

(Time: 3 hours)

Total Marks: 100

- N.B.: (1) All questions are compulsory.
 (2) Figures to the right indicate full marks.
 (3) Use of log table/ non-programmable calculator is allowed.

Q.1 **Attempt any four of the following.** **20**

- A) Explain the importance of quality concepts in industry.
 B) Calculate mass percent composition of each element in copper pyrites (CuFeS_2) molecule.
 (Given: atomic mass of Cu = 63.54, Fe = 55.85, S = 32)
 C) 30 g of glucose are dissolved in 250 g of water. Calculate the mole fraction of glucose in the solution.
 (Given: atomic mass of C = 12, O = 16, H = 1)
 D) What is purpose of sampling? Explain any one method used for reduction of sample size in sampling of solid.
 E) Discuss various grades of laboratory reagents.
 F) Explain any one method of sampling of stack gases, with a labelled diagram.

Q.2 **Attempt any four of the following.** **20**

- A) Mention any three desired properties of metallochromic indicators used in EDTA titrations. Give any two examples.
 B) Discuss the use of diphenylamine indicator in redox titration, explaining the reactions involved and role of H_3PO_4 in such titrations.
 C) Explain direct titration and back titration with respect to EDTA titrations.
 D) 10.0 cm^3 0.01 M Fe (II) solution is titrated with 0.01 M Ce (IV) in acidic medium Calculate the potential
 i) on addition of 5.0 cm^3 0.01 M Ce (IV)
 ii) on addition of 10.5 cm^3 0.01 M Ce (IV)
 Given: $E_{\text{Pt/Fe}^{3+}, \text{Fe}^{2+}}^0 = 0.771 \text{ V}$
 $E_{\text{Pt/Ce}^{4+}, \text{Ce}^{3+}}^0 = 1.44 \text{ V}$
 E) 10.0 cm^3 0.1 M Fe (II) solution is titrated with 0.02 M KMnO_4 at $\text{pH} = 2$, Calculate the potential at equivalence point.
 Given: $E_{\text{Pt/Fe}^{3+}, \text{Fe}^{2+}}^0 = 0.771 \text{ V}$
 $E_{\text{Pt/MnO}_4^-, \text{Mn}^{2+}}^0 = 1.510 \text{ V}$
 F) Name different methods to increase selectivity of EDTA. Describe any two in details.

Q.3. **Attempt any four of the following.** **20**

- A) With the help of a diagram explain the working of hollow cathode lamp.
 B) Describe the standard addition method for the estimation of a sample solution in FES.
 C) Explain Jablonski diagram of energy levels in a molecule.
 D) With the help of a neat diagram explain the working of phosphorimeter.
 E) Draw a schematic diagram of nephelometer and explain its working.
 F) What are the important factors affecting the scattering of radiation? Explain any two.

Q.4 **Attempt any four of the following.** **20**

- A) Explain $[pH]_{1/2}$ and discuss its importance using a graph of percentage extraction versus pH.
- B) What is solid phase extraction? Give any two advantages of solid phase extraction over solvent extraction.
- C) Explain the refractive index detector used in HPLC and give any two of its advantages.
- D) Explain the role of precolumn used in HPLC. Give any two applications of HPLC.
- E) What are the different types of detectors used in HPTLC? Explain any one in detail.
- F) What are the advantages and limitations of HPTLC.

Q.5 **A) Select the correct option and complete the following statements: (any five)** **05**

- a) _____ concerns operational techniques and activities to fulfil quality requirements.
 - i) Quality management ii) quality assurance iii) quality control
- b) The material which carries certificate of purity is _____.
 - i) RM ii) CRM iii) LR
- c) The normality of 0.05 M H_2SO_4 is _____ N.
 - i) 0.2 ii) 0.1 iii) 0.01
- d) 1 mg of solute dissolved in 1 litre of solution is _____.
 - i) 1 ppm ii) 1 ppb iii) 1 ppt
- e) _____ is used for sampling of cement and granular material.
 - i) Geo sampler ii) Concentric tube thief iii) Auger sampler
- f) Multiple tube sampler is used for sampling of _____ liquid.
 - i) Static ii) Flowing iii) immiscible
- g) _____ is used for dissolution of silicates.
 - i) Hydrochloric acid ii) Acetic acid iii) Hydrofluoric acid
- h) In sampling of solid, bulk ratio should be as _____ as possible.
 - i) large ii) small iii) minimum

Q.5 **B) State whether true or false: (any five)** **05**

- a) The plot of electrode potential of the system versus volume of titrant is called titration curve for redox reaction.
- b) Demasking is the process in which masked substance does not regain the ability to enter into reaction.
- c) Stability of M-EDTA complex depends on temperature of the ligand.
- d) Redox titrations involve transfer of electrons between reactant and titrant.
- e) $KMnO_4$ acts as self-indicator in Fe^{2+} versus $KMnO_4$ titration.
- f) Eriochrome black T indicator exhibits blue colour between pH 7 to 11.
- g) Calcium can be directly titrated with EDTA.

