d, 3H, \Delta, 1.1(d, 3H, \Delta, 2.1(m, 1H))$

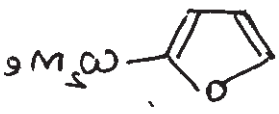
Q3) Write short notes on any three : [12]


- Time of flight analyzer in MS.
- Applications of NOE.
- Factor affecting  $^{13}C$  chemical shifts.
- Dirac model of spin-spin coupling

### SECTION - II

Q4) a) Explain the genesis of the ions for any four : [8]

- 

$181, 138, 101, 43, 22$
- 

$156, 46, 22, 27$
- 

$28, 30$

(b) Assign the chemical shifts to various carbon atoms. [4]

irradiation at  $\delta$  1.1  $\delta$  enhance the signal at 1.8  $\delta$  by 7%  
NOE expt :

changes 1.8 $\delta$ (bd)  $\leftarrow$  (bd) 1.2, 2 & 9.2 Hz

(ii) irradiation at  $\delta$  4.8  $\delta$  ts noitsibitri

(i) irradiation at  $\delta$  3.2  $\delta$  ts noitsibitri

2pin-decoupling expt :

4.8 (m, 1H)

4.30 (d, 3.2 Hz, 1H, exch.)

4.03 (m, 1H)

3.94 (bd, 6.2 & 2.2 Hz, 1H)

3.74 (bd, 1.3 & 1 Hz, 1H)

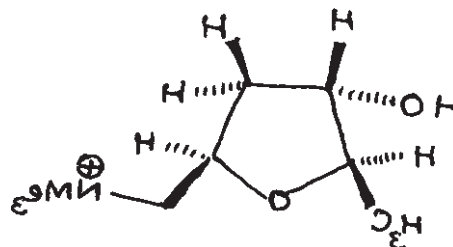
3.24 (bd, 1.3 & 3 Hz, 1H)

3.3 $\delta$  (s, 9H)

2.02 (bd, 1.2, 2, 6 & 2 Hz, 1H)

1.8 $\delta$  (bd, 1.2, 2, 9.2 & 2.2 Hz, 1H)

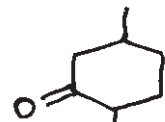
1.6 (b, 6.2 Hz, 3H)



(a) Assign the chemical shifts to various protons. Comment on the observed coupling constants and double resonance experiments. [8]

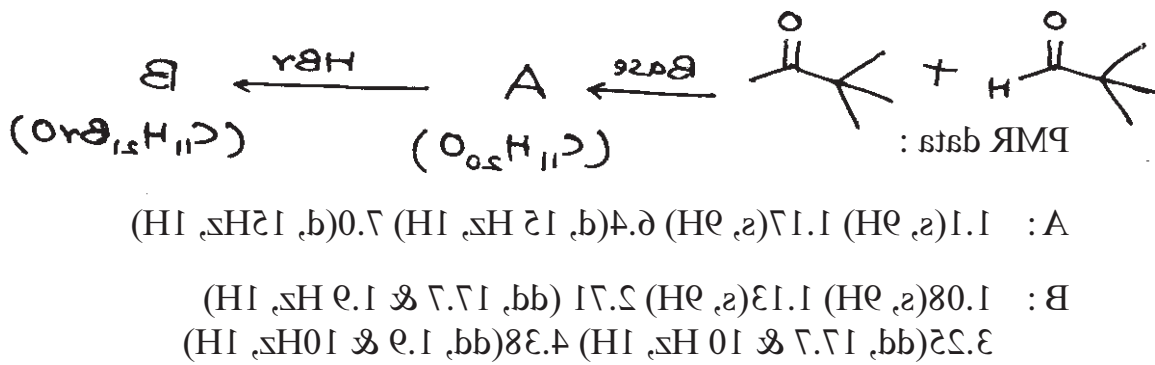
(b) The product of Friedel-Crafts reaction of benzene and ethylene oxide shows a strong peak at  $m/z = 92$ . Write the genesis of the same. [4]

(v) 1-Phenyl-2-propanone 128, 100, 83, 22, 39

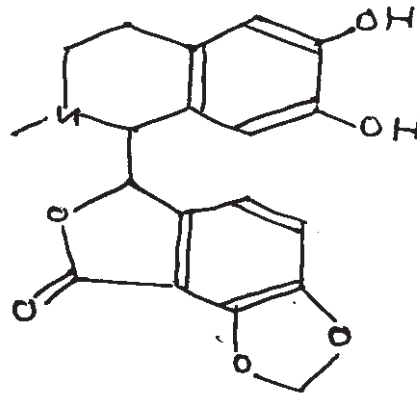


(vi) 112, 84, 69

Q6) The spectra of an unknown compound are shown on the adjacent page. Analyse the spectra and use this data to arrive at a structure of the unknown. Justify. [12]

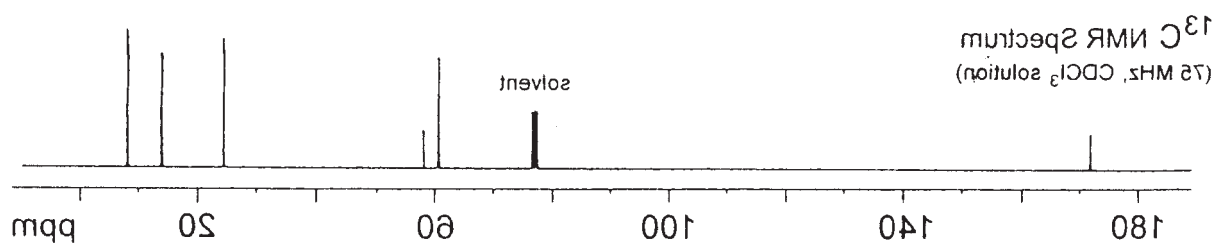
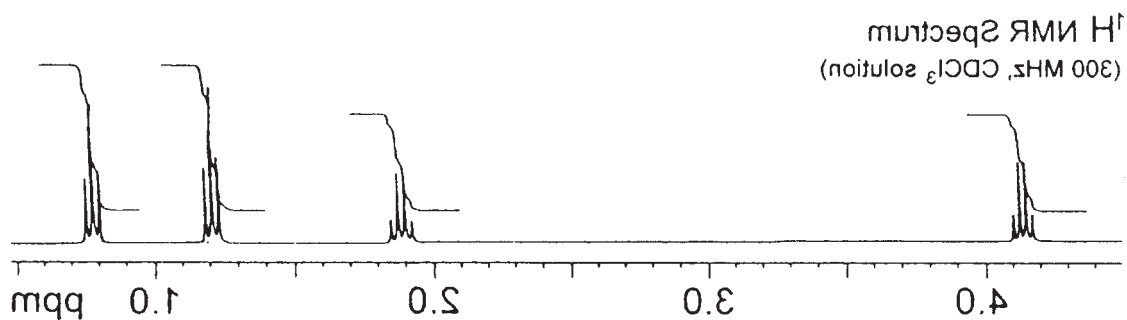


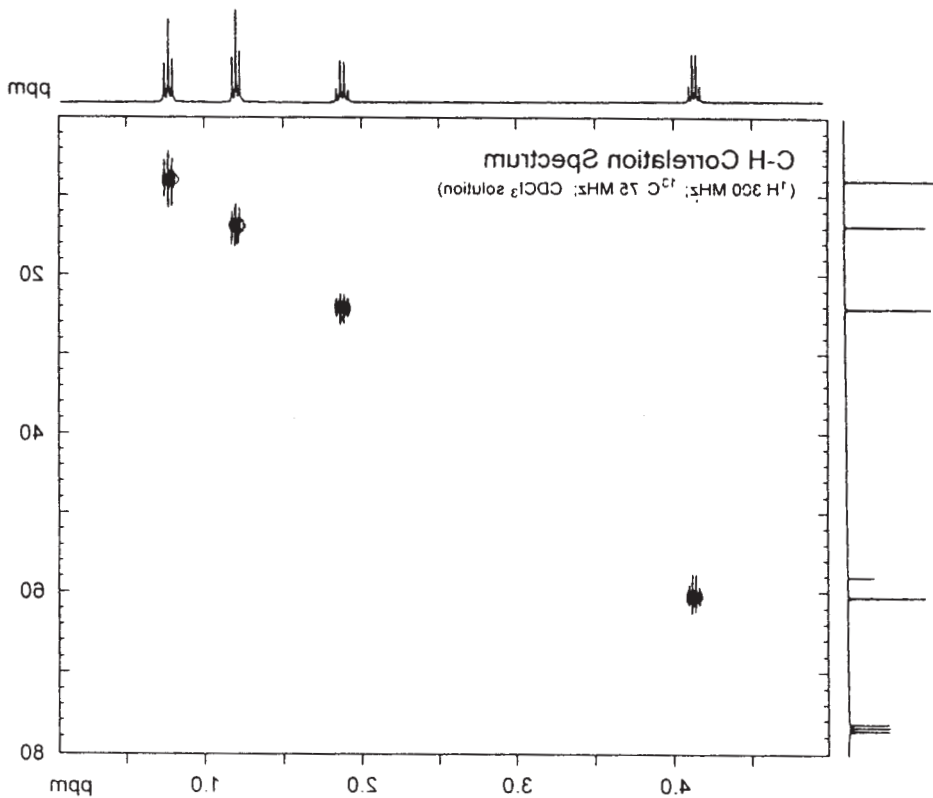
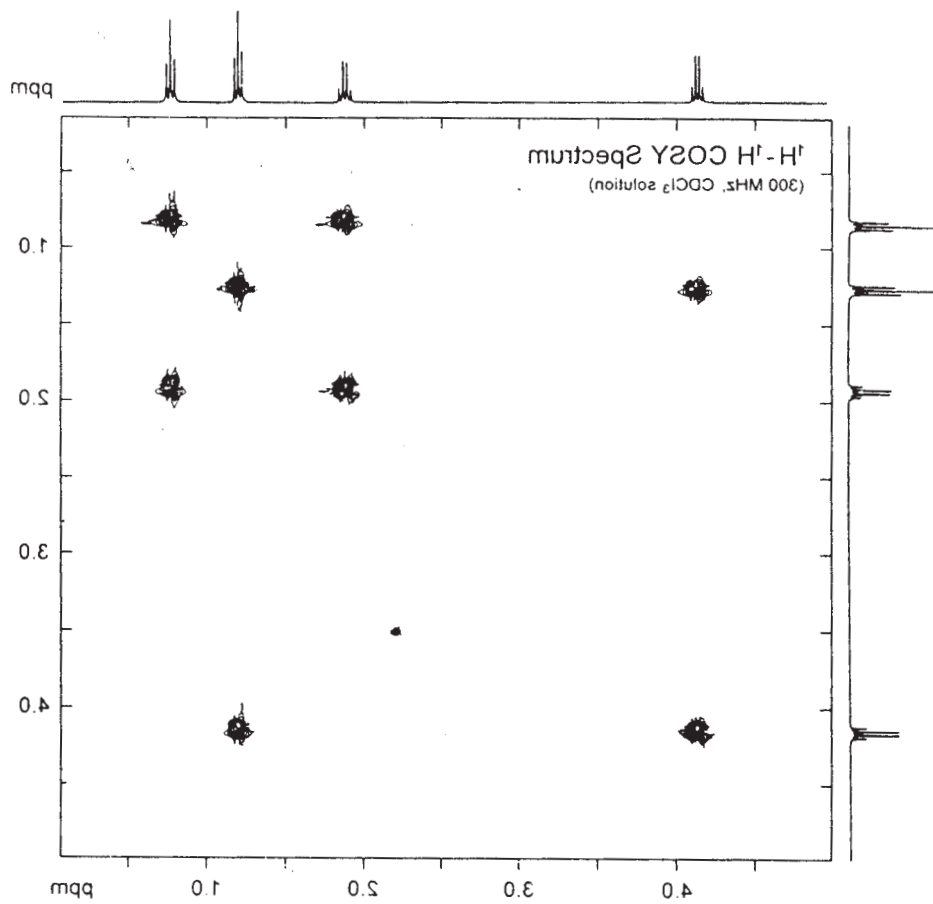
c) Complete the following sequence of reaction using the PMR data given below : [4]



- 123.0 (s), 128.9 (s), 140.2 (s)  
 167.6 (s), 114.2 (d), 142.1 (s), 143.2 (s)  
 112.6 (b), 109.8 (s), 144.2 (s), 149.0 (s)  
 84.6 (b), 103.2 (t), 113.3 (b), 112.1 (b)  
 22.8 (t), 44.7 (p), 49.0 (t), 52.4 (b)

Mol. For. :  $C_{11}H_{20}O_4$





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Total No. of Questions : 6]

SEAT No. :

P662

[Total No. of Pages : 4

[4325]-312

M.Sc. - II (Semester - III)

ORGANIC CHEMISTRY

CH-352: Organic Stereochemistry

(2008 Pattern)

Time : 3 Hours]

[Max. Marks : 80

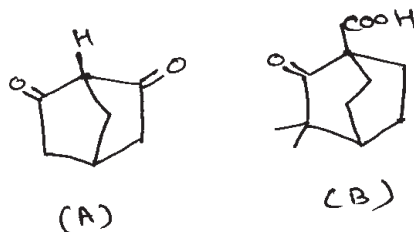
Instructions to the candidates :

- 1) All questions are compulsory.
- 2) Figures to the right indicates full marks.
- 3) Answers to the two sections should be written in separate answer books.

SECTION - I

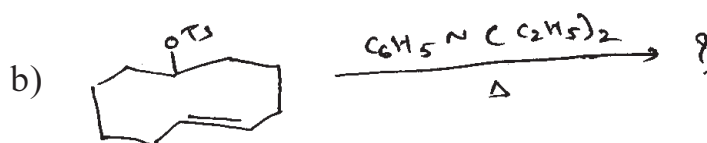
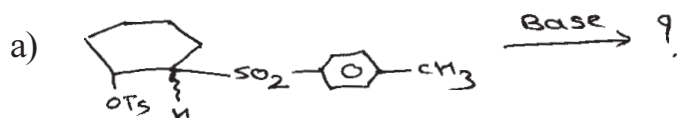
Q1) Answer any four of the following : [16]

- a) Discuss the dipole moments of cis and trans 1,2- dibromo cyclohexane.
- b) Which form of bicyclo [3.3.1] nonane is more stable? Why?
- c) Explain isomers of perhydrophenanthrene and their stability.
- d) Bicyclo [2.2.2] octane - 2, 6 - dione (A) does not show acidic properties while camphonic acid (B) does not readily undergo decarboxylation.

