

12. (a) (i) Discuss FBTR at kalpakkam. (5)  
(ii) Discuss briefly the fusion reactions involved in the release of stellar energy. (5)

Or

- (b) Describe various nuclear reactions that take place in the cosmic furnace. (10)

#### UNIT V

13. (a) What is BCC arrangement? (2)  
(b) What are the three important Crystallographic laws? (2)
14. (a) Give the conditions for the formation of Frenkel and Schottky defects. (6)

Or

- (b) Explain neutron diffraction experiment. (6)
15. (a) Explain with suitable examples of Perovskite structure. (10)

Or

- (b) Explain the work of Sommerfeld in explaining the conductivity of metals. (10)

5561/MC1

MAY 2011

#### Paper I – INORGANIC CHEMISTRY – I

(For those who joined in July 2003 and after)

Time : Three hours

Maximum : 100 marks

Answer ALL questions.

#### UNIT I

1. (a) What are the steps involved in hybridization process? (2)  
(b) Define overlap integral. (2)
2. (a) Brief an account on lattice energy. (6)
- Or
- (b) Explain the concept of three centre two electron bonding and three centre four electron bonding with examples. (6)
3. (a) Compare and contrast the VB and MO approaches to covalent bonding in molecules. Illustrate with examples. (10)

Or

- (b) Discuss in detail about valence shell electron pair repulsion theory. (10)

## UNIT II

4. (a) The lanthanides resemble much the alkaline earth metals than transition metals. Explain. (2)
- (b) How is it possible for uranium to show oxidation states from +3 to +6? (2)
5. (a) How is ion – exchange chromatography useful in the separating lanthanides? (6)

Or

- (b) The ground state term of  $\text{Er}^{3+}$  is  $^4\text{I}_{15/2}$ . Calculate the magnetic moment of  $\text{Er}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ . (6)
6. (a) What is separation factor? Discuss the modern methods of separation of lanthanides. (10)

Or

- (b) Calculate  $\mu_{\text{eff}}$  and  $\text{Eu}^{3+}$ . The observed value is 3.4 – 3.6 B.M. Is there any difference between  $\mu_{\text{cal}}$  and  $\mu_{\text{obs}}$  values? If yes give reasons for the difference. (10)

## UNIT III

7. (a) What is meant by Solvate formation? (2)
- (b) Why non – aqueous solvents are needed? (2)

8. (a) Give example for amphotericism in liquid  $\text{NH}_3$  and liquid  $\text{SO}_2$ . (6)

Or

- (b) Explain the solvent system of acid-base concept. (6)

9. (a) Outline the theory behind hard – hard and soft-soft interaction. (10)

Or

- (b) Describe the preparation and properties of sulphuric acid with suitable equations. (10)

## UNIT IV

10. (a) What kind of nuclei have magnetic moments? (2)
- (b) Fission products usually undergo  $\beta$  decay. why? (2)
11. (a) Discuss the Meson theory of binding forces of nucleon. (6)

Or

- (b) Give different nuclear shapes and electric quadrupole moments. (6)

Paper II – ORGANIC CHEMISTRY – I

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(For those who joined in July 2003 and after)

Time : Three hours

Maximum : 100 marks

Answer ALL questions.

UNIT I

1. (a) The calculated and observed heat of hydrogenation of benzene molecule differ – Explain. (2)
- (b) Cyclopentadiene is one of the most acidic hydrocarbons known. Why? (2)
2. (a) Discuss the factors that affect stability of carbocations. (6)

Or

- (b) Explain with suitable examples how steric effect influences the acidity and basicity of organic compounds. (6)

3. (a) Explain the following with suitable examples:

- (i) Kinetic controlled product
- (ii) Thermo dynamic controlled product
- (iii) Primary kinetic isotopic effect
- (iv) Secondary kinetic isotopic effect.  $(4 \times 2\frac{1}{2} = 10)$

Or

- (b) (i) Discuss how Craig's rule can be applied to determine aromaticity.
- (ii) Discuss the aromaticity of Tropolones and sydnones. (4+6)