Q.5 C) Fill in the blanks with correct alternatives given in the bracket: (any five) (UV light, singlet, delayed, right, acetylene, Turbidity, Nephelometer, colorimeter, AAS) 05

- _____ is used to detect toxic metals like Cu, Ni, Zn and Hg in food products.
- For most molecules, the electrons are paired in the ground state, such a state is called the _____ state.
- The fuel used in a premix burner in FES is _____.
- Secondary filter in fluorimetry absorbs _____.
- Phosphorescence is the _____ reemission of light absorbed by molecules.
- In nephelometry, the detector is usually, but not necessarily, placed at _____ angle to the incident radiation.
- A turbidimeter measures _____ as a function of concentration of suspension.
- The instrument used to measure scattered light is known as _____.

Q.5 D) Match the columns: (any five) 05

- | Column A | Column B |
|------------------------------------------------|----------------------------------------------------------|
| a) Partition coefficient | (i) Retention time |
| b) Extraction by Chelation | (ii) Retention factor |
| c) Parameter for quantitative analysis in HPLC | (iii) Applicable to solute exists in same molecular form |
| d) Parameter for Qualitative analysis in HPTLC | (iv) 8- hydroxy quinoline |
| e) Degasser in HPLC | (v) Silica gel |
| f) Parameter for qualitative analysis in HPLC | (vi) Peak area |
| g) Pre coated plates in HPTLC | (vii) To remove dissolved gases |

[Time: 3 Hours]

[Total marks: 100]

- N.B. :** (1) All questions are compulsory.
 (2) Figures to the right indicate full marks.
 (3) Use of logarithmic table/non-programmable calculator is allowed.

1. Attempt **any four** of the following:
- A. What is symmetry element? Discuss the following symmetry elements with one example each
- Plane of symmetry
 - Proper rotation axis
- 5**
- B. Discuss the point group assign to following molecules
- trans- dichloro ethylene
 - NH₃
- 5**
- C. Draw molecular orbital diagram for CO molecule. Discuss its bond order and magnetic behaviour. **5**
- D. Explain the triangular structure of H₃⁺ ion on the basis of molecular orbital theory. **5**
- E. Discuss the structure of BeH₂ molecule on the basis of molecular orbital theory and draw molecular orbital diagram showing the distributions of electrons in various molecular orbitals. **5**
- F. Write the comparison between homomononuclear and heteronuclear diatomic molecule. **5**
2. Attempt **any four** of the following:
- A. Define unit cell. Express the relationship between density of unit cell and lattice parameters. **5**
- B. What is atomic packing factor. Show that packing density of face centered cubic crystal [fcc] is 74%. **5**
- C. An element having atomic mass 27 g mol⁻¹ crystallises in cubic unit cell with edge length 405 pm and has density 2.7 g cm⁻³. Determine the type of cell. (Avogadro's constant is 6.023 x 10²³). **5**
- D. Explain Schottky and Frenkel defects in solids with suitable example. **5**
- E. Write a note on fullerenes and alkali metal fullerenes as a superconductor. **5**
- F. Give any five applications of superconductor. **5**
3. Attempt **any four** of the following:
- A. Define f-block elements. Name and give the electronic configuration of elements of second transition elements. **5**
- B. What do you mean by lanthanide contraction? Discuss the effects of lanthanide contraction with respect to:
- Decreasing basicity.
 - Variation in the properties of Lanthanides.
- 5**
- C. Explain the following:
- Magnetic moments of lanthanides are high. **3**
 - Lanthanides, preferably exhibit 3+ Oxidation states **2**
- D. Write a short note on spectral properties of lanthanides. **5**
- E. Discuss the principles involved in the separation of lanthanides by ion exchange method. **5**
- F. Discuss in brief commercial and nuclear applications of lanthanides. **5**