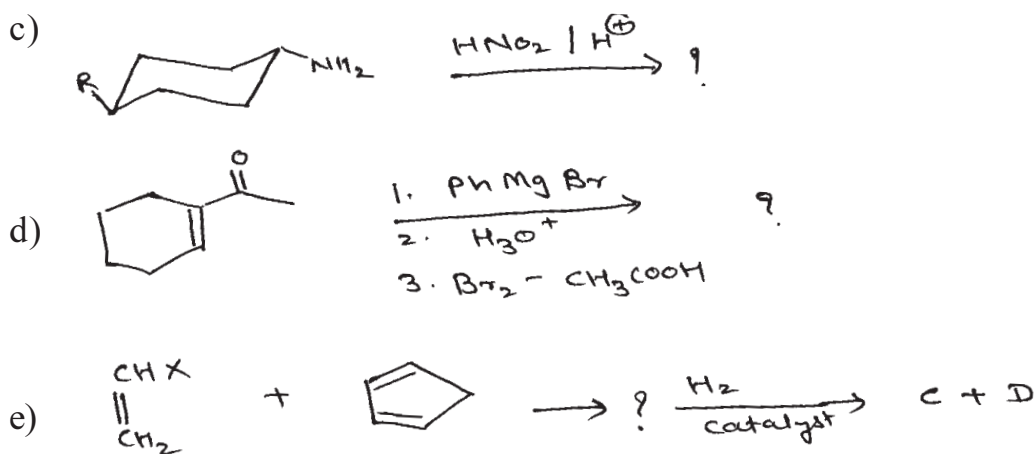


- e) Why trans decaline is more stable than cis decaline. Explain with stereo structure.

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

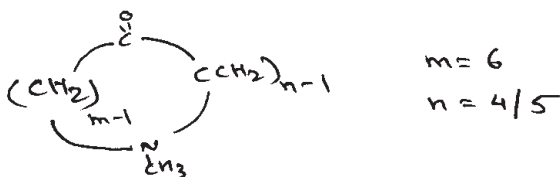


P.T.O.



**Q3)** Answer any three of the following : [12]

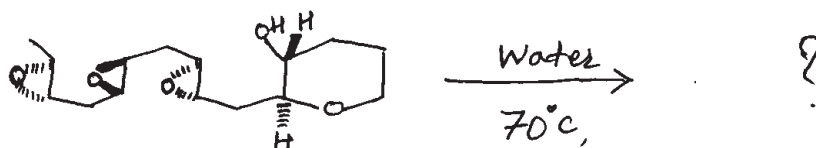
- Give the physical methods of resolution.
- What are the criteria for optical purity. Explain with examples.
- Explain the method for resolution of dl-alanine.
- In the IR spectra of following aminoketone the carbonyl absorption around  $1700 \text{ cm}^{-1}$  disappears on protonation. Explain.



### SECTION - II

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

- How NMR spectroscopy is used to find stereochemistry of lactone fusion in enhydrin?
- In cinchonine and quinine  $\text{C}_8\text{-C}_9$  bond and  $\text{C}_3\text{-Vinyl}$  bond are on the same side. Explain.
- Predict the product and explain stereochemistry of the product.

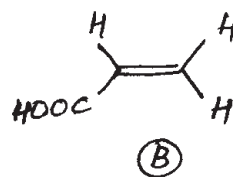
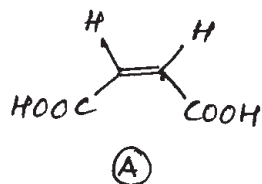


- Explain the stereochemistry of  $\text{C}_6$  &  $\text{C}_{13}$  in codeine. Give evidence.

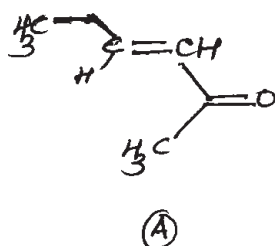
Q5) Attempt any four of the following :

[12]

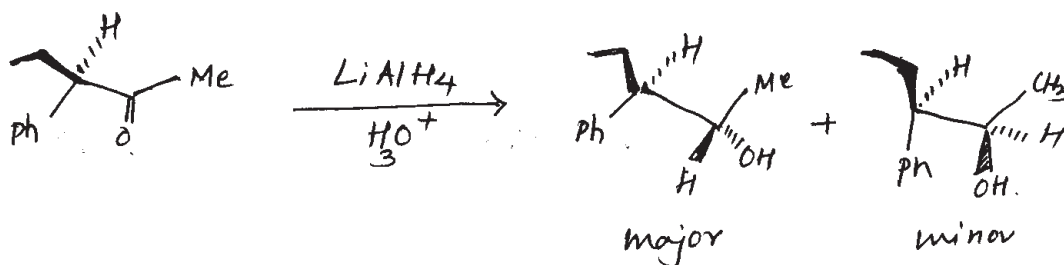
- a) Assign Re/Si configuration of each  $Sp^2$  hybridized carbon in following compound.



- b) With reasons, state whether the faces of the carbonyl groups in the following compounds are homotopic, enantiotopic or diastereotopic.

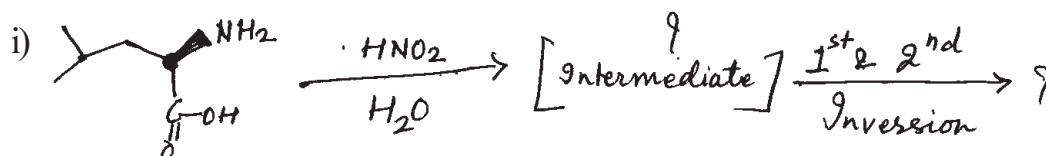


- c) Meso – 3, 4 dihydroxyhexane can be made from two alkenes that are geometric isomers. Outline the methods that makes this possible.
- d) Calculate the  $ee$  and the specific rotation of a mixture containing 6 gm of (+) 2-butanol and 4 gm of (–) 2-butanol. The specific rotation of enantiomerically pure (+) 2-butanol is  $+13.5^\circ$ .
- e) Using Felkin rule, explain the following transformation.

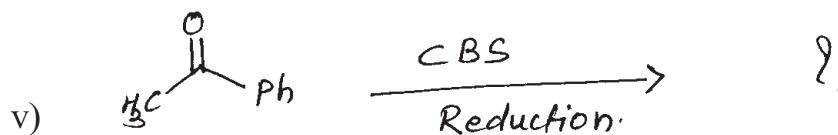
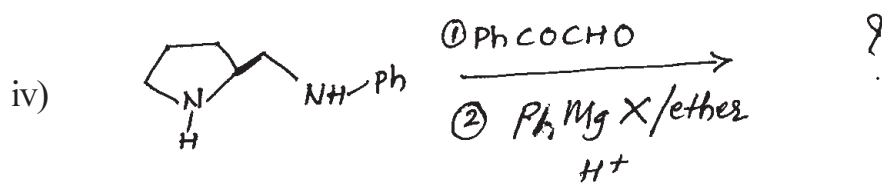
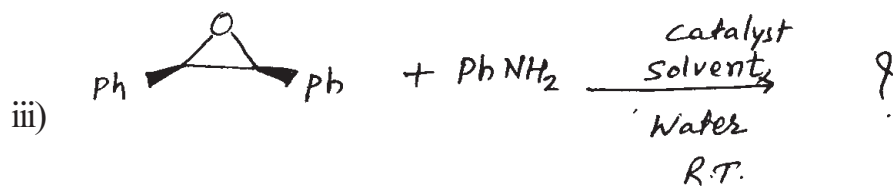
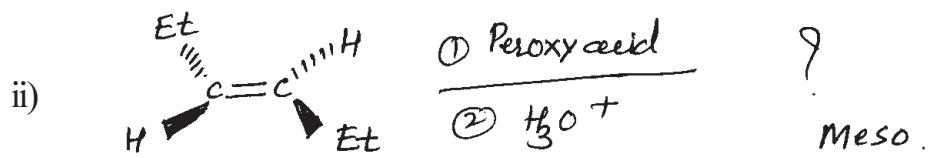


Q6) a) Predict the product/s and write stereochemistry of the following reaction (any four) :

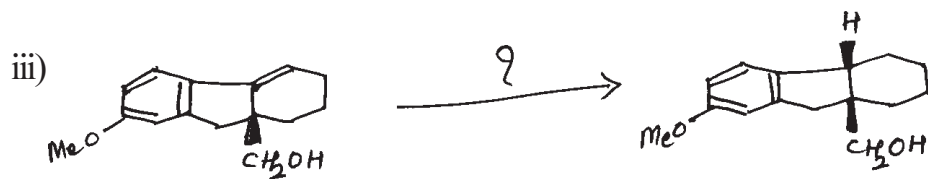
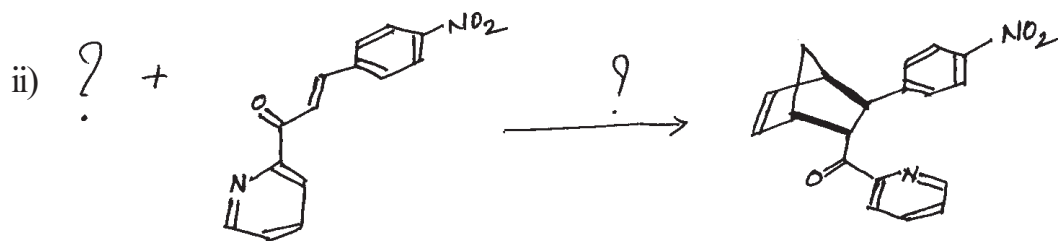
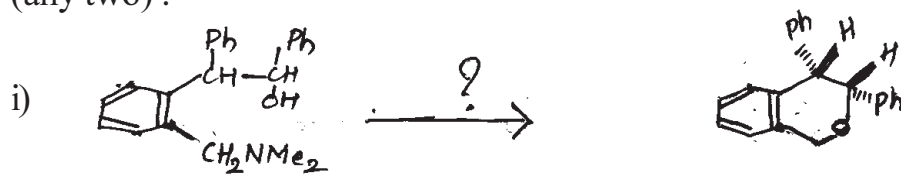
[8]







b) Suggest the reagent and stereochemistry of the following reaction (any two): [8]



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[4325]-313

M.Sc. - II (Semester - III)

ORGANIC CHEMISTRY

CH - 353: Free Radicals, Photochemistry and Pericyclic Reactions  
& their Applications  
(2008 Pattern)

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.

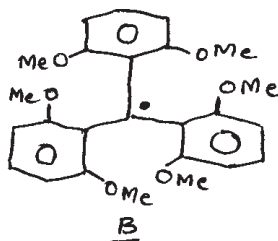
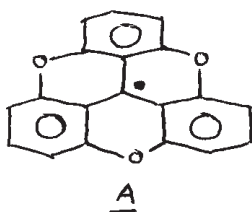
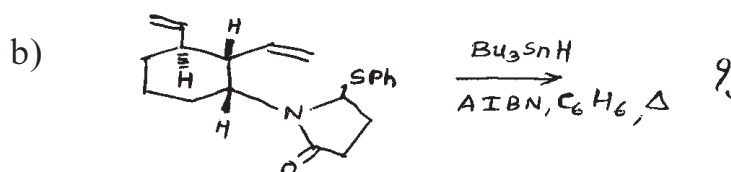
SECTION - I

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

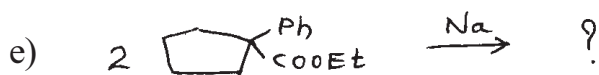
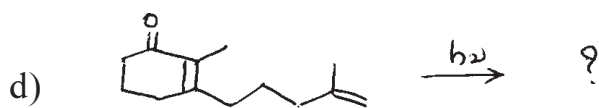
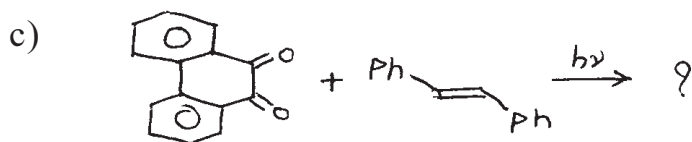
- i) Dienone-Phenol rearrangement.
- ii) Arylation of aromatic rings.
- iii) Sandmeyer reaction.

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

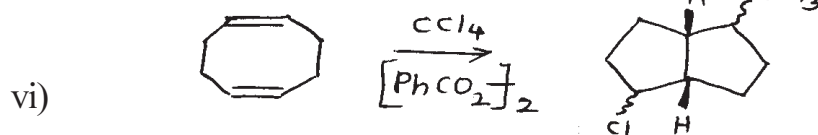
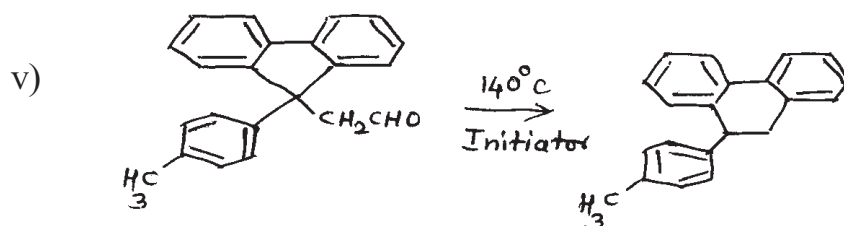
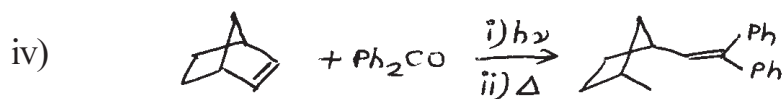
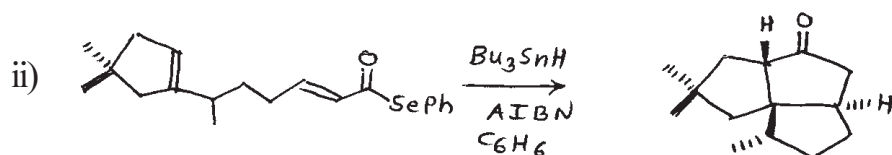
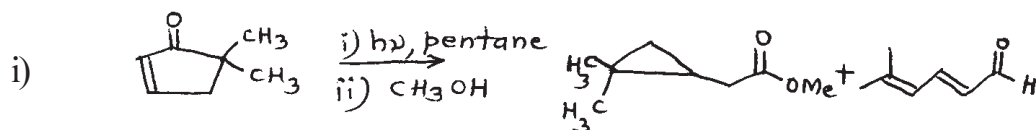
- i) Irradiation of benzophenone in the presence of  $(\text{Ph})_2\text{CHOH}$  gives benzpinacol as the only product.
- ii) Irradiation of 2, 2, 5, 5 - tetraphenyl cyclohexanone gives two products.
- iii) Compound A exists primarily in the dimeric form while compound B exists as a free radical even in the solid state.