UNIT II

4. (a) Solvolysis of 1 – phenyl ethyl chloride in 20% aqueous acetone proceeds with 2% inversion while the solvolysis of 1-cyclohexyl thyl chloride results in 66% inversion – Explain. (2)
- (b) 2-bromo -1,3, 5 - Trimethyl benzene does not react with potassium amide in liquid ammonia – Why? (2)

5. (a) Discuss Benzyne mechanism and give evidences for the same. (6)

Or

- (b) Discuss the different mechanisms available for nucleophilic substitution at a vinyl carbon atom. (6)

6. (a) On bromination anisole gives ortho and parabromo anisoles while nitrobenzene gives a meta product. Further anisole reacts faster than nitrobenzene during bromination. Account for these observations. (10)

Or

- (b) (i) Discuss the effect of solvents on  $SN^1$  and  $SN^2$  reactions.  
(ii) Discuss  $BAC^2$  mechanism of esterification and hydrolysis. (6+4)

### UNIT III

7. (a) Give the mechanism of the unimolecular elimination reactions. (2)  
(b) What is Wittig reagent? How is it prepared? (2)

8. (a) Write a note on :

- (i) Chugaev reaction  
(ii) Cope reaction. (4+2)

Or

- (b) State and explain Saytzeff and Hofmann's rule with suitable examples. (6)

9. (a) (i) Give an example for Michael addition reaction and discuss its mechanism.  
(ii) Discuss the preparation and synthetic applications of lithium dimethyl cuprate. (6+4)

Or

- (b) (i) How will you prove that dehalogenation of dihalides takes place through anti periplanar configuration?  
(ii) Write a note on Perkin's reaction. (6+4)

### UNIT IV

10. (a) Allenes do not possess an asymmetric carbon atom. But they are optically active – Explain. (2)  
(b) How dipole moment studies are used in assigning the configuration of geometrical isomers? (2)

11. (a) Write a note on :

- (i) Stability of free radicals
- (ii) Ullmann reaction. (4+2)

Or

(b) Explain stereoselective and stereospecific reactions with suitable examples. (6)

12. (a) (i) What is asymmetric synthesis? Give an example.

- (ii) State and explain Cram's rule with a suitable example. (2+8)

Or

(b) Write short notes on :

- (i) stereoisomerism of Truxilic acid and Truxinic acid
- (ii) Hunsdiecker reaction. (6+4)

#### UNIT V

13. (a) How Thiazole reacts with :

- (i)  $\text{Br}_2$  in chloroform
- (ii)  $\text{NaNH}_2$ . (2)

(b) How will you convert resorcinol to 7-hydroxy coumarin? (2)

14. (a) Write a note on :

- (i) Fischer Indole synthesis
- (ii) Baker-Venkataraman rearrangement. (4+2)

Or

(b) Starting from urea how will you prepare Uracil, Thymine and Cytosine. (6)

15. (a) Elucidate the structure of Uric acid. (10)

Or

(b) (i) What are anthocyanins and anthocyanidines? Give examples. How the structure of an anthocyanine is generally determined?

- (ii) Discuss the structure of Apigenin. (6+4)

12. (a) Write a note on the postulates of quantum mechanics. (10)

Or

- (b) Write down the schrodinger wave equation for a rigid rotor and solve it. (10)

#### UNIT V

13. (a) Write any two radial function equations. (2)
- (b) What is resonance integral? (2)
14. (a) Apply HMO procedure to the following:
- (i) Butadiene
  - (ii) Allyl system (3 + 3)

Or

- (b) Write the equation of Hamiltonian operator for the N-electron atom and explain the SCF method. (6)
15. (a) Describe in detail how perturbation method applied to  $\text{He}$  atom ground state. (10)

Or

- (b) Discuss the one particle orbital-angular momentum operators. (10)

#### PHYSICAL CHEMISTRY — I

(For those who joined in July 2003 and after)

Time : Three hours

Maximum : 100 marks

Answer ALL questions.