4. Attempt **any four** of the following:
- A. With reference to liquid dinitrogen tetroxide as a solvent give two balanced equations for each of the following type of reactions. **5**
 (i) acid-base (ii) reaction with metals
- B. Explain anomalous behaviour of Oxygen with reference to elements of group 16. **5**
- C. With the help of schematic diagram discuss the manufacture of sulphuric acid by contact process. **5**
- D. Based on electronic configuration of elements of Group 17, explain their oxidation states and oxidizing power. **5**
- E. Give any two methods of preparation of interhalogen compounds and discuss the structures of (i) XY_3 and (ii) XY_5 type interhalogen compounds. **5**
- F. Explain (i) Protic (ii) aprotic and (iii) amphiprotic solvents with suitable examples. **5**
5. Answer the following:
- A. Select whether the following statements are **true** or **false** (**Any five**) **5**
- Centre of symmetry is denoted by symbol 'i'.
 - The rotational axis C_n for water molecule is 2
 - The axis with the lowest order of symmetry operations is called principal axis.
 - Total number of electrons in NO is 14
 - Operation of doing nothing is called identity operation.
 - Molecular orbitals are regarded as monocentric.
 - Molecular orbitals with lowest energy give rise to antibonding molecular orbitals.
 - In triangular ion, nondegenerate orbitals are labelled as 'a'.
- B. Fill in the blank with appropriate words given in the bracket (**Any five**) **5**
 [zero, above, Schottky, unit cell, two, 0.52, fcc]
- is the fundamental building unit of the crystal.
 - Atomic packing factor in simple cubic cell is.....
 - Number of atoms per unit cell in body centered cubic crystal [bcc] is
 - ABC-ABC. Type packing results in unit cell.
 - Defects occurs in crystal due to cation and anion vacancy is
 - Superconductors has practically electrical resistance.
 - Superconductors whose critical temperature is 77 K are high temperature superconductors.
- C. Select and write the appropriate answer . (**Any five**) **5**
- The elements of actinide series are characterized by the preferential filling of ----- .
 a. 5f orbitals. b. 4s orbitals. c. 5p orbitals. d. 5s orbitals.
 - The ideal electronic configuration of lanthanum is ----- .
 a. $[Xe] 4f^7 5d^1 6s^2$. b. $[Rn] 4f^0 5d^1 6s^2$.
 c. $[Xe] 4f^0 5d^1 6s^2$. d. $[Ar] 4f^0 5d^0 6s^2$.

- c. Decreasing basicity is one of the important consequences of -----
 -.
 a. Lanthanide contraction b. Cracking
 c. Concentration d. Extraction.
- d. Cerium by exhibiting +4 oxidation state attains a stable configuration of -----
 a. $4f^0$ b. $4f^5$ c. $4f^{10}$ d. $4f^1$
- e. The method which involves the adsorption of Ln^{3+} ions on a cation exchange resin followed by preferential elution is -----
 a. spectrophotometric method. b. potentiometric method.
 c. ion exchange method. d. colorimetric method.
- f. An average separation factor reported for the adjacent lanthanides in 15.8 M nitric acid-100% TBP system is -----
 a. 0.5. b. 1.2. c. 1.5. d. 2.5
- g. The lanthanide compound used as catalysts in hydrogenation, dehydrogenation and oxidation reactions is -----
 a. Lanthanum oxides. b. Promethium nitrate.
 c. Samarium oxalate. d. Neodymium sulphate.
- h. The tripositive lanthanide ion that is colourless is -----
 a. Erbium b. Lutecium. c. Holmium d. Promethium.

D. Match the column (Any five).

5

- | | |
|---------------------------------------------|----------------------------|
| a. Acidic solvent | i. levels of acids |
| b. Rhombic sulphur | ii. V_2O_5 |
| c. Contact process | iii. $m + n$ |
| d. Steric number of AB_mE_n | iv. trigonal bipyramid |
| e. XY_5 interhalogens | v. Protionic solvents. |
| f. Metal-ammonia solution | vi. Square pyramidal |
| g. Liquid HF | vii. S8 rings |
| | viii. levels of bases |
| | ix. blue |

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[Total Marks: 100]

Please check whether you have got the right question paper.