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

P.T.O.



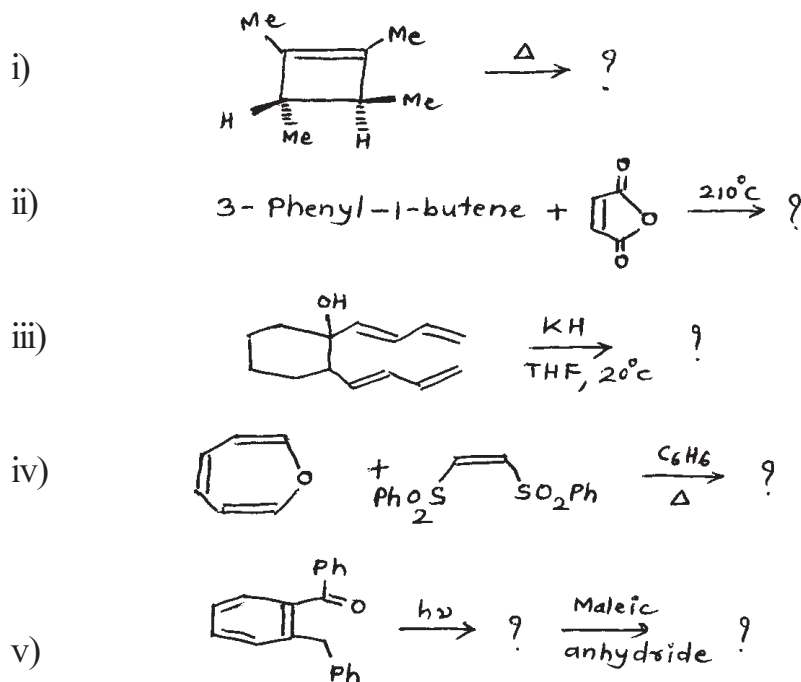
Q3) a) Suggest suitable mechanism for any five of the following : [10]



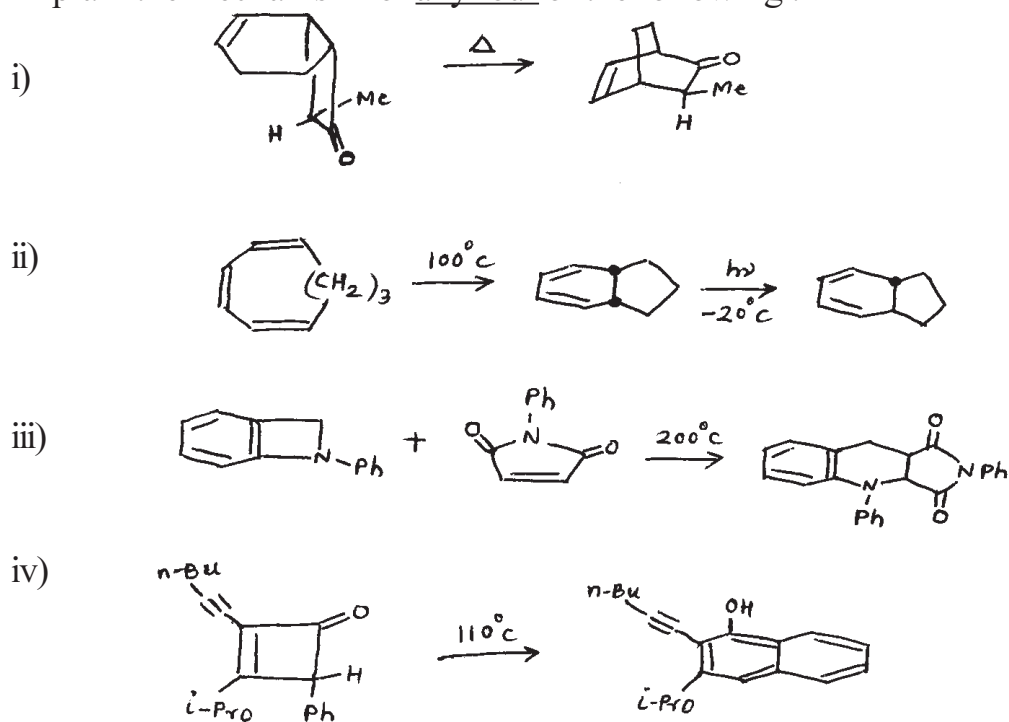
b) Explain the role of antioxidants in inhibition of autoxidation with suitable examples. [4]

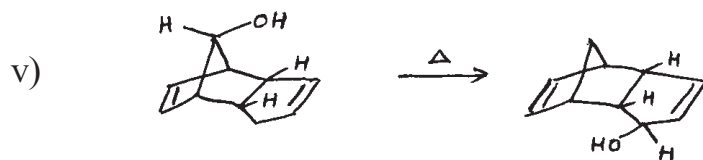
## SECTION - II

- Q4)** a) Draw the correlation diagram for disrotatory conversion of allyl carbonium ion to cyclopropyl carbonium ion and predict whether the reaction is thermally or photochemically allowed. [6]
- b) Predict the products in any four of the following. Explain the stereochemistry and mechanism. [8]

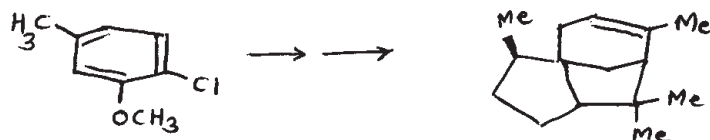


- Q5)** a) Using the Aromatic Transition state concept predict whether the  $\pi^4_s + \pi^2_s$  cycloaddition reaction is thermally or photochemically allowed. [4]
- b) Explain the mechanism for any four of the following: [8]

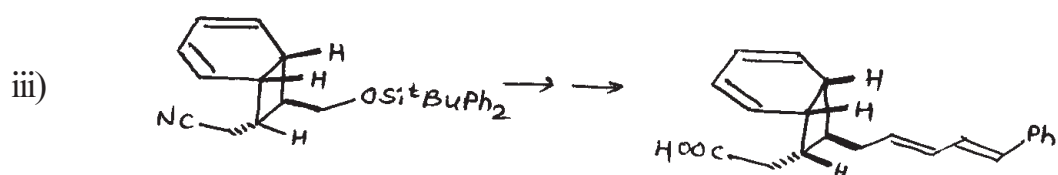
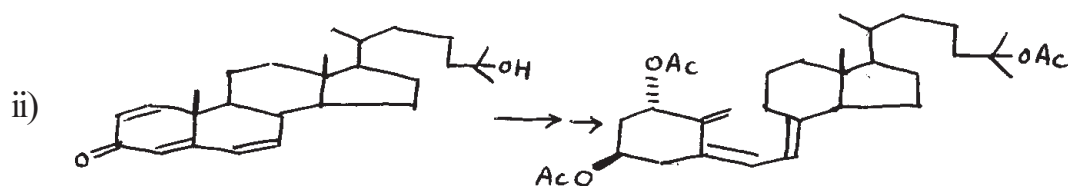
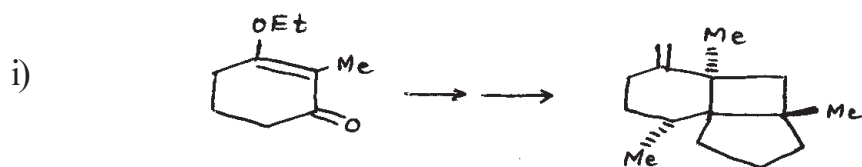




Q6) a) Complete the following synthetic sequence indicating all intermediates and reagents required. [6]



b) Complete any two of the following synthetic sequences indicating all intermediates and reagents required. [8]



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Total No. of Questions : 4]

SEAT No. :

P664

[Total No. of Pages : 3

[4325]-314

M.Sc. - II (Semester - III)

ANALYTICAL CHEMISTRY

CH - 390: Electro Analytical and Current Analytical Methods in  
Industries  
(2008 Pattern)

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 separate answer books.

**SECTION - I**

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

- a) Distinguish between Voltammetry and Polarography.
- b) Explain the following terms and give their significance in Polarographic analysis.
  - i) Limiting current
  - ii) Polarographic maxima
  - iii) Condenser current
- c) Explain construction and working of rotating platinum microelectrode. What are advantages of it over DME?
- d) The diffusion coefficient for  $Tl^+$  is  $2.00 \times 10^{-5} \text{ cm}^2/\text{s}$ , where as for  $Cd^{2+}$  is  $0.72 \times 10^{-5} \text{ cm}^2/\text{s}$ . If a  $1.00 \times 10^{-3} \text{ M}$  solution of  $Cd^{2+}$  gives a diffusion current of  $8.15 \mu\text{A}$ , predict the diffusion current for  $1.5 \times 10^{-3} \text{ M}$   $Tl^+$  under the same conditions.
- e) Anodic stripping voltammetry is used for the analysis of copper in a sea water sample using standard addition method. When a 50 ml sample is analysed it gave a peak current of  $0.886 \mu\text{A}$ . A  $5.00 \mu\text{dm}^3$  spike of 10 ppm  $Cu^{2+}$  is added to the sample and the resulting peak current is  $3.52 \mu\text{A}$ . Calculate the concentration of  $Cu^{2+}$  in ppm in the given sample of sea water.

P.T.O.

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

- a) Write a critical note on cyclic voltammetry.
- b) What are nano-materials? Explain its general applications.
- c) What are amperometric titrations? Explain the estimation of zinc by EDTA using this technique.
- d) Draw schematic diagram of cell used in coulometric titration. Discuss the application of coulometry for complexometric titration.
- e) A solution containing 0.50 g of nickel as  $\text{Ni}^{2+}$  requires 20 minutes for complete deposition of nickel at 1.50A. Calculate the quantity of electricity required.  
[At. Wt - Ni = 58.7]

### **SECTION - II**

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

- a) Explain the following terms :
  - i) Specific activity.
  - ii) Neutron flux.
  - iii) Neutron capture cross section.
- b) What is the principle of a radiometric titration? Discuss the nature of the titration curve of calcium by EDTA with solid radioactive silver iodate as an indicator.
- c) State and explain the principle of isotope dilution analysis. Give its applications.
- d) The vitamin B-12 content of multivitamin tablet was determined by dissolving 10 tablets in water. The solution was transferred to 100 ml volumetric flask and diluted to volume. A 50 ml portion was removed and treated with 0.5 mg of radioactive vitamin B-12 having an activity of 572 cpm. After homogenization, the vitamin B-12 in the sample was isolated and purified, producing 18.6 mg with an activity of 361 cpm. Calculate the amount of vitamin B-12 per tablet.
- e) 53.8 mg steel sample was analysed for its manganese content by neutron activation, 68.5 mg standard steel sample containing 0.9% manganese was irradiated along with the sample in neutron source and counted under same experimental conditions. Activities of sample and the standard counted for 5 minutes were 16597 and 21983 counts respectively. Calculate the percentage amount of manganese in the steel sample.

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

- a) Explain the principle and instrumentation of Nephelometry. Give the typical applications of nephelometric method.
- b) Explain the principle of DTA technique with suitable example. Describe the terms exotherm and endotherm in DTA.
- c) Draw a schematic diagram of a modern thermo balance and discuss the significance of each component.
- d) Explain the construction and working of optically transparent electrodes.
- e) The mass 250 mg hydrated sample of disodium hydrogen phosphate decreases to 153 mg after heating to 150°C by TGA. What is the number of water of hydration in hydrated sample?  
(Given: At.Wt. Na = 23, P = 31, H = 1, O = 16).





Total No. of Questions : 4]

SEAT No. :

P665

[Total No. of Pages : 3

[4325]-315

M.Sc. - II (Semester - III)

ANALYTICAL CHEMISTRY

CH-391: Environmental and Analysis of Industrial Materials

(2008 Pattern)

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 calculators is allowed.

**SECTION - I**

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

- a) Give the analytical procedure for the estimation of Potassium from fertilizer.
- b) What are colouring constituents of glass? How is iron estimated from coloured glass?
- c) Explain the general scheme of analysis of soap.
- d) Enlist the constituents of face powder. Describe the method for estimation of chloride from sample of face powder.
- e) Phosphate containing detergent weighing 0.57 gm was ignited to red hot to destroy organic matter. The residue was dissolved in hot HCl and gave  $H_3PO_4$ , the phosphate was precipitated as  $MgNH_4PO_4 \cdot 6H_2O$  by addition of  $Mg^{+2}$  ions followed by aqueous ammonia. After filtration, washing, drying and ignition at  $1000^\circ C$ , weight of residue,  $Mg_2P_2O_7$  was 0.441 gm. Calculate percentage of phosphorous in the given sample.  
[Given: At. wt: P = 30.97, Mg = 24.31, O = 15.99]

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

- a) What are explosives? How is moisture determined by Karl Fischer titration?
- b) Outline the procedure for determination of Chromium from pigments.

