

Reg. No. : .....

D 1652

Q.P. Code : [D 07 PCH 01]

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2010.

First Year

Chemistry

ORGANIC CHEMISTRY — I

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

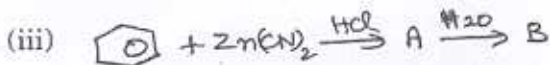
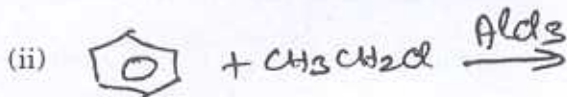
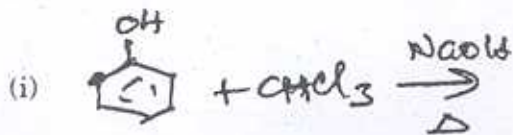
All questions carry equal marks.

(5 × 20 = 100)

1. (a) Discuss the aromatics of azulene with resonance structures.
- (b) Explain the use of Hammond postulate in the study of reaction mechanism.
- (c) Write an account of the following
  - (i) Primary kinetic isotopic effect
  - (ii) Hammett equation.

2. (a) What are the products formed when phenol and nitrobenzene are nitrated? Discuss the mechanism of their formation.

(b) Predict the products in the following



(c) Illustrate the orientation in the electrophilic substitution of disubstituted benzene with two examples. (6 + 6 + 8)

3. (a) Discuss the substitution reaction at allylic carbon.

(b) Account for the following

(i) Vinyl chloride does not undergo substitution reaction.

(ii) Alkyl fluoride is unreactive towards  $S_N1$  and  $S_N2$  reactions.

(iii)  $C_2H_5SCH_2CH_2Cl$  undergoes solvolysis  $10^4$  times faster than  $C_2H_5OCH_2CH_2Cl$ .

(c) Write a note on the following :

(i) Von-Brown reaction

(ii) Acid mechanism of ester hydrolysis.

(6 + 6 + 8)

4. (a) Give the mechanism of the following :

(i) Chugaev reaction

(ii) Hoffmann degradation

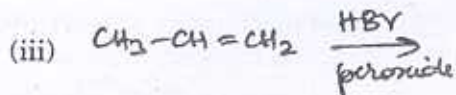
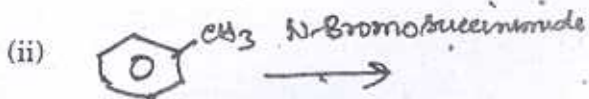
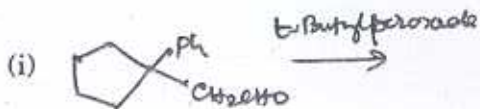
(b) How nitrenes are generated? Give any two reactions of nitrenes.

(c) Discuss the mechanism and stereochemistry of  $E_2$  and  $E_1$  elimination. (6 + 6 + 8)

5. (a) How short lived free radicals are generated?

(b) Discuss the mechanism of Pschorr reaction.

(c) Predict the products and justify their formation



(d) Write an account of the following

(i) Free radical rearrangement

(ii) Free radical elementation.

(3 + 3 + 6 + 8)

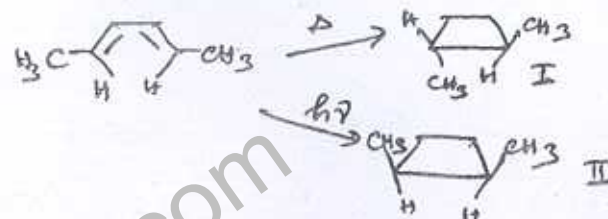
6. (a) Addition of bromine to cis and trans-2-butene is both stereoselective and stereospecific - Explain with the reactions.

(b) Describe the mechanism of Mannich and Stobbe reactions.

(c) Compare the mechanism of hydrogen of alkenes by oxymercuration-demercuration and hydroboration methods and discuss.

(6 + 6 + 8)

7. (a) Explain the formation of products I and II with the thermal and photochemical process using frontier orbital theory.