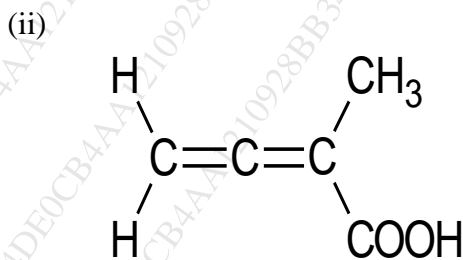
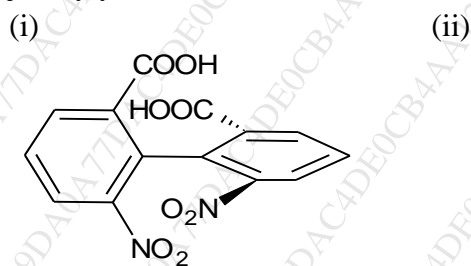
- N.B.**
1. All Questions are compulsory.
 2. Figures to the right indicate full marks.
 3. The use of log-table/non-programmable calculator is allowed.
 4. Answers for the same question as far as possible should be written together.

Q.1 Answer any four of the following:

- A** Explain the following with suitable examples: 5
1. Neighbouring Group Participation
 2. Electrocyclic reaction
 3. Electrophile
- B** Distinguish between 3
- i) Nucleophilicity and Basicity 3
 - ii) Reaction Intermediates and Transition state 2
- C** What are pericyclic reactions? Explain pyrolytic elimination of Xanthate esters and Acetates with suitable examples. 5
- D** Write a reaction for the esterification of acetic acid and explain its mechanism. 5
- E** Distinguish between Singlet and Triplet States. What are forbidden transitions? 5
- F** Write reactions to explain Norrish Type I cleavage of acetone at room temperature. 5

Q.2 Answer ANY FOUR of the following:

- A** Write a note on the following-
- a) Alternating axis of symmetry 3
 - b) Centre of symmetry 2
- B** a) Identify optically active and optically inactive molecules among the following, justify your answers- 3

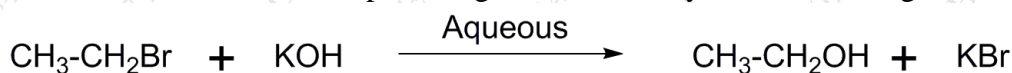


- b) Write the structure of meso-tartaric acid and identify the element of symmetry present in it. 2
- C**
- a) Write a note on biopesticides. 3
 - b) Give synthesis of Endosulfan 2

- D** a) Give advantages and disadvantages of Agrochemicals. **3**
 b) Discuss the action of mixture of fuming HNO₃ and concentrated H₂SO₄ on isoquinoline at 0°C. **2**
- E** Write Bischler- Napieralski synthesis for 1-methyl isoquinoline. **5**
- F** a) Explain: Pyridine-N-oxide gives electrophilic substitutions and nucleophilic substitutions at the same positions. **3**
 b) Write the reaction of following reagents with quinoline. **2**
 (i) alkaline KMnO₄, (ii) peracetic acid

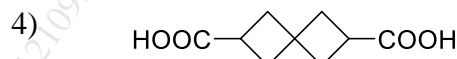
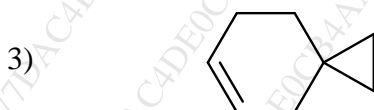
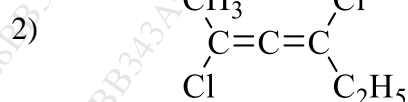
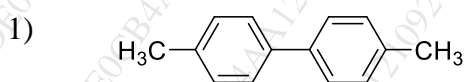
Q.3 Answer any four of the following:

- A** a) Explain Linear synthesis with a suitable example. **3**
 b) State any four principles of Green chemistry. **2**
- B** a) Give any two examples of a Chemoselective reaction. **3**
 b) Give any one use of dimethyl carbonate as a methylating agent in green chemistry. **2**
- C** Define E-factor? Calculate the percentage atom economy of the following reaction. **5**



Atomic Weight: C = 12, H = 1, O = 16, Br = 80, K = 39

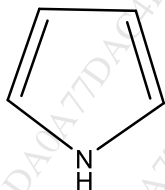
- D** Give the synthesis of the following compounds: **5**
 1) p-bromobenzoic acid from p-aminobenzoic acid
 2) 3-methyl-1-butanol using a suitable Grignard reagent
- E** Write the structural formula for each of the following compounds: **5**
 1. 3-Iodo spiro [4.5] decane
 2. Bicyclo [3.3.0] octane
 3. Bicyclo [2.2.1] heptan-2-one
 4. 2-Ethoxy quinoline
 5. Penta-2,3-diene-1-oic acid
- F** Give IUPAC names for each of the following compounds: **5**