**P.T.O.**

- c) Describe any one method for determination of calcium in propellant.
- d) Borosilicate glass weighing 0.308 gm was fused with sodium carbonate in platinum crucible, and the melt was converted into boric acid by suitable process. Mannitol is added in whole solution and titrated with 0.110 N NaOH using para nitrophenol as an indicator, and 29.40 ml of alkali required for complete neutralisation.  
Calculate percentage of  $B_2O_3$  in sample of glass.  
[Given At. wt : B = 10.81, O = 15.99]
- e) 1.507 gm of sample of Brass was dissolved in acid mixture and the solution was diluted to 250 ml. 150 ml aliquot was used for determination of Cu and Zn. Copper was determined electro gravimetrically. Weight of copper deposited after electrolysis is 0.615 gms. Zinc was determined gravimetrically as  $Zn_2P_2O_7$ . The weight of residue was 0.435 gm. Calculate percentage of Cu and Zn.  
[Given: At. wt: Zn = 65.38, P = 30.97, Cu = 63.54, O = 16]

### SECTION - II

- Q3)** Attempt any Four of the following : **[20]**
- a) What is steel? Explain the analytical procedure for the estimation nickel from steel.
- b) Explain the analytical procedure for estimation of calcium from Dolomite ore.
- c) Outline the analytical procedure for the determination of any one of the following.
- i) Ti from ilmenite ore.
  - ii) Si from bauxite ore.
  - iii) Cu from cupronickel alloy.
- d) 4.510 gm washing soda was dissolved in distilled water and diluted to 250 ml, A 25 ml aliquot of this solution was titrated with 0.110 N HCl using Methyl orange as an indicator, gave burette reading 30 ml. Calculate percentage of  $Na_2CO_3$  in given sample.  
[At. wt. Na = 22.98, C = 12, O = 15.99]
- e) Analysis of the components of 2.110 gm of shipnail brass yielded 0.0685 gm  $SnO_2$  and 0.2824 gm  $PbSO_4$ . Calculate percentage of Sn and Pb in alloy.  
[Given: At. wt. Sn = 118.7, Pb = 207.2, S = 32, O = 16]

**Q4)** Attempt any four of the following :

**[20]**

- a) Explain the method of determination of hexavalent chromium from waste water.
- b) Write note on (any one) :
  - i) Cyclone separator.
  - ii) Anaerobic decomposition.
- c) How  $\text{SO}_x$  is generated? Give its hazardous effects on materials. How is it controlled?
- d) Explain the terms COD and BOD. How is COD estimated from Waste water?
- e) Write note on safety measures in industries.





Total No. of Questions : 4]

SEAT No. :

P666

[Total No. of Pages : 3

[4325]-316

M.Sc. - II (Semester - III)

ANALYTICAL CHEMISTRY

CH - 392: Advanced Analytical Techniques

(2008 Pattern)

*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 calculators is allowed.*
- 5) *Use of graph paper is allowed.*

**SECTION - I**

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

- a) State and explain Faraday's laws of electrolysis. Give its important application.
- b) Explain the following terms :
  - i) Resistor.
  - ii) Conductance.
  - iii) Capacitors.
  - iv) Inductors.
  - v) Transformers.
- c) What is rectification? Describe the working of a diode as a full wave rectifier.
- d) Write a critical note on Flow injection analyzers.
- e) Calculate the binary equivalent of 7497 and decimal equivalent of 1110001011.

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

- a) Explain the properties of ideal amplifier as differentiator and integrator.
- b) Draw the outline of microprocessor control in X-ray spectrometer.
- c) Draw a block diagram of digital computer and explain the function of each component.

**P.T.O.**

- d) Calculate the resistance of  $0.02 \mu f$  capacitor of a frequency 4kHz and 4MHz.
- e) A metallic cube of length 5 cm is to be copper plated, if the cube is immersed in a copper electrolyte. The current is adjusted to 5A and passed for 30 min. What will be the thickness of deposited copper?  
(Given: At. wt. of Cu - 63.54 gm.  
Faraday's Const. (F) - 96487 (Coulomb))

### **SECTION - II**

**Q3)** Attempt any four 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) Write a note on Resonance ionization spectroscopy.
- c) Mention the elements required as micronutrients for the growth of plants. Explain any one suitable method for determination of Zinc from soil.
- d) Compare the ICPS and Direct current plasma emission spectroscopic techniques of analysis with respect to principle and method of analysis.
- e) A 40.0 mg sample of mineral is dissolved in HCl and diluted to 250 ml and analysed for Calcium by FES. The emission signal is 2.6 units on the emission scale. Standard Calcium gave the following results.

<u>Ca ppm</u>	<u>E.R.</u>
5.0	13
10.0	25
15.0	37

Calculate the percentage of Calcium in mineral.

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

- a) Write a note on :
- i) Immunoelectrophoresis.
  - ii) Immunoblotting.
- b) Compare RIA and ELISA techniques. Explain their relative merits and demerits.

- c) Explain the role of Supercritical Fluid Chromatography as an analytical tool in pharmaceutical analysis.
- d) Explain clinical applications of radioimmuno-assay of Esterogen.
- e) 5 ml sample of blood was treated with trichloroacetic acid to precipitate proteins. After centrifugation the resulting solution was brought to pH 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 0.532 and 0.290 5ml of aliquot of standard solution containing 0.400 ppm and 0.600 ppm of lead were treated in same way yielding absorbance 0.396 and 0.599 calculate ppm of lead in blood sample.



Total No. of Questions : 4]

SEAT No. :

**P667**

[Total No. of Pages : 2

**[4325]-317**

**M.Sc. - II (Semester - III)**

**ANALYTICAL CHEMISTRY**

**CH-380: Pharmaceutical Analysis**

**(Optional) (2008 Pattern)**

*Time :3 Hours]*

*[Max. Marks :80*

*Instructions to the candidates :*

- 1) *All questions are compulsory and carry equal marks.*
- 2) *Answers to the two Sections should be written in separate answer books.*
- 3) *Use of logarithmic table/non-programmable calculator is allowed.*

**SECTION - I**

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

- a) Discuss, the unadequate storage conditions and their effects on pharmaceutical products.
- b) Write a note on “prediction of shelf- life of pharmaceutical products”.
- c) Explain any one method for biological assay of Insuline.
- d) Give limit test for arsenic.
- e) Write a note on dry heat steralisation.

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

- a) Explain the analytical procedure for determination of moisture from pharmaceutical products using K.F. method.
- b) Discuss disintegration test for tablets.
- c) How sulphated ash from vegetable drug is determined?
- d) Explain microbial limit test with respect to preliminary testing and media.
- e) Explain in detail ‘tube-assay’ method used in microbial assay.

**SECTION - II**

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

- a) Discuss in detail clinical study in the development of new drugs.
- b) Give brief account of diluents and lubricants used in tablets.
- c) Give an account of Gels and Lotions.

**P.T.O.**



- d) What are aerosols? State the disadvantages of aerosols.
- e) 0.33 gm sulphadiazine [ $C_{10}H_{10}N_4O_2S$ ] was dissolved in 10.0 ml concentrated hydrochloric acid and 50.0 ml water. After cooling this solution to 15°C, it was titrated with 0.1 N  $NaNO_2$  using acriflavin indicator. The burette reading recorded was 10.2 ml. Calculate percentage of sulphadiazine in the given sample.  
[Given At. wt. C = 12, H = 1, N = 14, O = 16, S = 32]

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

- a) What are additives? Explain in detail.
- b) What are emulsions? How are they prepared?
- c) Write a note on FDA.
- d) Give an assay of salbutamol.
- e) 0.50 gm sample containing calcium lactate [ $C_9H_{10}O_6Ca \cdot 5H_2O$ ] was dissolved in 150 ml of water and 2 ml HCl. After dissolution solution was neutralised with NaOH. This solution was titrated with 0.05 M EDTA using Muroxide and naphthol green indicator, gave burette reading 18.2 ml. Calculate percentage of calcium lactate in the given sample.  
Given : (At. wt. of C = 12, H = 1, O = 16 and Ca = 40.08).



Total No. of Questions : 6]

SEAT No. :

P668

[Total No. of Pages : 3

[4325]-401

M.Sc. (Semester - IV)

PHYSICAL CHEMISTRY

CH-410: Molecular Structure and Spectroscopy

(2008 Pattern)

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) Neat diagrams must be drawn wherever necessary.
- 4) Figures to the right indicate full marks.
- 5) Use of logarithmic tables/calculator is allowed.

**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	$\beta_e$	=	$-9.274 \times 10^{-24} \text{ J T}^{-1}$
12. Nuclear magneton	$\beta_n$	=	$5.051 \times 10^{-27} \text{ J T}^{-1}$
13. Mass of an electron	$m_e$	=	$9.11 \times 10^{-31} \text{ kg}$

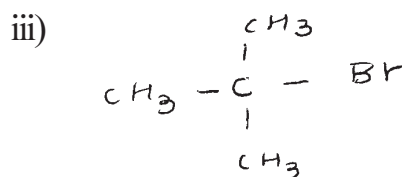
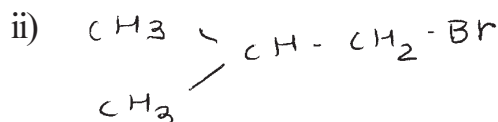
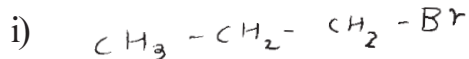
P.T.O.

## SECTION - I

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

a) Explain in brief the origin of NMR spectrum. Would Deuterium nucleus exhibit NMR spectrum? Explain.

b) Differentiate on the basis of their  $^{13}\text{C}$  NMR :



c) Write a brief note on: ESR of triplet state.

d) Outline in brief the factors those affect chemical shift in NMR spectrum. Give suitable example in each case.

e) Discuss applications of PAS.

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

a) Write a brief note on (any one) :

i) Kramers degeneracy.

ii) Zero-field splitting.

b) What is the g-factor in ESR? Why the g-factor in many ionic crystals is close to that of the free electron.

c) What is McConnell equation? Explain its importance.

d) What is the origin of fine structure in the ESR spectra?

e) Write a short note on ELDOR.

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

a)  $^{32}\text{S}$  has a nuclear spin of  $3/2$ . Calculate the energies of the nuclear spin states in a magnetic field of 7.50 T ( $\frac{g}{g_s} = 0.4289$ ).

b) The chemical shift of the  $\text{CH}_3$  protons in acetaldehyde is 2.20 and that of CHO proton is 9.80. What is the splitting between the methyl and aldehyde proton resonance in a spectrometer operating at 350 MHz?

- c) The ESR spectrum of  $\text{Cu}^{2+}$  in  $\text{Cs C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  shows four lines of equal intensity at 268.9 mT, 282.3 mT, 295.5 mT, and 307.2 mT. Determine the effective spin and nuclear spin of  $\text{Cu}^{2+}$ .

### SECTION - II

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

- a) Give a brief account of Bragg's method used in the elucidation of crystal structure. State its limitations.
- b) Compare the usefulness of XRD and electron diffraction techniques.
- c) State and explain the phase problem observed in XRD. Outline the techniques to overcome it.
- d) Define the structure factor and relate it to the reflection intensities in X-ray diffraction pattern.
- e) State and explain X-ray diffraction and interference of wave motions.

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

- a) Derive the Wierl equation for a diatomic homonuclear molecule.
- b) Discuss the advantages of X-ray diffraction technique over neutron diffraction technique.
- c) Distinguish between ferromagnetism and antiferromagnetism.
- d) Describe the experimental procedure of Gouy technique.
- e) Derive the Langevin equation for the determination of atomic susceptibility.

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

- a) Calculate the volume and mass susceptibility of a sample of a complex with two unpaired electrons at  $0^\circ\text{C}$ .  
[Given: density =  $1.56 \text{ gcm}^{-3}$ , molar mass =  $174.8 \text{ gmol}^{-1}$ ]
- b) Calculate the length of unit cell of NaCl crystal having density  $2.163 \text{ gcm}^{-3}$ .  
[Given: Atomic weight of Na = 23, Cl = 35.5]
- c) Using Pascal constants and constitutive corrections calculate the molar susceptibility of toluene.  
[Given:  $\chi_A$  of C =  $-6.0 \times 10^{-6}$  cgs unit  
 $\chi_A$  of H =  $-2.93 \times 10^{-6}$  cgs unit  
 $\lambda$ :C (in ring) =  $-0.24 \times 10^{-6}$  cgs unit]



Total No. of Questions : 6]

SEAT No. :

P678

[Total No. of Pages : 4

[4325]-410

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

SECTION - I

Q1) a) Explain the following (any three) : [9]

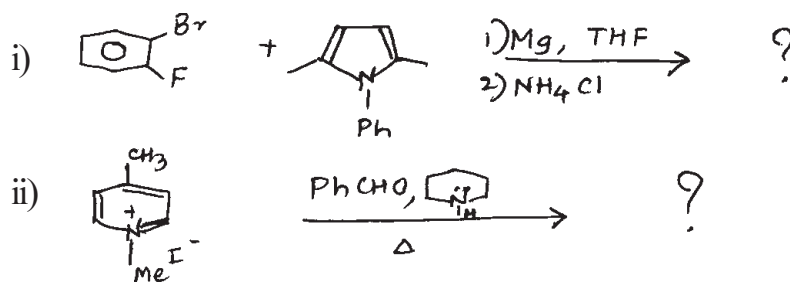
- i) Thiophene is resistant to ring opening than furan & Pyrrole.
- ii) Indole on reaction with chloroform in alkali gives 3-chloroquinoline as one of the product.
- iii) Purine (pKa 8.9) is much more acidic than imidazole or benzimidazole.
- iv) Pyridine N-oxide readily undergoes electrophilic substitution at the 4-position.

b) Give applications of Supramolecular Chemistry in medicine, data storage and processing. [3]