(b) Write a note on the following :

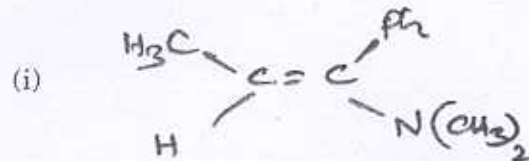
(i) Sigmatropic reaction

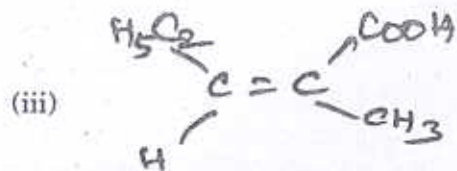
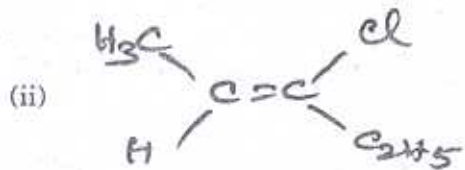
(ii) Claisen rearrangement

(iii) Di-pomethane rearrangement. (8 + 12)

8. (a) Discuss the optical isomerism exhibited by any two nitrogen compounds.

(b) Designate the following as E and Z and explain





- (c) Draw the most stable conformation of perhydrophenanthrene, perhydroanthracene and 1,3-dimethyl cyclohexane. Explain their stability.

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Reg. No. : .....

**D 1653**

**Q.P. Code : [D 07 PCH 02]**

(For the candidates admitted from 2007 onwards)

**M.Sc. DEGREE EXAMINATION, DECEMBER 2010.**

First Year

Chemistry

**INORGANIC CHEMISTRY — I**

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

(5 × 20 = 100)

1. (a) Give an account on the metal clusters formed by heavier members of groups 14, 15 and 16.  
(b) Write notes on inorganic rings.
2. (a) What are called thermodynamic defects? Explain.  
(b) How is borazine prepared? Give the uses of boron nitride.

3. (a) What is called the Meissner effect? Explain.  
(b) Write notes on the dielectric properties of solids.
4. (a) Discuss the important applications of the liquid drop model.  
(b) What do you mean by packing fraction? Discuss the Aston's packing fraction curve.
5. (a) What do you mean by nuclear fragmentation? Explain.  
(b) What are known as nuclear isomers? How are they classified?
6. (a) Write a detailed notes on the atomic power projects in India.  
(b) Give an account of the regeneration and breeding of fissile material.
7. (a) What is called a bubble chamber? How does it operate?  
(b) Explain the photographic detection of ionizing particles.
8. (a) Sketch the arrangement of temperature sensors in DTA. Explain.  
(b) What is called Koopman's theorem. Explain the technique of UPs.
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D 1654

Q.P. Code : [D 07 PCH 03]

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2010.

First Year

Chemistry

PHYSICAL CHEMISTRY — I

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

(5 × 20 = 100)

1. (a) Define the properties of a group. (10)
- (b) Distinguish between a point group and space group. (3)
- (c) Explain the identity and centre of symmetry. (7)

2. (a) Construct  $C_{3v}$  character table. (10)
- (b) What is called an irreducible representation? (3)
- (c) Discuss the method of determining orbitals contribute to bonding. (7)
3. (a) Discuss the postulates of quantum mechanics. (10)
- (b) The speed of a projectile of mass 1.2 g is known to within  $1 \mu \text{ms}^{-1}$ . Calculate the minimum uncertainty in its position. (3)
- (c) Describe the Born's interpretation of the wave function. (7)
4. (a) Discuss the method of normalizing a harmonic oscillator wave function. (10)
- (b) What do you mean by a cyclic boundary condition? (3)
- (c) Explain the property of orthogonality. (7)
5. (a) Give the salient features of the time-independent perturbation theory. (10)
- (b) What is called the space quantization? (3)
- (c) Discuss bond polarity using the variation principle. (7)
6. (a) How do you calculate the activity of solvent from that of solute? (10)
- (b) How is fugacity related to the compression factor? (3)
- (c) How is fugacity of a gas determined by graphical method? (7)
7. (a) State MB law. How are  $\alpha$  and  $\beta$  are evaluated. (10)
- (b) State Stirling's approximation. (3)
- (c) Explain the concept of ensemble. (7)
8. (a) Derive an expression for equilibrium constant in terms of partition function. (10)
- (b) Give an expression for electronic partition function. (3)
- (c) Obtain the relationship between entropy and partition function. (7)



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**D 1655**

**Q.P. Code : [D 07 PCH 04]**

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2010.