Q.4 Answer any four of the following:

- A** a) Define the following terms used in UV-Visible spectroscopy **3**
 i) Chromophore
 ii) Auxochrome
 iii) Red shift
 b) Explain the effect of solvent on λ_{max} with a suitable example. **2**

- B** a) Explain the mass spectral fragmentation pattern of 2- Methyl but-2-ene. **3**
 b) Give the basic principle of mass spectroscopy. **2**
- C** a) Give the synthesis of adrenaline from catechol. **3**
 b) Define hormones. Give any two functions of adrenaline. **2**
- D** a) What are terpenoids? Give analytical evidence to prove that Citral is an unsaturated terpenoid. **3**
 b) Give analytical evidence to prove that Nicotine has a pyridine ring with a side chain containing $>N-CH_3$ group. **2**
- E** a) Give the synthesis of citral from 6- methyl hept-5-en-2-one. **3**
 b) State and explain Special isoprene rule as applied to Citral. **2**
- F** a) Give the reaction for Hofmann exhaustive methylation and degradation of : **3**

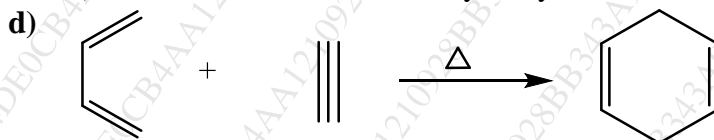


- b) What are the harmful effects of nicotine? **2**
- Q5 A** **Fill in the blanks with the most correct given alternative. Rewrite the completed statements. (Any five)** **5**

- a) To show the movement of a pair of electrons is used.



- b) The term is associated with NGP?
 (saponification; pericyclic reaction; anchimeric assistance; cycloaddition)
- c) The products of Cope elimination are alkene and
 (amine oxide; substituted hydroxyl amine; tertiary amine; amide)



The above reaction is reaction.

(Diel's Alder; Saponification; Claisen; Chugaev)

- e) Group transfer reactions are most closely related to reactions.
 (Electrocyclic; Cheletropic; Cycloaddition; Sigmatropic)
- f) The wavelength of phosphorescence is than fluorescence and has energy.
 (longer, more; longer, lesser; shorter, more; shorter, lesser)
- g) Di- π -methane reaction is an example of photochemical.....
 (reduction; rearrangement; isomerization; elimination)
- h) In photosensitization the energy of the excited state Donor molecule should be the excited state of Acceptor molecule.
 (more than; less than; approximately equal to; identical to)

B **State whether following are True or False- (ANY FIVE)** **5**

- a) Always an optically active compound must contain at least one chiral carbon atom.
 b) In an allene compound, the central carbon atom is sp hybridized.
 c) Indole-3-acetic acid is a plant hormone from auxin class.

- d) Fungicides are the chemicals that destroy, prevent or inhibit the growth of weeds.
 e) Oxidation of pyridine using peracid gives pyridine-N-oxide.
 f) Electrophilic substitution reactions on quinoline take place preferably at positions 5 and 8.
 g) Isoquinoline is also known as 1-azanaphthalene.

C Fill in the blanks (Any five)**5**

- a) In the nomenclature of spirans, the ----- ring is not given the preference.
 b) To name the fused and bridged ring systems the numbering starts from the ----- carbon atom.
 c) Quinolines belongs to the class of condensed ----- compounds.
 d) ----- is the term used when the reactions are carried out by using Ultra sound.
 e) Benadryl is prepared by ----- synthesis.
 f) Alkyl lithium reacts with alkyl halides to form higher -----.
 g) The concept of atom economy was developed by -----.
 h) ----- is an example of a green solvent used in industry for recycling of waste.

Q 5 D Match the following columns (Attempt any five)**5**

| | | | |
|----------|-----------------------------|----------|-----------------------|
| a | Adrenaline | 1 | Odd mass number |
| b | Lemon grass oil | 2 | Quinoline alkaloid |
| c | Amino acid derivative | 3 | Epinephrine |
| d | Quinine | 4 | Citral |
| e | Odd number of nitrogen atom | 5 | Thyroid hormones |
| f | n to π^* | 6 | Tobacco leaves |
| g | Nicotine | 7 | $>C=O$ group |
| | | 8 | Phenanthrene alkaloid |
