St. Aloysius College (Autonomous)
Mangaluru

SEMESTER I- P.G. Examination – M.Sc. Analytical Chemistry
January- 2023
INORGANIC CHEMISTRY

Time: 3 Hrs   Max. Marks: 70

PART – A

1. **Answer any <u>FIVE</u> sub-divisions of the following**   **(5x2= 10)**

   a. The molecules CH_4, NH_3 and H_2O are isoelectronic but have different bond angles. Why?

   b. What are the coordination numbers of metal ions in the crystals of CsCl and ZnS?

   c. Give an example of solvolytic reaction in liq. SO_2.

   d. CsF readily reacts with LiI even though both are ionic. Why?

   e. Electrons in borazine are partially delocalized. Give reason.

   f. Give the topological structure of B_5H_9 and predict its STYX number.

   g. Write the structure of $(NPCl_2)_3$ and mention the hybridization of N and P.

   h. What is Wij's reagent? Mention its significance

PART – B

Answer any <u>FIVE</u> of the following choosing at least one   (5x12= 60) full question from each unit

UNIT-I

2. a. What are Slater's rules? What will be the effective nuclear charge felt by a 2p electron of a nitrogen atom?   (4)

   b. Elucidate the principle upon which lattice energy of an ionic crystal calculated from Born –Haber cycle.   (4)

   c. Discuss why bond strength in a N_2 molecule is greater than that in a F_2 molecule using MO theory.   (4)

3. a. Based on the concept of hybridization, illustrate the shapes of SF_6 and XeF_6 molecules.   (4)

   b. Calculate the minimum radius ratio for trigonal and tetrahedral arrangement.   (4)

   c. Compare and contrast structural features of zinc blend and wurtzite structures of ZnS.   (4)

UNIT-II

4. a. Discuss Pearson's principle of HSAB and any two applications of it. (4)

   b. Which of the following can act as Lewis acid? Explain why? (4)

   i) $CaCl_2$ ii) SO_3 iii) CO_2 iv) Ag^+

   c. Describe the role played by molten salts as non-aqueous solvents. (4)

5. a. Explain the following concepts of acids and bases with suitable examples

   i) Usanovich   ii) Lux-Flood (4)

   b. Discuss briefly the reactions in anhydrous sulphuric acid. (4)

   c. Give an example each for the following reactions in liq. NH_3

   i) Precipitation   ii) Acid-Base iii) Reduction

   iv) Oxidation (4)

UNIT-III

6. a. Discuss the MO theory of B-H-B bonding in boranes. (4)

   b. Explain the structure of boron nitride. How is it similar and different from graphite? (4)

   c. Discuss the utility of Wade's rules in the classification of boranes (4)

7. a. Draw the structure of basic unit in pyroxenes and explain. Mention two examples with formulae. (4)

   b. What are zeolites? Mention the general formula and discuss its role in catalytic and water softening processes. (4)

   c. How is synthesis of dicarbacloso dodecacarborane achieved? Discuss its reactions. (4)

UNIT-IV

8. a. Give one method of preparation of S_4N_4 and discuss its reaction with silver and sodium hydroxide. (4)

   b. Explain the structure of hexachlorotriphosphazene. (4)

   c. Discuss the following

   i) Preparation of hyponitrous acid.

   ii) Structure of H_2SO_4. (4)

9. a. What are interhalogens? Give an example of AX_5 type and explain its geometry. (4)

   b. Give the method of preparation and discuss the structure of I_3^- (4)

   c. Discuss the following

   i) Structure of XeO_2F_2.

   ii) Preparation of any two pseudohalogens (4)

****

St Aloysius College (Autonomous), Mangaluru

SEMESTER I– P.G Examination – M.Sc. Analytical Chemistry

January - 2023

ORGANIC CHEMISTRY

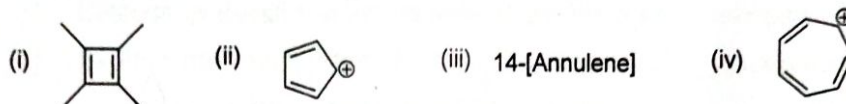Time: 3 Hours   Max. Marks: 70

PART-A

1. **Answer any FIVE subdivisions of the following**   (5x2=10)

a) Classify the following into aromatic, non-aromatic and anti-aromatic compounds.

   (i) [structure]   (ii) [structure]⊕   (iii) 14-[Annulene]   (iv) [structure]⊕

b) Arrange the following in the decreasing order of their acid strengths. Justify the answer.