Second Year

Chemistry

ORGANIC CHEMISTRY - II  
(ORGANIC SYNTHESIS AND NATURAL PRODUCTS)

Time : Three hours

Maximum : 100 marks

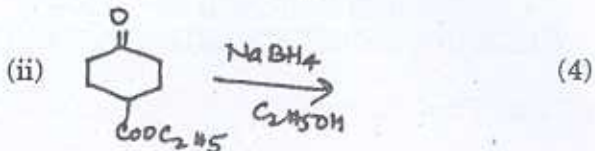
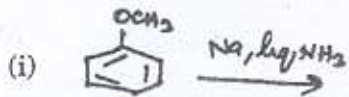
Answer any FIVE questions.

All questions carry equal marks.

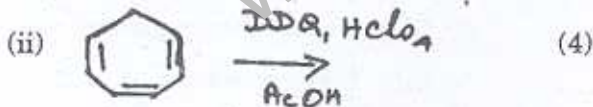
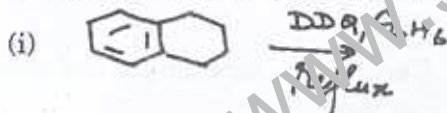
(5 × 20 = 100)

1. (a) Discuss the migratory aptitude in Baeyer-Villiger rearrangement with suitable examples. (5)
- (b) Describe the mechanism and synthetic use of the following :
  - (i) Neber rearrangement
  - (ii) Stevens rearrangement
  - (iii) Favorskii rearrangement. (3 × 5 = 15)

2. (a) Illustrate a photosensitized reaction with an example. (4)
- (b) Discuss cis-trans photoisomerisation of stilbene. (6)
- (c) Distinguish between Clemmensen reduction and Wolff-Kishner reduction. (6)
- (d) Complete the following :



3. (a) Give the preparation and synthetic applications of the following :
- (i) DCC (8)
- (ii) Crown ethers. (8)
- (b) Predict the product of the following :



- (c) Explain the mechanism of Barton reaction. Discuss its application. (8)

4. (a) Elucidate the structure of eudesmol. (10)
- (b) Give the synthesis of the following :
- (i) Caryophyllene.
- (ii) Zingiberene. (2 × 5 = 10)
5. (a) How the structure of estrone is established? (10)
- (b) How will you synthesise equilemin? (6)
- (c) Give the reactions involved in the conversion of cholesterol of testosterone. (4)
6. (a) Discuss the structure elucidation of quinine. (10)
- (b) How 2-ethyl pyridine is obtained from tropine? (4)
- (c) Give the synthesis of glaucine. (6)
7. (a) Write an account of biological importance of RNA and DNA. (4)
- (b) How will you synthesise the following :
- (i) Oxytocin.
- (ii) Adenine. (8)

- (c) Discuss the reactions of cyanic. (4)
- (d) Explain the primary and secondary structures of protein. (4)
8. (a) Illustrate axial haloketone rule. (4)
- (b) Discuss the applications of octant rule. (4)
- (c) Give the fragmentation pattern for phenol, benzaldehyde and benzamide. (9)
- (d) Illustrate McLafferty rearrangement with an example. (3)
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Reg. No. : .....

D 1656

Q.P. Code : [D 07 PCH 05]

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2010.

Second Year

Chemistry

INORGANIC CHEMISTRY — II

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

Each question carries 20 marks.