#### UNIT I

1. (a) Partial molar volume can be positive or negative. Explain. (2)
- (b) Show that an ideal gas has zero internal pressure. (2)
2. (a) Derive Gibbs-Duhem equation and indicating its applications. (6)

Or

- (b) How may one measure activities from partial pressure in a binary mixture? (6)
3. (a) Discuss the third law. (10)

Or

- (b) Explain the concept of fugacity and acidity. (10)

## UNIT II

4. (a) Define Debye-Huckel constants A and B. (2)  
(b) Define electrochemical series. (2)
5. (a) Explain any two applications of conductivity measurements. (6)

Or

- (b) Discuss the theory of corrosion. How is corrosion prevented? (6)
6. (a) Derive Butler-volmer equation for an electrode process involving one electron transfer and deduce tafel equation. (10)

Or

- (b) (i) What are fuel cells? and discuss the working of any one fuel cell. (5)  
(ii) How are electrodes classified? Give examples. (5)

## UNIT III

7. (a) What is steady state approximation? How does it simplify the reaction scheme? (2)  
(b) Under what conditions does a chain reaction become explosive? (2)

8. (a) Explain the origin of lower and upper explosion limits in the  $H_2-O_2$  reaction. (6)

Or

- (b) Discuss the principle and experimental details of relaxation technique. (6)

9. (a) Discuss the mechanism of decomposition of acetaldehyde and derive the rate expression. (10)

Or

- (b) Discuss briefly the effect of dielectric constant and ionic strength on the rates of ion-ion reactions. (10)

## UNIT IV

10. (a) For a particle in a box explain how the quantization of energy depends on the size of the box. (2)  
(b) Discuss the deBroglie's equation. (2)
11. (a) Write a note on photoelectric effect. (6)

Or

- (b) What are the average and most probable distances of the electron in H-like atom if

$$\psi_{1s} = \left( \frac{z^3}{\pi} \right)^{\frac{1}{2}} e^{-z.r}. \quad (6)$$

**Paper IV — ANALYTICAL CHEMISTRY**

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(For those who joined in July 2003 and after )

Time : Three hours

Maximum : 100 marks

Answer ALL questions.

**UNIT I**

1. (a) What is transition probability in uv spectroscopy and give selection rules. (2)
- (b) What is shift reagent? Give any two examples. (2)
2. (a) What is chemical shift? Explain what are the factors influencing chemical shift. (6)

Or

- (b) Sketch and explain the FTIR spectrometer. (6)

3. (a) (i) Describe the various applications of UV Spectroscopy. (5)
  - (ii) Explain the types of vibrations of molecules in IR spectroscopy. (5)
- Or
- (b) Explain in detail spin-spin splitting and the factors affecting spin-spin splitting in NMR spectroscopy. (10)

**UNIT II**

4. (a) What are the precautions to be taken in paper chromatography? (2)
- (b) What is a mass spectrum? Give example. (2)
5. (a) Explain the types of paper chromatography. (6)

Or

- (b) Explain cotton effect with suitable examples. (6)

6. (a) Discuss on Mc lafferty rearrangement in mass spectroscopy. (10)

Or

- (b) Describe the following.

- (i) HPLC (4)  
(ii) TLC experimental technique (6)

### UNIT III

7. (a) Write the advantages of potentiometric acid–base titrimetry. (2)

- (b) Define reversible cell. (2)

8. (a) What are the advantages and disadvantages of dropping mercury electrode? (6)

Or

- (b) Give a brief account of cyclic voltametry. (6)

9. (a) (i) Write briefly about Tafel's equation. (5)  
(ii) Describe Butler – Volmer equation (5)

Or

- (b) Discuss in detail about coulometric analysis. (10)

### UNIT IV

10. (a) Define mean and median. (2)

- (b) How is a two dimensional array read? Give example. (2)

11. (a) Explain the rules for computation. (6)

Or

- (b) Develop a program to draw the structure to toluene. (6)

12. (a) (i) Write notes on statistical functions in Excel. (5)
- (ii) Explain the various components and part of a worksheet. (5)

Or

- (b) (i) Explain ON GO TO statement with an example. (5)
- (ii) Explain single line and multiline functions with examples. (5)

#### UNIT V

13. (a) What are the advantages of emission spectroscopy? (2)
- (b) What is eutrophication? (2)
14. (a) Discuss the basic principles of flame photometry. (6)

Or

- (b) How is quinine determined by fluorimetric method? (6)

15. (a) Discuss the applications of thermogravimetry. (10)

Or

- (b) Discuss the applications of atomic absorption spectroscopy. (10)
-

13. (a) What is catenation? (2)  
(b) How do you prepare  $B_5H_{11}$ ? (2)