   CH_3COOH, Cl_3CCOOH, $ClCH_2COOH$, $Cl_2CHCOOH$

c) What are singlet and triplet carbenes?

d) How the mechanism of the clasein rearrangement

e) What is meant by stereo specific and stereo selective synthesis?

f) Assign E/Z configuration to each of the following

   [structures with H, CH₃, H₃C, Cl and Br, Cl, I, H]
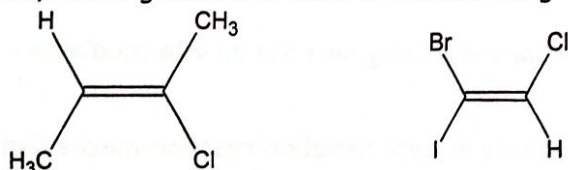
g) Differentiate between configuration and conformation of monosaccharides

h) What is Deoxy sugar? Give example

PART-B

Answer any FIVE of the following choosing at least one   (5x12=60)
full question from each unit:

UNIT- I
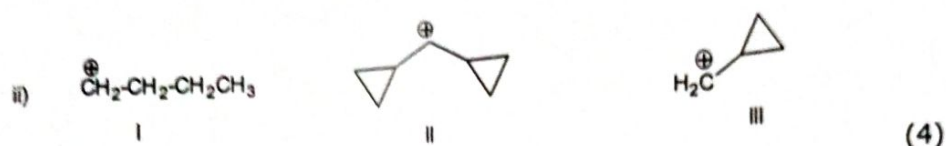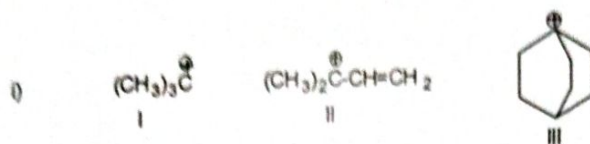
2. a) Apply polygon rule to determine the aromaticity of the following

          (i) Cyclopentadiene anion   (5)

          (ii) Cycloheptatriene cation

    b) Discuss the aromaticity of non-benzenoid compounds.   (4)

    c) Discuss the various factors affecting the strength of organic bases
       taking suitable examples.   (3)

3. a) Explain in detail hyper conjugation and inductive effects by taking
       suitable examples   (4)

    b) Write a note on (i) Catenanes

                       (ii) Fluxional molecules   (4)

    c) Discuss the effect of hydrogen bonding & inductive effect on the
       strength of organic acids   with appropriate examples.   (4)

PH542.1

UNIT II

4. a) Arrange the following carbocations in order of their increasing stability with reasoning

i) $(CH_3)_3\overset{\oplus}{C}$ $(CH_3)_2\overset{\oplus}{C}-CH=CH_2$

   I   II   III

ii) $\overset{\oplus}{CH_2}-CH_2-CH_2CH_3$

   I   II   III   (4)

   b) With suitable examples explain the determination of reaction mechanism by cross over experiments   (4)

   c) Discuss the following

      i) Stereochemical evidences to determine the reaction mechanism   (4)

      ii) Any two reactions involving nitrenes as intermediates

5. a) Explain the following

         i) Kinetic evidences in determination reaction mechanism

         ii) Stability of carbanions   (5)

   b) Explain generation, structure and reactions of arynes   (4)

   c) Predict the product and propose a mechanism for the below reaction

                                                                          (3)
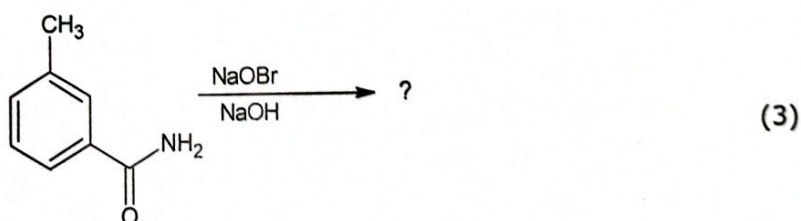
UNIT III

6. a) Describe various methods used for the separation of optical isomers from racemic mixture.   (5)

   b) Discuss the optical activity exhibited by biphenyls and allenes   (4)

   c) Write a brief note on conformational analysis of cyclohexane.   (3)

7. a) Explain cram's rule and Prelog's rule with suitable examples.   (4)

   b) What are the various strategies used in executing a stereoselective synthesis?   (4)

   c) Describe R, S notations used in fixing the positions of groups in an optically active compound   (4)

UNIT IV

8. a) Elucidate the structure of fructose   (4)

    b) Explain how following compounds can be synthesized and discuss
        the   mechanism
        i) Benzoin   ii) Epoxyester   (5)

    c) Predict the product and propose suitable mechanism for the
        following reaction