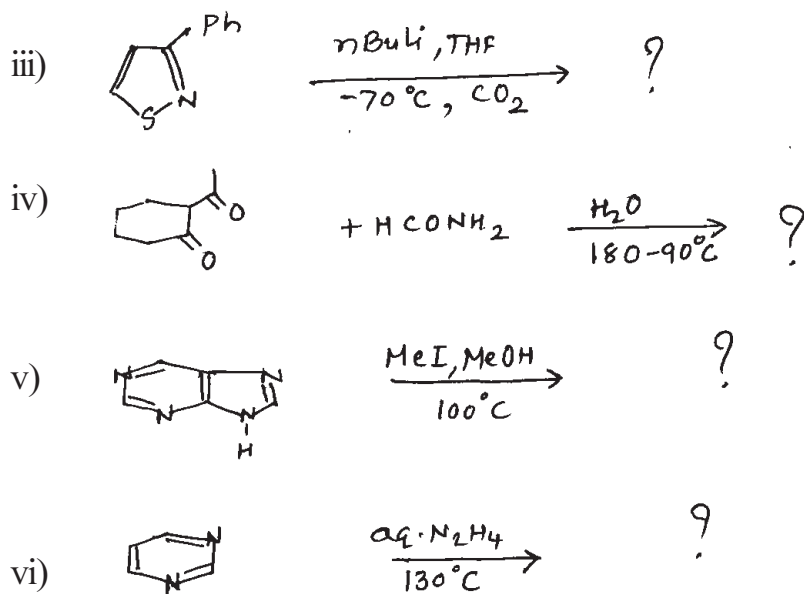
Q2) a) Give the reactions of following reagents with Quinoline. [4]

- i) 30% Oleum, 90°C
- ii) KNH<sub>2</sub>, NH<sub>3</sub>(liq.), -66°C
- iii) LAH, Et<sub>2</sub>O
- iv) TsCl, KCN, CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>O R.T

b) Predict the product/s in any five of the following : [10]



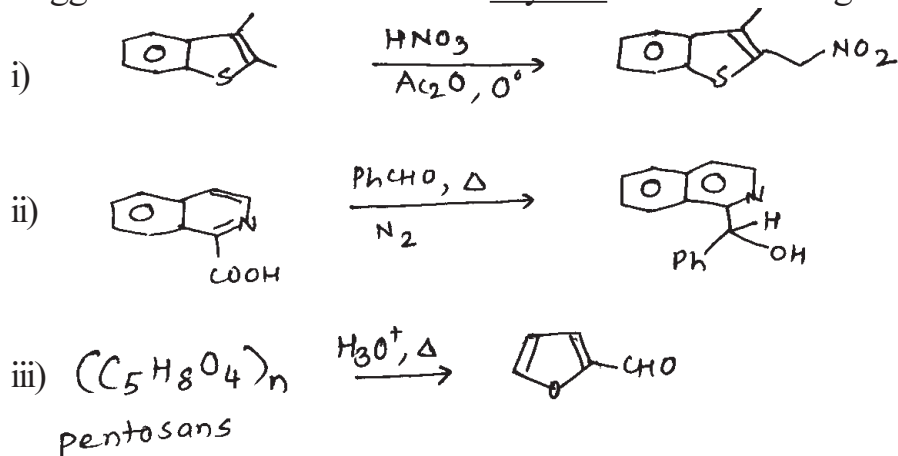
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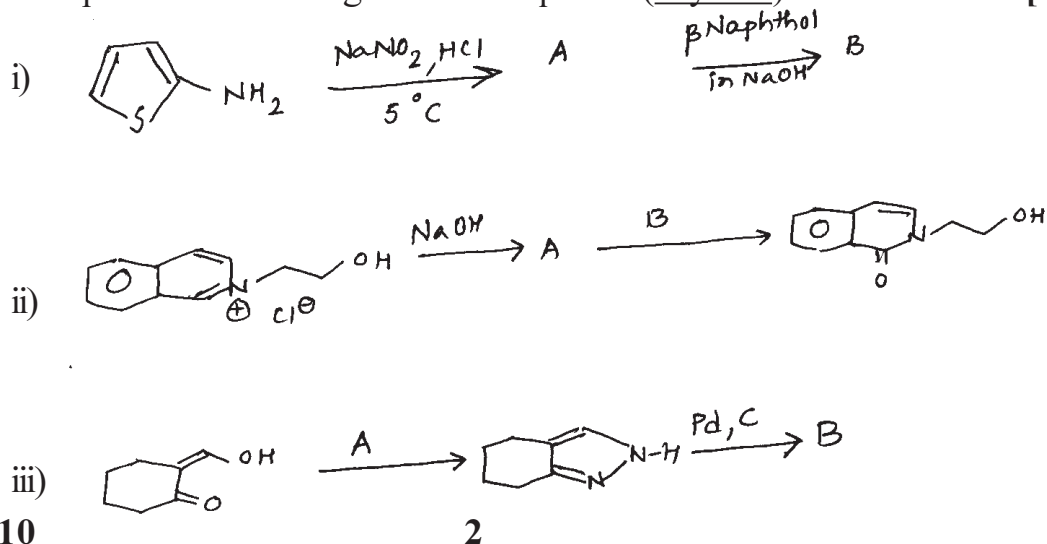
Q3) a) Write notes on (any two) : [4]

- Hantzsch Pyridine synthesis.
- Use of Thiourea in thiazole synthesis.
- Fiest Benary furan synthesis.

b) Suggest suitable mechanism for any two of the following : [6]



c) Complete the following reaction sequence (any two) : [4]



## SECTION - II

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

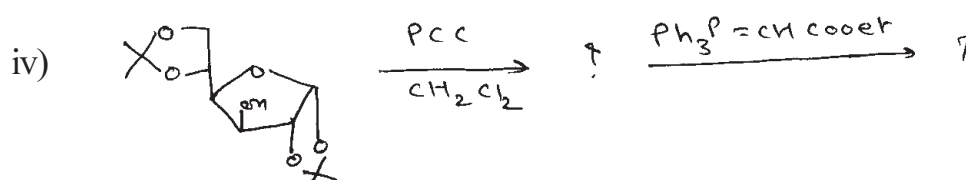
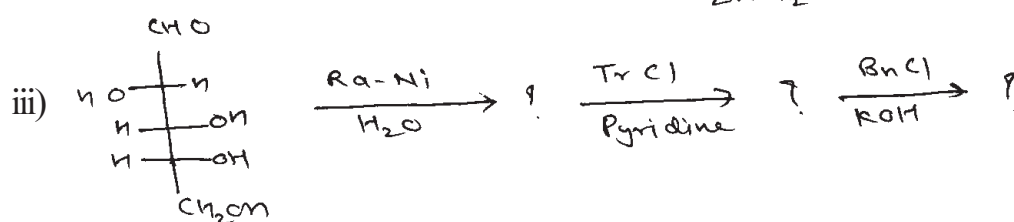
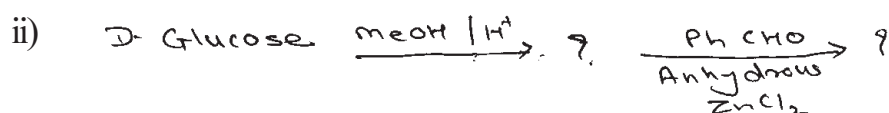
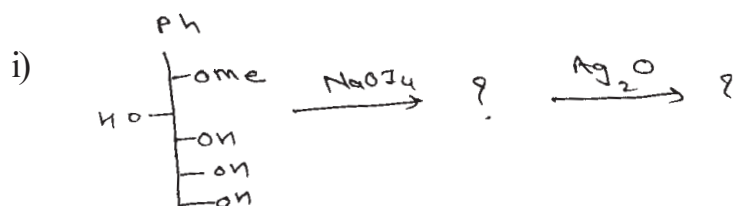
- a) Write  ${}^1C_4$  and  ${}^4C_1$  conformation of D-Mannose and L-mannose
- b) Two isomeric compounds A & B having MF  $C_4H_8O_4$  gives following reactions.
  - i) Both A & B forms oximes.
  - ii) Both A & B forms triacetate.
  - iii) A on oxidation with  $HNO_3$  gives optically inactive acid while B gives optically active acid. Deduce the structure of A & B.
- c) Write Ruff degradation of aldopentose to aldotetrose.
- d) Comment on stability of D- Gluco Furanose and D-Gluco pyranose with special note on anomeric effect.

**Q5)** a) How will you convert D-mannitol to R-epichlor hydrin. **[3]**

b) Give the synthesis of L(+)-Alanine. **[3]**

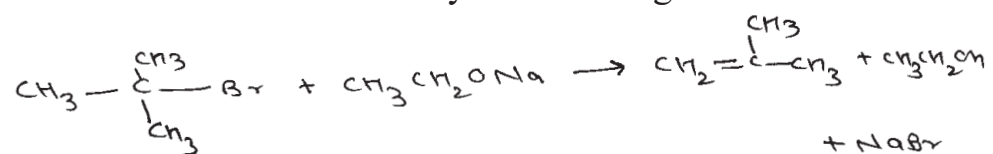
c) Write the Retrosynthetic analysis of (-) shikimic acid. **[2]**

d) Predict the products (Any three) : **[6]**



Q6) a) Describe the basic principles of green chemistry. [4]

b) Calculate the % atom economy for following reaction. [2]



c) Answer the following (any two): [8]

i) Explain in brief the pharmacokinetics (ADME) of the drug action.

ii) Explain active transport of drug absorption.

iii) Give the theoretical aspect of drug design.





Total No. of Questions : 6]

SEAT No. :

P669

[Total No. of Pages : 4

[4325]-402

M.Sc. (Semester - IV)

PHYSICAL CHEMISTRY

CH - 411: Surface and Electrochemistry

(2008 Pattern)

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) Neat diagrams must be drawn wherever necessary.
- 4) Figures to the right indicates full marks.
- 5) Use of logarithmic table/calculator is allowed.

**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	$\beta_e$	=	$-9.274 \times 10^{-24} \text{ J T}^{-1}$
12. Nuclear magneton	$\beta_n$	=	$5.051 \times 10^{-27} \text{ J T}^{-1}$
13. Mass of an electron	$m_e$	=	$9.11 \times 10^{-31} \text{ kg}$

P.T.O.

## SECTION - I

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

- a) Derive the relation  $\pi\sigma = KT$  for the film of adsorbed solute in dilute solutions.
- b) Explain the term wetting and nonwetting. Explain wetting as a capillary action phenomenon.
- c) Describe with neat labelled diagram gravimetric method for measurement of adsorption of gas on solid.
- d) Discuss briefly adsorption of gas on porous solids.
- e) Give a critical comparison of various models used for multilayer adsorption.

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

- a) What are Zeolites? Explain with example how they are used to isolate radionuclides.
- b) Write a short note on heterohomogeneous catalysis.
- c) Explain what is catalyst deactivation. Describe different ways of catalyst deactivation.
- d) What is specific surface area of solid? Discuss various methods used to determine it.
- e) Discuss geometrical theory of heterogeneous catalysis.

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

- a) One gram of activated charcoal has surface area of  $1000 \text{ m}^2$ . Considering complete coverage as well as monomolecular adsorption, how much ammonia in ml of STP would be adsorbed on the surface of 2.5 g charcoal? Diameter of ammonia molecule is 0.3 nm.
- b) The adsorption of p-xylene on KC-8 adsorbent is studied at various temperatures. The equilibrium constant varies with temperature according to the equation in  $\ln K = -122.88 \times \frac{1}{T} - 4.88$ . Calculate the adsorption activation energy.
- c) The surface tension of an aqueous solution varies with concentration of solute according to equation  $\gamma = 70 - 350C$ ,  $C = 0.05$ . Calculate the value of K for the variation of surface excess of solute with concentration. Where K is defined by equation  $K = \Gamma \cdot \sqrt{C}$ . The temperature is  $25^\circ\text{C}$ .

## SECTION - II

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

- a) Describe the structure of water when ion is present in it.
- b) Explain the term ionic strength. How does it affect i) thickness of ionic atmosphere ii) the mean activity coefficient of an electrolyte?
- c) Deduce the extended Debye-Huckel equation for appreciable concentration.
- d) Write the Butler-Volmer equation and explain the terms involved in it. How current density varies with overpotential?
- e) Discuss the electrical double layer theory using storn model.

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

- a) Explain the terms :
  - i) Galvani potential
  - ii) Outer potential
  - iii) Surface potential
  - iv) Electrochemical potential
- b) Discuss the Wagner-Traud mechanism for corrosion of ultrapure metals.
- c) Write short note on Li ion battery.
- d) Explain the terms :
  - i) Fradic efficiency
  - ii) Voltage efficiency
  - iii) Maximum efficiency
  - iv) Overall efficiency
- e) Discuss the electrosynthesis of benzene from phenols and aniline from benzene.

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

- a) Evaluate the constants A and B for water at 25°C. Hence calculate mean activity coefficient of  $\text{KNO}_3$  in water at 25°C when ionic strength is 0.01, dielectric constant of water is 78.3 and ion size parameter  $a = 3\text{Å}$ .
- b) When dilute potassium hydroxide was electrolysed using nickel cathod, the over potential was found to be 0.394 V to maintain a current density  $0.01\text{ A cm}^{-2}$  and 0.148 to maintain a current density  $0.0001\text{ A cm}^{-2}$ .

Calculate the transfer coefficient and exchange current density for hydrogen/hydrogen ion equilibrium at nickel cathod in the given medium at 298 K.

- c) Calculate the Zeta potential in Helmholtz double layer in a solution having dielectric constant 78, ionic charge density  $10^{15}$ esu and separation between the Helmholtz layer is  $10^{-5}$  cm.



Total No. of Questions : 4]

SEAT No. :

P670

[Total No. of Pages : 3

[4325]-403

M.Sc. (Semester - IV)

PHYSICAL CHEMISTRY

CH-414: Biophysical Chemistry and Related Techniques

(2008 Pattern) (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	=	$6.022 \times 10^{23} \text{ mol}^{-1}$
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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	$\beta_e$	=	$-9.274 \times 10^{-24} \text{ J T}^{-1}$
12. Nuclear magneton	$\beta_n$	=	$5.051 \times 10^{-27} \text{ J T}^{-1}$
13. Mass of an electron	$m_e$	=	$9.11 \times 10^{-31} \text{ kg}$

P.T.O.

## SECTION - I

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

- a) Discuss the strategies adopted to study biophysical chemistry in cell processes.
- b) Calculate the  $pK_a$  of a buffer system showing pH 4.5 if the base component is 0.17M and acid component is 0.15M.
- c) What are good and poor solvents? What is the measure of the effectiveness of a solvent to dissolve a macromolecule?
- d) Write a note on the role of ATP to fuel cell processes.
- e) Discuss the role of Caldesmon in smooth muscle contraction.
- f) Explain the role of Osmotic pressure in cell biology.