- (a) What are the important assumptions in crystal Filed Theory? (4)

(b) Calculate the total pairing energy for  $\text{Cr}^{2+}$  complex in high spin and low spin states. Mean pairing energy =  $23,000 \text{ cm}^{-1}$ . (6)

(c) Draw the M.O picture for  $[\text{CoF}_6]^{3-}$  showing all the  $\sigma$  and  $\pi$  bonds. Give a brief explanation. (10)

2. (a) What is the ground state term symbol for  $d^2$  configuration? How is it split in octahedral field? (4)
- (b) State Jahn-Teller theorem. Draw the orbital energy diagram for tetragonal field both for Z-out and Z-in. (10)
- (c) Briefly explain charge transfer spectra. (6)
3. (a) Write any two methods for the preparation of metal carbonyls. (4)
- (b) How is Ziese's salt prepared? Discuss the salient features of the structure of it. (6)
- (c) Give a comparison between the structure of hemoglobin and myoglobin. Write the significant differences between them in their action. (6 + 4)
4. (a) Explain trans effect and its importance in synthetic chemistry. (6)
- (b) Explain hydrogenation reaction using Wilkinson's catalyst under homogeneous conditions. (10)
- (c) Explain the terms :
- (i) Coordinative unsaturation and
- (ii) Electron transfer reaction. (4)
5. (a) Write a note on metal oxygen complexes. (6)
- (b) Discuss the bonding in nitrosyl complexes. (8)
- (c) Write a note on complexes of alkenes. (6)
6. (a) Give an account of benzene complex. (4)
- (b) Discuss about the bonding in ferrocene. (6)
- (c) Discuss the structure of cytochrome C. How cytochromes are classified? Explain the role of cytochrome in respiration. (10)
7. (a) Explain the concept of isolabel analogy. What are isolabel fragments? (10)
- (b) The reaction of chloroform with  $\text{Co}_2(\text{CO})_8$  yields a compound of formula  $\text{Co}_3(\text{CH})(\text{CO})_9$ . Spectroscopic data indicate only one terminal CO and presence of a CH group. Propose a structure. Propose a structure consistent with the spectroscopic observations and the correlation of CVE (Cluster valence Electron Count) with structure. (10)
8. (a) Give a comparison between X-ray diffraction and neutron diffraction. What are the significant differences between them? (10)
- (b) Discuss about the columns and detector used in HPLC. (10)

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D 1657

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(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2010.

Second Year

Part III — Chemistry

PHYSICAL CHEMISTRY – II

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

(5 × 20 = 100)

1. (a) How will you determine  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for a reaction by using ARRT? (5)  
(b) Explain the Kinetic Isotopic effect. (5)  
(c) Discuss in detail the Collision theory of bimolecular reactions. (10)
2. (a) Describe the stopped flow method for studying Kinetics of fast reactions. (5)  
(b) Explain the significance of volume and entropy of activation. (5)  
(c) Illustrate the influence of ionic strength and the nature of the solvent on the rates of ionic reactions. (10)

3. (a) Derive Gibbs adsorption Isotherm equation. (5)
- (b) Explain the Langmuir - Rideal Elay mechanism. (5)
- (c) Derive rate expressions for enzyme catalysed reactions. How  $K_m$  can be evaluated. (10)
4. (a) Explain Guoy-Chapman model of the electrical double layer. (5)
- (b) Derive the Debye Huckel limiting law equation. How can this equation be verified. (5)
- (c) Derive the Debye - Huckel onsag on equation and explain its significance. (10)
5. (a) Explain amperometric titrations taking suitable examples. (5)
- (b) What do you understand by constant current coulometer? How end point can be determined in constant current coulometry? (5)
- (c) Explain the following. (10)
- (i) Half Wave Potential
- (ii) Diffusion Current
- (iii) Migration Current.
6. (a) What is the principle of TGA? Discuss the factors that affect thermograms. (5)
- (b) Discuss the axial halo Ketone rule with examples. (5)
- (c) What is Cotton effect? Discuss the applications of ORD and CD. (10)
7. (a) Explain the principle and applications of Auger electron spectroscopy. (5)
- (b) Explain the techniques of GL C with special reference to the detection systems employed. (5)
- (c) Discuss how photo electron spectrum is helpful in the study of binding energy. (10)
8. (a) How is neutron diffraction useful in distinguishing between ferro magnetic and antigerromagnetic substances? (5)
- (b) What is the main difference between X-ray scattering and neutron scattering. (5)
- (c) Explain the structure of fluorite and antifuoride. (10)