(3)
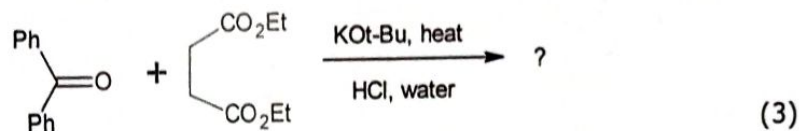
9. a) Discuss in detail the structures of cellulose and glycogen   (5)

    b) Explain the mechanism of Sharpless asymmetric epoxidation and   (4)
        comment on the selectivity of the reaction

    c) Give the mechanism of Stephen reaction   (3)

****

St Aloysius College (Autonomous), Mangaluru

SEMESTER I– P.G Examination – M.Sc. Analytical Chemistry

January - 2023

PHYSICAL CHEMISTRY

Time: 3 Hours   Max. Marks: 70

PART A

1. **Answer any FIVE sub divisions of the following   (5x2=10)**

   a. Write the combined form of first and second law of thermodynamics. Mention its significance.

   b. 133 kg of an aqueous solution containing 0.33 kg of ethylene glycol is cooled to -18°C. If K_f is 1.86 deg mol^{-1}, how much ice will separate out?

   c. Write the role of inhibitor for the reaction of Hydogen and chlorine

   d. Collision theory fails to explain chain reactions. Give reason.

   e. Draw the graph to show the effect of substrate and hence mark V_{max} and K_m.

   f. Depict the behaviour of Langmuir's equation at the limits of low and high pressure.

   g. State and explain Walden's rule.

   h. What is ionic atmosphere? How is the radius of ionic atmosphere determined?

PART B

Answer any FIVE of the following choosing at least one   (5x12=60) full question from each unit:

UNIT-I

2. a. Give the physical significance of entropy and discuss the entropy changes in an ideal gas.   (3)

   b. Discuss the application of third law of thermodynamics for the calculation of absolutè entropies.   (5)

   c. Deduce the van't Hoff equation for osmotic pressure.   (4)

3. a. Define Chemical potential. Derive the expression for variation of chemical potential with temperature.   (4)

   b. What is meant by activity and activity co-efficient of a substance? The activity of 2.5mol of a substance change from 0.05 to 0.35.   (4) What would be the change in its free energy?

   c. Formulate Gibbs-Duhem equation. How do you evaluate the activity coefficient of a component using Gibbs-Duhem equation?   (4)

UNIT-II

4. a. Discuss the Hinshelwood modification of unimolecular theory   (4)

   b. Explain the mechanism of oscillatory reactions with a suitable example.   (4)

   c. Discuss the variation in the rate constant of an ionic reaction with ionic strength of the solutions.   (4)

PH543.1

5. a. Obtain the expression for rate constant of reversible reactions which are first order in both directions. (6)

   b. Discuss the Hammett equation and the Taft equation. (6)

UNIT-III

6. a. State the postulates of B.E.T. adsorption isotherm. Discuss the application of this isotherm in determination of surface area. (8)

   b. Write a note on semiconductor catalysis. (4)

7. a. Discuss the kinetics of unimolecular surface reaction (4)

   b. Outline the kinetics of acid base catalysis using prototropic mechanism. (4)

   c. At 0°C and 1 atm pressure, the volume of nitrogen gas required to cover a sample of silica gel, assuming Langmuir monolayer adsorption, is found to be 130 cm^3g^{-1} of the gel. Calculate the surface area per gram of silica gel. Given that the area occupied by a nitrogen molecule is 0.162 $(nm)^2$ (4)

UNIT-IV

8. a. Discuss the Debye-Huckel theory of mean ionic activity coefficients. Derive the Debye Huckel limiting law. (8)

   b. Draw and discuss the phase diagram of water system. (4)

9. a. Calculate ionic strength of a solution containing 1M Na_2SO_4 and 0.5M NaCl. (4)

   b. Discuss Bjerrum theory of ion association. (4)

   c. Describe the Debye Huckel theory of strong electrolytes. (4)

****

St Aloysius College (Autonomous)
Mangaluru
SEMESTER I – P.G. Examination –M.Sc. Analytical Chemistry
January - 2023
PRINCIPLES OF ANALYTICAL CHEMISTRY AND SEPARATION TECHNIQUES

Time: 3 Hours   Max. Marks: 70

PART - A

1. **Answer any <u>SEVEN</u> sub-divisions of the following:**   (7 x 2 =14)

a) A chemist determined the percentage of iron in an ore and obtained the following results: Mean: 12.31, standard deviation = 0.10 and n = 4 Calculate the 90% confidence interval of the mean. (Table value = 2.35)

b) Differentiate between gross sample and laboratory sample.

c) Give the importance of digestion of precipitates in Gravimetric Analysis.

d) Give two examples for metallochromic indicators and draw their structures.

e) Differentiate between masking and unmasking agents.

f) Justify why in the titration of HCl with NaOH, the pH at equivalence point is 7.0, but when acetic acid is titrated with NaOH, the pH at equivalence point is greater than 7.0

g) In the extraction of Ce(IV) with 2-thenoyl trifluroacetone in benzene, the distribution ratio was 999. If the volume of organic phase was 20ml and that of aqueous phase was 50ml, calculate the percentage extraction.

h) Mention any two advantages of using H_2 as carrier gas in GC.

i) Why is guard column used in HPLC?