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

- a) Explain the cage structure of the water molecules around a solute molecule.
- b) Explain the primary, secondary, tertiary and quaternary structures of proteins in brief.
- c) Discuss the role of heat-shock proteins to facilitate refolding of proteins.
- d) Comment on the ability of water to form H bonds with polar solutes like the  $HCO_3^-$  anion.
- e) Write a note on 'flickering clusters'.
- f) What is buffering capacity of a buffer system. When is it maximum? Explain acidosis.

## SECTION - II

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

- a) Discuss briefly the composition of a cell membrane.
- b) Draw and explain the graph showing various events of action potential.
- c) What is all or none law? Explain.
- d) Discuss briefly the factors affecting 'enzyme activity'.
- e) Derive Michaelis-Menton equation for enzyme catalysis.
- f) What are biopolymers? State their characteristics and applications.

**Q4)** Attempt any four of the following :

**[20]**

- a) Describe the diffraction method for determination of molecular weight of a biopolymer.
- b) State the principle of X-ray diffraction. How is it used to determine the molecular weight of an asymmetric macromolecule?
- c) What is Electrophoresis? State its types. Explain any one.
- d) Discuss the theory of optical rotatory dispersion.
- e) Discuss the applications of circular Dichroism.
- f) What are micelles and bilayers? Differentiate between these.







Total No. of Questions : 5]

SEAT No. :

P671

[Total No. of Pages : 3

[4325]-404

M.Sc. (Semester - IV)

PHYSICAL CHEMISTRY

CH-415: Special Topics in Nuclear Radiation Chemistry

(2008 Pattern) (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	=	$6.022 \times 10^{23} \text{ mol}^{-1}$
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	$\beta_e$	=	$-9.274 \times 10^{-24} \text{ J T}^{-1}$
12. Nuclear magneton	$\beta_n$	=	$5.051 \times 10^{-27} \text{ J T}^{-1}$
13. Mass of an electron	$m_e$	=	$9.11 \times 10^{-31} \text{ kg}$

P.T.O.

## SECTION - I

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

- a)  $^{99m}\text{Tc}$  is called as a work horse of nuclear medicines'. Explain.
- b) Write a note on radiation therapy.
- c) Discuss the principle and procedure of Positron Emission Tomography technique.
- d) Outline the procedure for Li-6 isotope separation.
- e) What are the advantages and disadvantages of food irradiation by ionizing radiations?

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

- a) Write a brief note on pre-mordial nucleosynthesis.
- b) Discuss p, r and s processes in nucleosynthesis.
- c) Write down the properties of quark confinement era, GUT era and inflation era.
- d) Define maximum permissible dose. How much is the value of MPD for radiation workers for different organs.
- e) Give an account solid and gaseous radioactive waste management.

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

- a) Write down the reactions in C-N-O bicycle.
- b) In technetium generator, activity of loaded  $^{99}\text{Mo}$  is 12,000 cpm. What will be the activity of  $^{99m}\text{Tc}$  if extracted after 5 hours of loading? Given  $t_{1/2}$  of  $^{99}\text{Mo} = 66\text{h}$  &  $^{99m}\text{Tc} = 6.01\text{h}$ .
- c) Find out thickness of lead required to reduce a dose from 10Gy/h to 10mGy/h. Given :  $e^{-\mu} = 0.211$  b/e, A of Pb = 207, Z of Pb = 82, density of Pb = 11.35 g/cm<sup>3</sup>.

## SECTION - II

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

- a) Discuss the phenomenon of radiolysis of hydrocarbons.
- b) Write the possible reactions occurring in the radiolysis of methanol.
- c) Discuss the problems encountered in the preparation of target by reactor irradiation.

- d) Explain the necessity of thin targets and techniques for their preparation.
- e) Write a note on carriers used in nuclear reaction.
- f) Discuss Sworski and Schwarz relationships for the yield of molecular products and the solute concentration.

**Q5)** Answer any four of the following : **[20]**

- a) Define Scavenging. Explain the phenomenon of radical Scavenging with a suitable example.
- b) Describe a typical radiometric titration curve obtained in precipitation reaction where in substance and reagent both are labelled. Write the experimental procedure for the same.
- c) Explain the principle and technique of radiometric titration curves based on interaction of  $\beta$ -particles with the substance.
- d) Discuss applications of radiometric titrations.
- e) Explain competition kinetics with a suitable example.
- f) 10 cc of LiCl labelled with radioactive chloride was titrated with 0.01 M  $\text{AgNO}_3$ . Addition of 2.0 cc of titrant showed a loss in activity from 10,000 counts per min to 10,000 counts per two min. Calculate the concentration of lithium chloride.



Total No. of Questions : 4]

SEAT No. :

P672

[Total No. of Pages : 2

[4325]-405

M.Sc. - II (Semester - IV)

INORGANIC CHEMISTRY

CH-430: Inorganic Solids and Heterogenetics Catalysis

(2008 Pattern)

Time :3 Hours]

[Max. Marks :80

Instructions to the candidates :

- 1) All questions are compulsory.
- 2) Figures to the right indicate full marks.
- 3) Draw neat figures wherever necessary.

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

- a) How are heterogeneous catalysts classified? Give two examples each.
- b) Explain the formation of  $\text{SO}_2$  in the presence of a vanadium (V) catalyst.
- c) "Metal nanoparticles are effective catalysts for hydrogenation". Justify.
- d) Giving suitable examples differentiate between linear and cyclic inorganic polymers.
- e) Explain with the help of MOT the structure and conductivity of polythiazylion.

**Q2)** Attempt any Four : **[20]**

- a) Write an account on "Synthesis of Zeolites".
- b) What is meant by photocatalysis? Explain one photocatalysed reaction in detail.
- c) What are peroxyacids? Explain the acidic properties of these compounds.
- d) Explain the basic principles involved in heterogeneous catalysis.
- e) Draw the structures of the following :
  - i)  $[\text{NSCl}]_3$
  - ii)  $[\text{Si}_4\text{O}_{12}]^{8-}$
  - iii)  $[\text{Si}_2\text{O}_5]^{2-}$
  - iv)  $[\text{V}_{10}\text{O}_{28}]^{6-}$
  - v)  $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$

**P.T.O.**

**Q3)** Answer any Four : **[20]**

- a) Explain the use of X-Ray Diffraction technique for determining the structure of zeolites.
- b) Explain the significance of volcano diagram in heterogeneous catalysis.
- c) Write an account on Heteropolyanions of Molybdenum.
- d) Explain the role of sulphides as catalysts.
- e) Explain the following terms :  
Polysilylenes, Silicones, Silicon rubber and Feldspar.

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

- a) ALPO & SAPO.
- b) MCM-41.
- c) Structural features of SN compounds.
- d) Ultramarines.
- e) Fixed bed reactor.



Total No. of Questions : 4]

SEAT No. :

**P673**

[Total No. of Pages : 2

**[4325]-406**

**M.Sc. - II (Semester - IV)  
INORGANIC CHEMISTRY  
CH-431: Material Science  
(2008 Pattern)**

*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 & calculator is allowed.*

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

- a) What is the difference between soft wood and hard wood? Explain with example. Describe the different layers in the cross section of a tree stem.
- b) Explain the type of diffusion mechanism in solids.
- c) Explain the different types of plots of  $\alpha$  vs T in solid state reactions?
- d) Explain the mechanism of fluorescences and phosphorances with the help of energy level diagram.
- e) What are nanomaterials? Name the various method for synthesis of nanomaterials. Why these methods are important?

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

- a) Explain the BCS theory for superconductor.
- b) What is point defect? Explain the Schottky and Frenkel defect in solids?
- c) What is Biomaterials? Explain classification of Biomaterials.
- d) Explain the how thermocopal operate on the basis of principle of Peiter and Seebeck effect?
- e) What are the different types of magnetism?

**P.T.O.**

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

- a) What is hysteresis loop? Saturation magnetisation of F.C.C. iron is 1750 KA/m<sup>2</sup>. Calculate the net magnetic moment per iron atom in the crystal.  
Given : Lattice parameter of F.C.C. is 2.87°A  
and 1BM =  $9.273 \times 10^{-24}$  A/m<sup>2</sup>.
- b) Derive the expression of Curie law.
- c) In 'Ge' energy gap is 0.75 eV. What is wavelength of which starts absorption of light?
- d) Calculate the conductivity of pure silicon at room temp. when concentration of carrier is  $1.6 \times 10^{10}$  per cm<sup>3</sup>, Take  $\mu_e = 1500$  cm<sup>2</sup>/V.S and  $\mu_n = 500$  cm<sup>3</sup>/V.S.
- e) In an n-type semiconductor, the fermi level lies 0.3 eV below the conduction band at room temp. If the temp. is increased to 330°K. Find the position of fermilevel. (Room temp = 300°K)

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

- a) What do you mean by a transistor? Give its types and explain any one of them.
- b) Write a short note on Hall effect and Hall coefficient.
- c) What is crystal growth? Explain the crystal growth of hydration reaction.
- d) What are Main types of synthetic fiber's used to produce fiber reinforced plastic composite materials?
- e) Write a note on oil well cement and Sol gel process.



Total No. of Questions : 9]

SEAT No. :

P674

[Total No. of Pages : 3

[4325]-407

M.Sc. - II

INORGANIC CHEMISTRY

CH-445: Inorganic Applications in Industry, Biotechnology and  
Environmental Chemistry  
(Semester - IV) (2008 Pattern)

*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**

**Inorganic Applications in Industry**

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

- a) What is meant by term pigment? Explain the following properties of Inorganic pigments.
  - i) Colour and tints.
  - ii) Reactivity with vehicle.
  - iii) Resistance to light.
  - iv) Chemical resistance.
- b) Explain the methods for electroplating of precious metals.
- c) Give an account of preparation of copper dyes from O-hydroxy diaryl azo compounds and O-halogeno-O-hydroxy diaryl azo compounds.
- d) Explain the microstructure of soft and hard wood.

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

- a) What is the difference between a pigment and dye? Explain the use of chromium in dyeing of wool using azo dyes? Give the structure of the compounds involved.

**P.T.O.**



- b) How are redox centers to PVP electrode coating? Explain the effect of increasing the positive potential of the platinum electrode on electrodeposition.
- c) Which types of isomerisms are seen in chromium and cobalt complexes of tridentate azo compounds? Explain any one type of isomerism.
- d) Explain two methods of electroplating of tin.

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

- a) Explain the production and properties of glass fibers.
- b) Write a note on - Luminous and Fluorescent pigments.
- c) How do complexes such as Prussian blue and Ferrocene modify the behaviour of electrodes during electroplating.

### SECTION - II

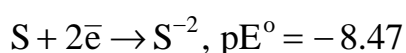
#### Environmental Chemistry

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

- a) What is powerball? Draw a schematic diagram of plant for producing powerball. How is the hydrogen gas liberated from a powerball. How is the power ball manufactured.
- b) What does tertiary treatment in a sewage treatment plant remove from the waste stream?
- c) Draw a schematic diagram that shows all the components of an AAS. How is an aqueous sample introduced into AAS? The metal ion analyte has a positive charge, how does it become a neutral atom?
- d) 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?

**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 pE for waste water that contains  $5 \times 10^{-4} \text{MS}^{-2}$ . Does this waste water favour oxidation or reduction?



- c) Draw a schematic diagram of a Phosphoric Acid Fuel Cell (PAFC). What reactions are occurring at the cathode and anode? Show over all reaction.
- d) What is meant by point and nonpoint sources of pollution? Give an example of each.

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

- a) Which principles of Genetics are used in biotechnology?
- b) Give an overview of chemical reactions involved in the production of biohydrogen.
- 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.

**Q8)** Attempt the following (any three) : **[15]**

- a) Describe the steps involved in the synthesis of insulin from clone DNA segment.
- b) How are variations induced in plants? Explain one method in detailed.
- c) Discuss the ethical and socio-economic issues related with impacts of Biotechnology.
- d) Write an account on production of lactic acid.

**Q9)** Write short notes on any two : **[10]**

- a) DNA mapping.
- b) Applications of single cell proteins.
- c) Vaccines.



[4325]-408

M.Sc. - II (Semester - IV)

ORGANIC CHEMISTRY

CH - 450: Chemistry of Natural Products

(2008 Pattern)

Time : 3 Hours]

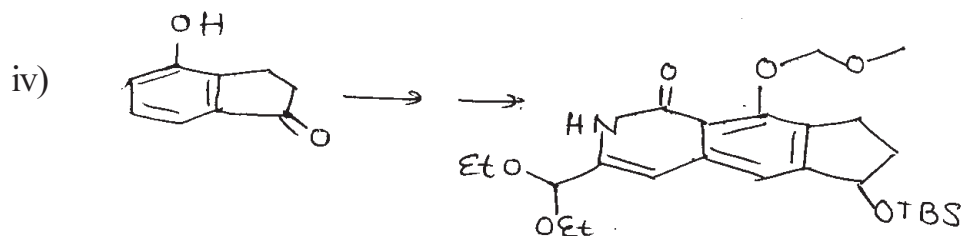
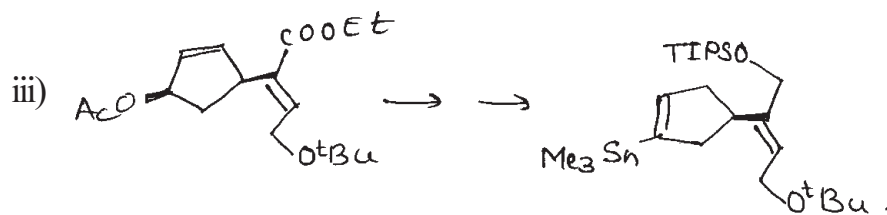
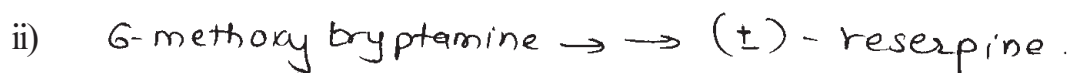
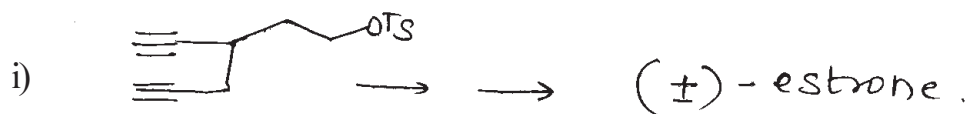
[Max. Marks : 80

Instructions to the candidates :

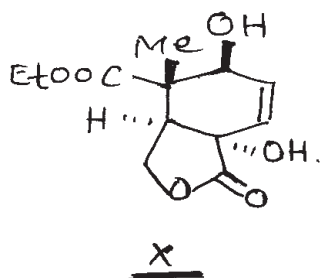
- 1) All questions are compulsory.
- 2) Figures to the right indicate full marks.
- 3) Answers to the two sections should be written in separate answer books.