14. (a) Discuss the structure of 12-heteropoly anion,  
 $[(PMO_3O_{10})]^{3-}$  (6)

Or

- (b) Explain the structures of mica and talc. (6)

15. (a) (i) What are metallocene carboranes?  
How are they prepared? (4)  
(ii) Explain the structure of  $Re_2X_8^{2-}$ . (6)

Or

- (b) Explain in detail about phosphonitrilic compounds. (10)

5565/MC5

MAY 2011

INORGANIC CHEMISTRY — II

(For those who joined in July 2003 and after)

Time : Three hours

Maximum : 100 marks

Answer ALL questions.

UNIT I

1. (a) Why are d-d transitions weak? (2)  
(b) Write a brief note on stabilization of unusual oxidation states of metal ions by complexation. (2)

2. (a) Outline the uses of chelates. (6)  
Or

- (b) Write a note on Dynamic Jahn-Teller effect. (6)

3. (a) (i) Explain the terms nephelauxetic effect and nephelauxetic ratio. What is the significance of nephelauxetic effect? (5)  
(ii) Explain the molecular orbital (diagram) theory for square planar complexes. (5)

Or

- (b) Explain in detail about isomerism in coordination compounds. (10)

## UNIT II

4. (a) Write a note on kinetic stability and thermodynamic stability. (2)  
(b) What are labile and inert complexes? Give one example of each. (2)
5. (a) Define 'stepwise stability constant' and 'overall stability constant'. How are they related? (6)

Or

- (b) Explain the spectroscopic method of determination of stability constant of a metal complex. (6)
6. (a) What are electron transfer reactions? Explain in detail about inner sphere and outer sphere reactions with mechanism. (10)

Or

- (b) Describe the following :  
(i) Aldol condensation and imine formation.  
(ii) Anation reaction. (5 + 5)

## UNIT III

7. (a) Why are Nickelocene and Cobaltocene unstable? (2)  
(b) Give examples of selectivity of Wilkinson's catalyst. (2)

8. (a) Give the preparation and properties of cyclobutadiene complexes. (6)

Or

- (b) Write notes on "Carbonyl hydrides"? (6)

9. (a) Discuss the use of IR spectra in metal carbonyls. (10)

Or

- (b) (i) Discuss the structure of Zeise's salt?  
(ii) Describe briefly metal cyanide complexes. (5 + 5)

## UNIT IV

10. (a) State Jahn - Teller theorem. (2)  
(b) What is doppler shift? (2)
11. (a) What are selection rules for electronic transitions? (6)

Or

- (b) Evaluate all the terms for  $d^2$  configuration. (6)

12. (a) (i) Write a brief account of Auger emission spectroscopy. (5)  
(ii) Explain the basic principles of MB Spectroscopy. (5)

Or

- (b) (i) Describe Koopman's theorem. (5)  
(ii) Describe XPS of  $O_2$  molecule. (5)

Paper VI – ORGANIC CHEMISTRY – II

(For those who joined in July 2003 and after)

Time : Three hours

Maximum : 100 marks

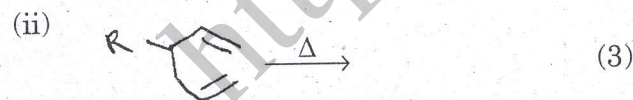
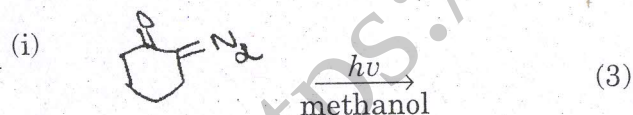
Answer ALL questions.

UNIT I

1. (a) What is the stereochemical requirement for  $E_2$  elimination reaction? (2)
- (b) Write the possible isomeric products that can be obtained when 3-methylcyclohexane oxime is subjected to Beckman rearrangement. (2)
2. (a) Discuss the mechanism or Hoffman rearrangement. (6)

Or

- (b) Predict the products in the following reactions. Name the rearrangement reaction.