PART – B

Answer any <u>FOUR</u> of the following choosing atleast (4 x 14 = 56) one full question from each unit

UNIT – I

2. a) Explain how determinate errors are detected and minimized.   (5)

   b) Write a note on precipitation from homogenous solution.   (5)

   c) Write a note on sampling of liquids   (4)

3. a) Differentiate between co-precipitation and post-precipitation   (3)

   b) Explain the mechanism of precipitation in gravimetric analysis   (4)

   c) Explain the steps to be taken for obtaining a representative sample   (3)

   d) In a set of measurements, the following concentrations of Fe (ppm) were reported: 202, 20.4, 20.3, 20.1, 19.9, 20.0 and 19.8 Calculate i)Average deviation (ii) Standard deviation (iii) Relative standard deviation (iv) Coefficient of variation   (4)

UNIT – II

4. a) Construct a titration curve when 25ml of 0.1M Maleic Acid is
        titrated against 0.1M NaOH.   (5)

    b) Write a note on types of EDTA titrations   (5)

    c) Write the analytical applications of permanganate titrations   (4)

5. a) Construct a titration curve for 50ml of 0.05M Fe^{2+} with 0.1M
        Ce^{4+} solution in presence of 1M H_2SO_4 (5)

    b) Write a note on determination of water hardness through
        complexometric titrations   (5)

    c) Distinguish between absolute formation constant and
        Conditional formation constant   (4)

UNIT-III

6. a) Explain the application of Ion-exchange chromatography in
        de-mineralization of water   (5)

    b) Explain batch extraction of mixtures with Active Solvents in
        detail   (5)

    c) Outline the working principle of electron capture detector used
        in GC. List any two of its advantages over other detectors.   (4)

7. a) Write the applications of HPLC   (5)

    b) Explain the factors affecting Ion-exchange capacity   (5)

    c) Explain the effects of salting out and masking agents in the
        process of solvent extraction   (4)

****

PS 546.1   Reg No:. ☐☐☐☐☐☐

St Aloysius College (Autonomus)
Mangaluru
SEMESTER I –PG Examination –M.Sc. Analytical Chemistry
January - 2023
RESEARCH METHODOLOGY

Time: 3 hours   Max. Marks: 70

PART – A

1. **Answer any <u>SEVEN</u> sub-divisions of the following:**   (7 x 2 = 14)

a) Highlight on importance of research.

b) What is abstract? Give its significance.

c) What is H-index? Mention one way to improve researcher's H-index.

d) Provide a method to safely store hazardous chemicals.

e) Mention the importance of reuse of laboratory chemicals.

f) Give an insight on transportation of hazardous chemicals.

g) Whether intellectual honesty is necessary? Justify your answer.

h) What is patent? Differentiate between patent publication and grant.

i) If someone copies your company logo which has been secured under IPR. Which form of IPR violation does he make and why?

PART – B

Answer any <u>FOUR</u> of the following choosing at least one (4x14=56)
full question from each unit:

UNIT – I

2. a) What is research? Describe the objectives and characteristics of research.   (5)

   b) Discuss the points to be observed while selecting the research problem.   (5)

   c) Differentiate between review article and original article.   (4)

3. a) Correlate concept of theory and theory building methods.   (5)

   b) What is literature review? Explain the sources for literature review.   (5)

   c) Give an elaboration on use of search engines and databases.   (4)

UNIT – II

4. a) Describe the Safe working procedure and protective environment.   (5)

   b) Write a note on procedures for working with gases at above or below atmospheric pressures   (5)

   c) Explain the method involved in disposal of chemicals in the sanitary sewage systems.   (4)

5. a) What are the steps to be taken while working with substances that pose hazards, flammable or explosive hazards?

    (5)

    b) Explain the process involved in recovery and recycling of waste chemicals.

    (5)

    c) What is incineration? Mention briefly this process of handling waste chemicals

    (4)

UNIT – III

6. a) Explain scientific conduct of ethics with respect to science and research.   (5)

    b) Write a note on origin and development of IPR.   (5)

    c) Differentiate between plagiarism and self-plagiarism.   (4)

7. a) Explain the various guidelines implemented by UGC to control plagiarism in various forms.   (5)

    b) How is falsification different from fabrication of scientific data? Explain.   (5)

    c) Write any four forms of IPR with suitable example.   (4)

****