SECTION - I

Q1) a) Outline the steps involved in the following synthetic sequences. Indicate the reagents and discuss the mechanism and stereochemistry involved (any three) : [12]



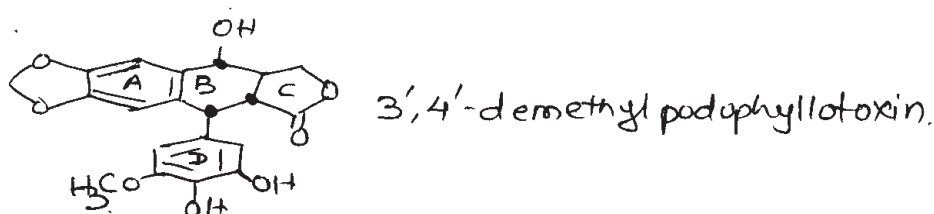
- b) Explain the importance of Navasaka's boron template methodology in construction of molecule X already possessing four contiguous stereogenic centres. [4]



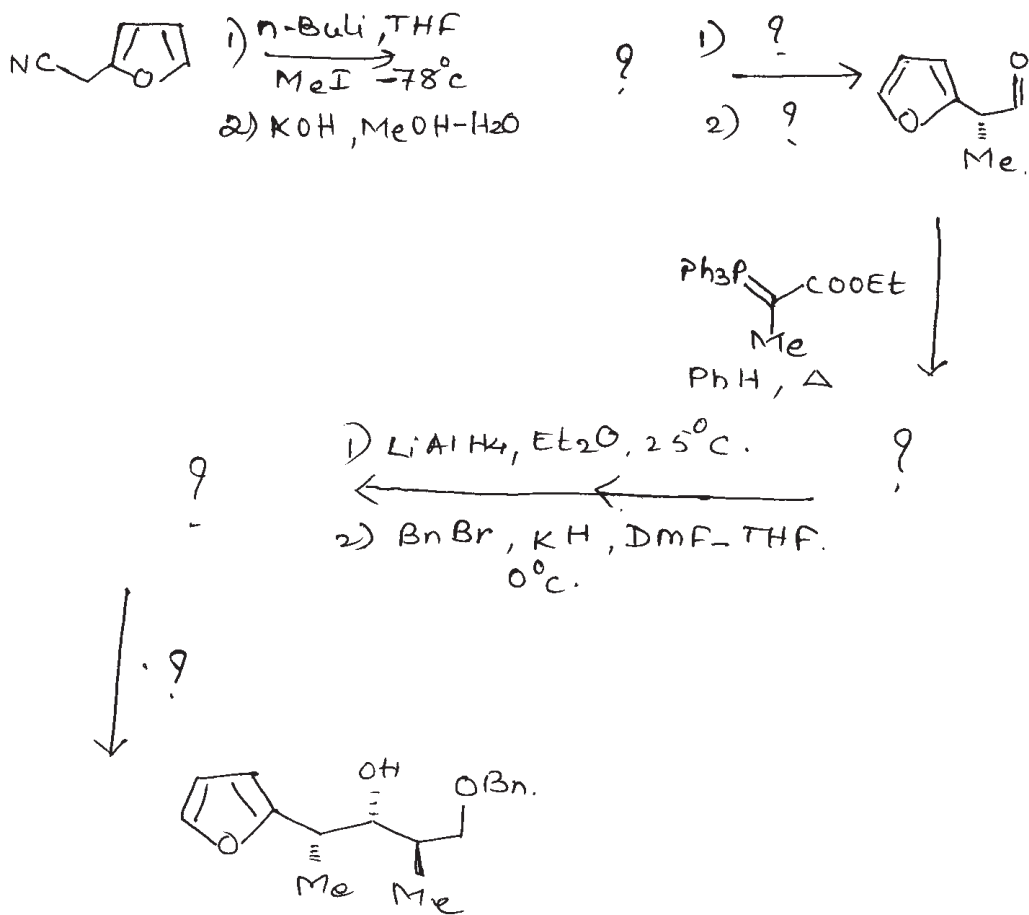
**Q2)** Answer the following (any three): [12]

- What is Dieckmann cyclisation? How this cyclisation helps in establishing stereochemistry of ring fusion in Hardwickiic acid?
- Give evidences to establish the presence of i)  $\text{Ar}-\text{CH}_2-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-$  group and ii) presence and position of ethyl group in hydroxy camptothecin.
- What is the role of acetic anhydride, chloroacetic anhydride,  $30\text{Cl}_2$  in structure determination of camptothecin?
- "Podophyllotoxin and picropodophyllin are stereoisomers and not structural isomers". Justify.

**Q3)** a) 3', 4'-demethyl podophyllotoxin has the following structure. [6]

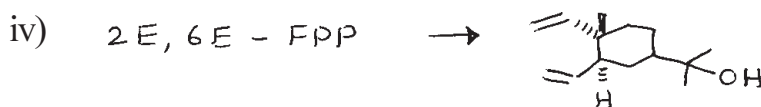
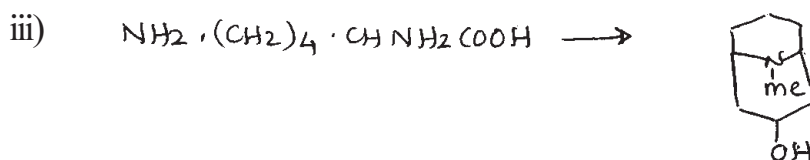
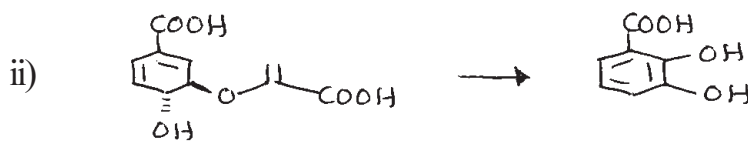


- How will you prove the trans B/C ring fusion?
  - How will you distinguish between the  $-\text{OH}$  group from ring B and ring D chemically and by physical methods?
  - How will you separate podophyllotoxin from 3', 4'-demethyl podophyllotoxin by chemical method?
- b) Complete the following synthetic sequences using appropriate reagents and intermediates. Justify. [6]



### SECTION - II

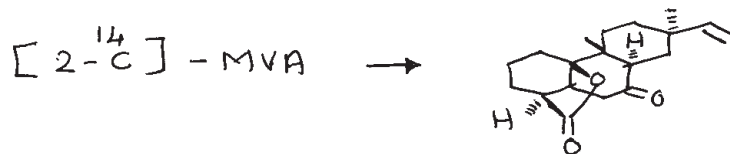
- Q4) a) Discuss the transamination reaction and the role of pyridoxal phosphate in the reaction. [4]
- b) Suggest biogenetic scheme for any three of the following : [12]



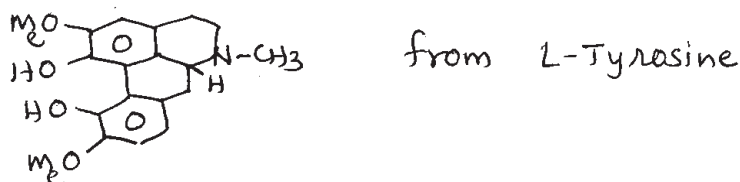
Q5) Answer any two of the following :

[12]

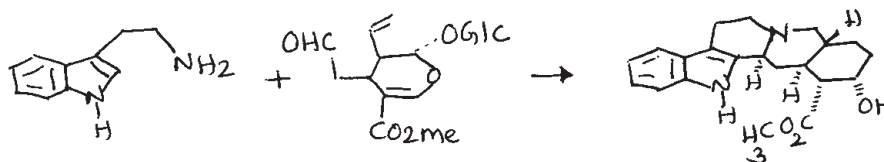
- a) Indicate the position of label in each step and in the final product from the following biogenetic conversion.



- b) Suggest the biogenetic pathway for




- c) Write all steps in the following conversion.



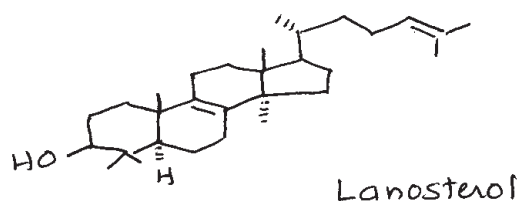
Q6) a) Answer any one of the following :

[6]

- i) Discuss the biogenesis of  from Ornithine  $[2-^{14}\text{C}]$ .

Clearly indicate the position of label in each step.

- ii) Outline the steps involved in the conversion of Farnesyl pyrophosphate to lanosterol and discuss the mechanism involved.



- b) Indicate the position of label in each step and in the final product from the following biogenetic conversion. [6]



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[4325]-409

M.Sc. - II (Semester - IV)

ORGANIC CHEMISTRY

CH - 451: Synthetic Methods in Organic Chemistry

(2008 Pattern)

Time : 3 Hours]

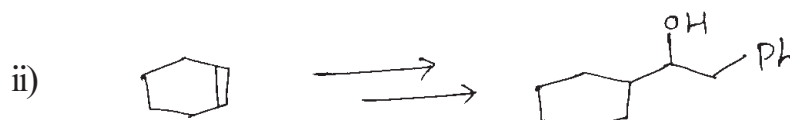
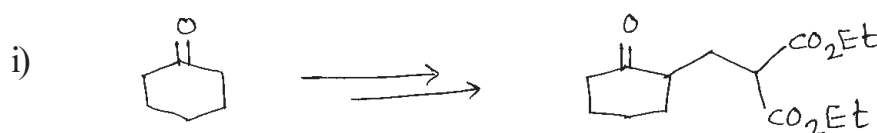
[Max. Marks : 80

Instructions to the candidates :

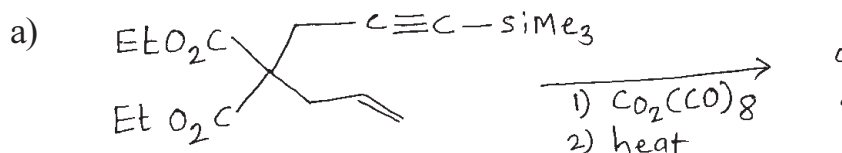
- 1) All questions are compulsory.
- 2) Figures to the right indicate full marks.
- 3) Answers to the two sections should be written in separate answer books.

SECTION - IQ1) a) Explain any two of the following : [6]

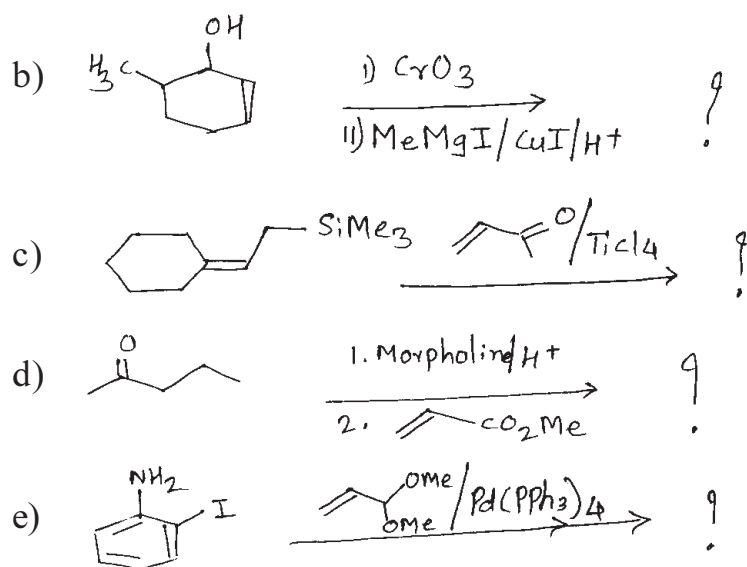
- i) Advantage of Fmoc as a protecting group over BOC.
- ii) Aldol style condensation by using silyl triflate.
- iii) Isotactic propene polymerisation by using titanium- aluminium catalyst.

b) Complete any two of the following conversions by using suitable reagents. [6]Q2) Predict the product in any four of the following:

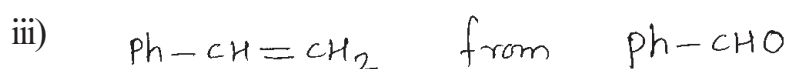
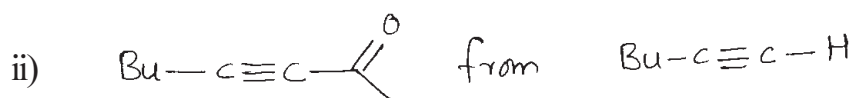
[12]



P.T.O.



- Q3)** a) Write short notes on any two of the following : [6]
- Solid phase peptide synthesis.
  - Grubb's catalyst.
  - Wacker oxidation.
- b) Explain any one of the following : [4]
- Synthesis of 1, 2-dicarbonyl compounds involve umpolung of reactivity.
  - Use of 9-BBN in organic synthesis.
- c) Provide a suitable synthesis using organo silanes as one of the step. Write all the reagents and intermediates (any two) : [6]



### SECTION - II

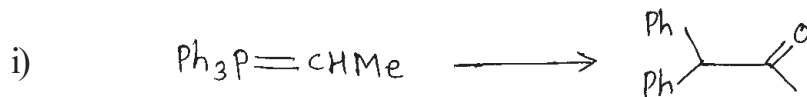
- Q4)** a) Explain any two of the following : [6]
- Olefination by Peterson's reaction.
  - Acyl anion equivalent can be prepared from enol ethers.
  - Synthetic applications of tetracarbonyl ferrate dianion.