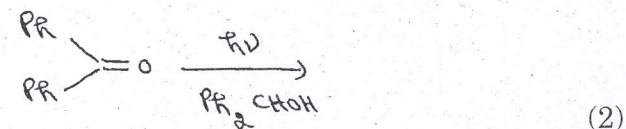
3. (a) Discuss the mechanisms of Baeyer-villiger rearrangement. (10)

Or

- (b) Explain how conformational affect the reactivity of acyclic systems towards substitution and elimination reaction. (10)

UNIT II

4. (a) Outline the mechanism of photoreduction. (2)
- (b) Predict the product in the following reaction.



5. (a) Explain with the help of Jablonski diagram the various photophysical processes of an excited state. (6)

Or

- (b) Write a note on di- $\pi$  methane rearrangement. (6)

6. (a) What are Woodward-Hoffman rules? Analyse the stereochemical course of pericyclic reactions with the help of them. (10)

Or

- (b) Discuss the common reaction of an excited Ketone. (10)

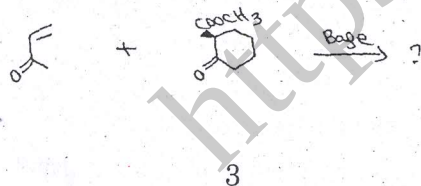
### UNIT III

7. (a) Explain the term 'synthons' with suitable example. (2)
- (b) What are activating groups? Give examples. (2)

8. (a) Write notes on :
- (i) Robinson – Annellation (3)
- (ii) Umpolung synthesis. (3)

Or

- (b) Predict the product and explain the reaction mechanism. (6)



3

5566/MC6

9. (a) Discuss various stereochemical problems associated with organic synthesis. (10)

Or

- (b) Outline a synthetic route for the synthesis of 2, 4 – dimethyl – 2 – hydroxy pentanoic acid from readily available starting material. (10)

### UNIT IV

10. (a) Write the product with its stereochemistry.



(2)

- (b) How will you convert acetophenone to phenylacetate? (2)

11. (a) Bring the mechanism of oxidation of alcohol to carbonyl compounds using DMSO and oxalyl chloride. (6)

Or

- (b) Write a note on oxidation by DDQ. (6)

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5566/MC6

[P.T.O.]

12. (a) Compare the mechanistic aspects of prevost and woodward hydroxylation. (10)

Or

- (b) Write a detailed note on Heterogeneous and Homogeneous hydrogenation. (10)

#### UNIT V

13. (a) What are the ring system present in  $\alpha$ -pinene? (2)

- (b) How many double bond present in zingiberene and how will you account for it? (2)

14. (a) What happens when?

- (i) Camphor is distilled with zinc chloride. (3)
- (ii)  $\alpha$ -piene is treated with hydrogen chloride. (3)

Or

- (b) Give the synthesis of codinene. (6)

15. (a) Elucidate the structure of camphor. (10)

Or

- (b) Discuss the structure of maltose. (10)

- (b) (i) Drive stern-volmer equations also mention the application of stern-volmer equation. (6)
- (ii) Discuss how one can measure quantum yield using chemical actinometry. (4)

#### UNIT V

13. (a) Define  $\overline{M}_n$  and  $\overline{M}_w$ . (2)

- (b) Write a note on kinetic chain length. (2)

14. (a) Write a note on poly condensation. (6)

Or

- (b) Discuss the kinetic of step polymerization. (6)

15. (a) Describe the method of determining reactivity ratios. (10)

Or

- (b) Discuss the mechanism and the kinetics of cationic polymerisation. (10)

**5567/MC7**

**MAY 2011**

#### Paper VII — PHYSICAL CHEMISTRY — II

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(For those who joined in July 2003 and after)

Time : Three hours

Maximum : 100 marks

Answer ALL questions.

#### UNIT I

1. (a) Define abelian and abelian group. (2)

- (b) What is meant by order of a group? (2)

2. (a) Discuss briefly reductions formula. (6)

Or

- (b) Construct the  $C_{2v}$  character table. (6)

3. (a) Discuss briefly

- (i) The products of symmetry operations and equivalence of atoms. (5)

- (ii) Rules for orientation of the molecule of identification of symmetry elements. (5)

Or

- (b) Explain with suitable example how group theory is applied to vibrational spectroscopy. (10)

## UNIT II

4. (a) Explain Fermi resonance. (2)  
(b) What are the advantages of FT-IR spectroscopy? (2)
5. (a) Show that  $I = \mu r^2$ . (6)

Or

- (b) Explain and distinguish between SHM and harmonic oscillator. (6)
6. (a) (i) Discuss spin-spin and spin-lattice relaxation times and mechanism. (5)  
(ii) State and explain rule of mutual exclusion principle. (5)

Or

- (b) Write notes on :  
(i) FT-NMR spectroscopy. (10)  
(ii) Zero field splitting.

## UNIT III

7. (a) Define chemisorption. (2)  
(b) What are the applications of X-ray photoelectron spectroscopy? (2)

8. (a) Deduce Gibb's adsorption isotherm. (6)

Or

- (b) Write notes on micro emulsion. (6)
9. (a) Derive the rate expression of langmuir adsorption isotherm. (10)

Or

- (b) (i) Explain ultra-violet spectroscopy. (5)  
(ii) Write notes on surfactants. (5)

## UNIT IV

10. (a) Draw the Jablonski diagram and explain different types of deactivation process? (2)  
(b) The quantum yield for some reaction is less than 1 and for some reaction it is very much larger than 1 why? (2)
11. (a) Explain flash photolysis. (6)

Or

- (b) Discuss in detail the different types of delayed fluorescence. (6)
12. (a) Write note on :  
(i) Fricke dosimeter. (5)  
(ii) Bose-Einstein statistics. (5)

Or

12. (a) What are enzymes? What functions do they perform in biological system? Explain with two examples. (10)

Or

- (b) Describe four example of chelate therapy.

#### UNIT V

13. (a) Explain the term 'limit cycle behaviour'. (2)  
(b) Define energy flux. (2)
14. (a) Write a note on bioenergetics. (6)

Or

- (b) State and explain the rule of singlet oxygen in biology. (6)

15. (a) How will you obtain 3-D NMR images of various organs in living beings? (10)

Or

- (b) Explain the general principles of nmr spectroscopy. (10)

5568/MC8

MAY 2011

#### Paper VIII – CHEMISTRY OF BIOMOLECULES

(For those who joined in July 2003 and after)

Time : Three hours

Maximum : 100 marks

#### UNIT I

1. (a) Differentiate between enzymes and harmones. (2)

- (b) What are N-terminal and C-terminal amino acids? (2)

2. (a) What are conjugated proteins? How are they classified? (6)

Or

- (b) Distinguish DNA and RNA. (6)

3. (a) Write a note on genetic code. (10)

Or

- (b) How is  $K_m$  value determined? What is the significance of  $K_m$  value? (10)

## UNIT II

4. (a) What happens when pyridoxine methyl ether is oxidised with (2)

- (i)  $\text{KMnO}_4$   
(ii)  $\text{Ba}(\text{MnO}_4)_2$

- (b) Draw the structure of  $\alpha$ -tocopherol and indicate the nature of the ring system and substituents. (2)

5. (a) Give the synthesis of Vitamin A<sub>1</sub>. (6)

Or

- (b) Elucidate the structure of adrenaline. (6)

6. (a) How are the following synthesised?

- (i) Ascorbic acid (Haworth and Hirst) (5)  
(ii) Vitamin K<sub>1</sub>. (5)

Or

- (b) Elucidate the structure of PGE<sub>1</sub>. (10)

## UNIT III

7. (a) What happens when Narcotine is treated with

- (i)  $\text{Zn-HCl}$  and  
(ii) Dilute acid (2)

- (b) Draw the structure of cholesterol and estone. (2)

8. (a) Give the structure of estrone. (6)

Or

- (b) How is the position of  $-\text{CH}_2-\text{CH}_2-\overset{|}{\text{N}}-\text{Me}$  chain of morphine established? (6)

9. (a) Establish the structure of norcotine. (10)

Or

- (b) Give the structure and synthesis of progesterone. (10)

## UNIT IV

10. (a) Explain how  $\text{CO}/\text{CN}^-$  acts as a poison in living system. (2)

- (b) What is a metallothionein? Give one example. (2)

11. (a) Specify the role of manganese in photosynthesis. (6)

Or

- (b) How will differentiate between various types of cytochromes? (6)