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


- i) Sonogashira coupling in organic synthesis.
- ii) MOMCl and MEMCl
- iii)  $\text{Bu}_3\text{S}_n\text{H}$

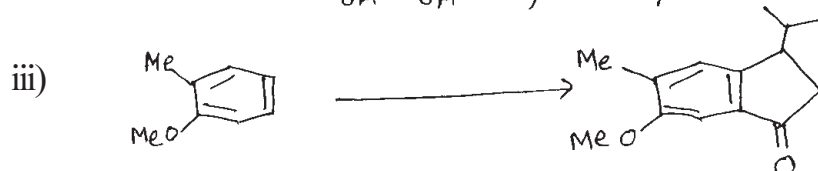
Q5) a) Complete the following transformation using the reagents given below. Arrange the reagents in proper order (any two) : [6]



$\text{MeLi}$  ;  $\text{Phscl}/\text{THF}/\Delta$  ;  $\text{TiCl}_4/\text{AcOH}$  ;  $\text{PhCHO}$  ;  $\text{MeI}$

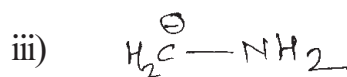
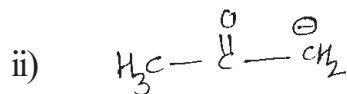
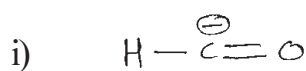


$\text{NaOEt}$  ;  $\text{HCN}$  ;  $\text{LAH}$  ;  $\text{CH}_2(\text{CO}_2\text{Et})_2, \ominus\text{OEt}$  ;  $\text{Tscl}, \text{Py}$  ;  
 $\text{HCl}, \text{EtOH}$  ;  ,  $\text{H}^+$  ;  $\text{DMF}/\text{NaCl}$  .

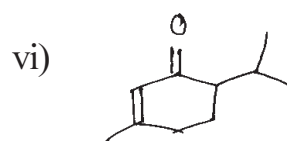
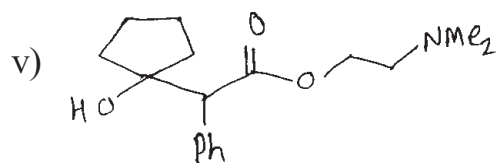
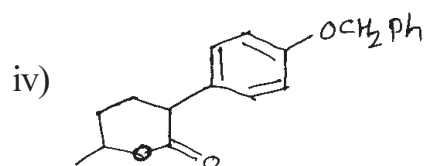
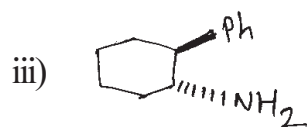
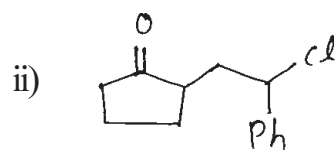
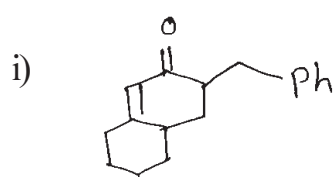


$\text{H}_2(\text{COOH})_2, \text{Py}$  ;  $i\text{-PrMgCl}, \text{CuSPh}$  ;  $\text{Me}_2\text{SO}_4, \text{K}_2\text{CO}_3$  ;  
 $\text{PPA}$  ;  $\text{Me}_2\text{NCHO}, \text{POCl}_3$  ;  $\text{MeOH}, \text{HCl aq.}$

b) Give the synthetic equivalent of (any three) the following synthone. Illustrate your answer with one example of each. [6]



**Q6)** Using retrosynthetic analysis, suggest a suitable method to synthesize of the following (any four): **[16]**



\* \* \*

Total No. of Questions : 4]

SEAT No. :

P679

[Total No. of Pages : 2

[4325]-411

M.Sc. - II (Semester - IV)

ANALYTICAL CHEMISTRY

CH-481: Bioanalytical and Forensic Science

(2008 Pattern)

*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 of the following : **[20]**

- a) How is benzoic acid estimated from food sample?
- b) Write note on 'Sweetening tablet'.
- c) What is Pasteurization? How is it verified?
- d) Describe analytical method for estimation of pectin content from Jam.
- e) Sulphite containing food sample 31.8 gm was subjected to Tanner method and the titre value obtained with 0.01 M NaOH was 8.9 ml. Calculate the amount of SO<sub>2</sub> in the sample. [At. wt. S = 32, O = 16]

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

- a) Discuss the microkjeldahl method for estimation of protein.
- b) Explain suitable method for estimation of glucose.
- c) Define Saponification value of oil. Discuss the method used for the estimation of the saponification value of oil.
- d) Explain the procedure for estimation of vitamin-C.
- e) How is HMF content of honey estimated? Calculate HMF content of sample of honey (100g) if absorbance of unit path length was 0.190.

**P.T.O.**

## SECTION - II

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

- a) How are barbiturates isolated from biological samples by 'procedure A'.
- b) State the principle and explain the procedure for extraction of caffeine from biological sample.
- c) Outline 'Procedure Type B' for isolation and identification of amphetamine.
- d) How is heroin isolated from sample?
- e) Biological sample was analysed for amphetamine content using gas chromatographic method, which gives following observations :-
  - i) Internal standard concentration = 1.6 µg/ml.
  - ii) Peak height for amphetamine = 8.3
  - iii) Peak height for amphetamine in standard reference solution = 4.30.
  - iv) Peak height for standard in specimen = 2.5.
  - v) Peak height for internal standard in reference solution = 1.62.
  - vi) Volume correction factor = 0.6.Calculate the concentration of amphetamine in the given sample.

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

- a) Define the terms :
  - i) Opium derivative
  - ii) Manufacture
  - iii) Coca-leaf
  - iv) Alcohol.
- b) Explain rules related to manufacture of manufactured drugs.
- c) How are dutiable goods transferred from one bonded warehouse to another bonded warehouse?
- d) Write note on offences and penalties in psychotropic substance acts.
- e) Give and explain the types of Ayurvedic preparations containing alcohol.



Total No. of Questions : 4]

SEAT No. :

P680

[Total No. of Pages : 2

[4325]-412

M.Sc. - II (Semester - IV)

ANALYTICAL CHEMISTRY

CH-490: Analytical Spectroscopy

(2008 Pattern)

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 of the following : **[20]**

- a) Explain the following terms used in instrumental analysis.
  - i) Dispersive power
  - ii) Resolving power
  - iii) Period
- b) Enlist the electromagnetic spectral regions that are useful for chemical analysis with electromagnetic radiation spectrum.
- c) Draw schematic diagram and explain working of single beam spectrophotometer.
- d) Calculate molar absorptivity for the complex formed between bismuth (III) and thiourea having  $3.7 \times 10^{-5}M$  concentration of complex, gave transmittance of 78.3% in a 1.0 cm path length at 470 nm.
- e) A certain photomultiplier tube has ten dynodes and each dynode emits an average of 4.2 electrons for impinging electrons. Calculate the amplification factor of a photomultiplier tube.

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

- a) Enlist the diffraction methods of crystal analysis. Describe Bragg's method for crystal analysis. How the reflection for different order are noted by this technique.
- b) Explain the origin of chemical shift in ESCA lines. Describe the use of chemical shift in quantitative analysis.
- c) Explain the principle of chemiluminescence. Describe it's analytical applications.
- d) Describe X-ray absorptive method for crystal analysis.

**P.T.O.**

- e) Calculate 1s electron binding energy of Nitrogen in nitrate ion from the incident X-ray photon that was used to create the inner-shell vacancy had a wavelength of 0.952 nm. The work function of spectrometer was 7.2 eV and the kinetic energy of measured electron was 889.4 eV.  
[Given: Planck's constant =  $6.625 \times 10^{-34}$  Js,  $C = 2.998 \times 10^8$  MS<sup>-1</sup>]

### SECTION - II

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

- a) Distinguish between proton magnetic resonance spectra and non-protonic resonance spectra.
- b) What is meant by Larmor precession? Explain the principle of NMR spectroscopy based on classical theory.
- c) What is meant by relaxation? Explain Spin-Spin and Spin-lattice relaxation.
- d) A proton appears at a quartet at  $4.5\delta$ ,  $J = 6$  Hz on a 300 MHz instrument, indicates the line position in Hz of each line and give its relative intensities.
- e) Calculate the chemical shift in PPM of a particular nucleus in a 60 MHz instrument if the reference nucleus absorbs at a magnetic Flux density that is 0.063 G which is greater than the sample nucleus.  
[Given: For <sup>1</sup>H nucleus 14000G required to cause absorption at 60MHz).

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

- a) Describe with suitable example the applications of ESR Spectroscopy in qualitative and quantitative analysis.
- b) Draw a schematic diagram of SEM, label its components. Describe how the image of a surface of solid sample is obtained using a Finely Focussed beam of electrons.
- c) Explain the following terms :
  - i) ELDOR
  - ii) ENDOR
- d) Distinguish between NMR and ESR spectroscopy with reference to its principle, sources, reference compounds, applied magnetic fields and detectors.
- e) if a resonance was observed for an unpaired electron at a magnetic flux density 0.33 T and a frequency of 9.5 GHz, calculate g-factor for unpaired electron.

[Given: Planck's constant =  $h = 6.625 \times 10^{-34}$  Js

Bohr Magnetron =  $\mu_B = 9.285 \times 10^{-24}$  J T<sup>-1</sup>].



Total No. of Questions : 4]

SEAT No. :

P681

[Total No. of Pages : 3

[4325]-413

M.Sc. - II (Semester - IV)  
ANALYTICAL CHEMISTRY  
CH-491: Polymer Technology  
(2008 Pattern)

Time : 3 Hours]

[Max. Marks : 80

Instructions to the candidates :

- 1) All questions are compulsory and carry equal marks.
- 2) Answers to the two sections should be written in separate answer books.
- 3) Draw diagram wherever necessary.

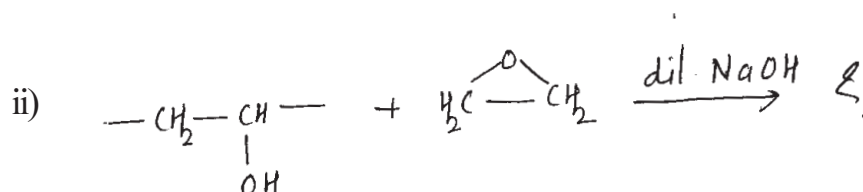
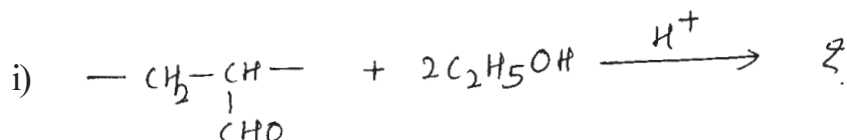
SECTION - I

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

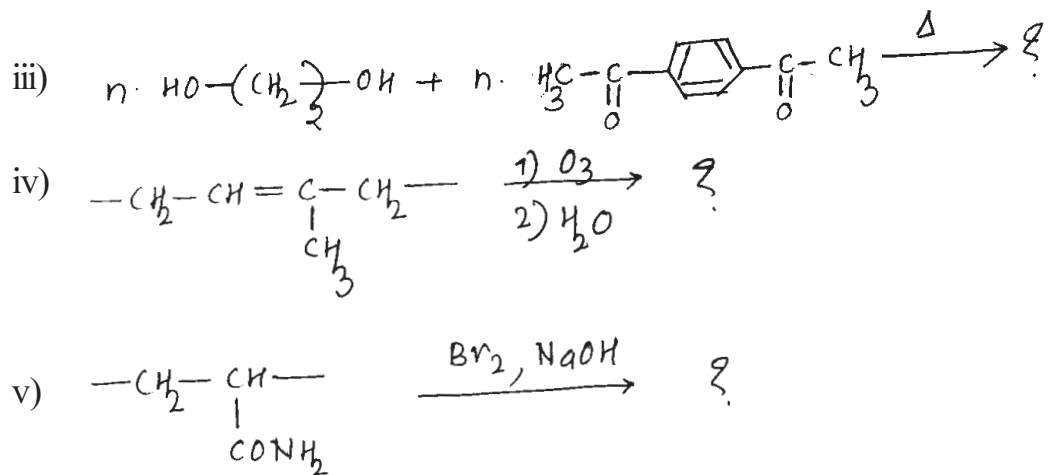
- a) How polymers are classified on their morphological behaviour?
- b) Write a note on Emulsion polymerisation.
- c) Derive kinetic rate equation for living chain polymerisation.
- d) Discuss the effect of radiation on Teflon.
- e) What is polymer degradation? Explain degradation by high energy radiation.

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

- a) Give salient features of suspension polymerisation.
- b) Give method of preparation, types and uses of silicone polymers.
- c) Complete the following reactions.



P.T.O.



- d) Discuss two types of termination reactions in free radical chain polymerisation.
- e) State, giving reasons the type of copolymer formed when the two monomers have the following reactivity ratios.

	$r_1$	$r_2$
Case I	0.02	0.01
Case II	55.0	0.01
Case III	1.0	1.0

### SECTION - II

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

- Explain softening temperature and flammability of the polymers.
- Write a note on calendering.
- Give types of fibres. Explain Wet spinning method.
- Explain the following terms :
  - Resistance to solvents.
  - Vapour permeability and weathering.
- A suspension containing equal masses of particles of molecular weights 30,000 and 40,000 respectively. Calculate the number average molecular weight ( $\bar{M}_n$ ) and weight average molecular weight ( $\bar{M}_w$ ).  
(Given :  $M_1 = 30,000$  g/mole,  $M_2 = 40,000$  g/mole)

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

- Explain the role of X-ray diffraction in structure determination of polymers.
- Describe in detail an ebulliometry method used for determination of  $\bar{M}_n$  of polymers.



- c) Explain the role of carbon black in reinforcement of elastomers.
- d) What is sol-gel? Explain aqueous chemistry of metal alkoxides.
- e) A 0.4378 gm of carboxy terminated and hydroxy terminated polybutadiene dissolved in mixture of ethanol and toluene. It was titrated against 0.1314 N alcoholic KOH. The burette reading was 6.2 ml. Calculate average molecular weight of polymer.

