PH 541.1

Reg. No. | | | | | | |

St Aloysius College (Autonomous)

Mangaluru

Semester I – P.G. Examination - M.Sc. Analytical Chemistry

February - 2022

INORGANIC CHEMISTRY

Time: 3 Hours **Max. Marks: 70**

PART – A

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

a. State Bents rule.

b. Define Radius ratio. What is its significance?

c. Write the autoionisation reaction for sulphur dioxide.

d. Li_2O is more stable than Cs_2O: Justify using HSAB concept

e. STYX number of tetraborane(10) is 4012. Justify

f. Give one method of preparation of borazine

g. XeF_6 cannot be stored in glass vessels. Justify the answer.

h. Give reason:Interhalogen compounds are diamagnetic in nature.

PART – B

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

UNIT-I

2. a) Explain the geometry of ClF_3 molecule using VSEPR theory and justify its geometry. **(3)**

b) Explain the postulates of Fajan's rule and explain how these rules help in predicting covalent character in ionic bonds. **(4)**

c) Construct a Molecular orbital diagram for O_2 molecule and predict its bond order and magnetic property. Also comment on the stability of O_2^+ , O_2^- and O_2^{2-} ions. **(5)**

3. a) Derive Born-Lande Equation. **(5)**

b) Explain the structure of NaCl and calculate the number of Na^+ and Cl^- in the unit cell. **(3)**

c) Construct a molecular orbital diagram for CO and calculate its bond order. **(4)**

UNIT – II

4. a) Arrange the halides of boron in the increasing order of their acid strength. Explain the observed trend. **(4)**

b) What are super acids? How is their acidic strength measured? **(4)**

c) Explain Levelling and differentiating solvents. **(4)**

Contd...2

5. a) Explain Drago-Wayland equation for the Lewis acid-base interactions. (4)

b) Give HSAB principle and comment on the feasibility of the reaction : $ZnO + 2\,LiC_4H_9 \rightleftharpoons Zn(C_4H_9)_2 + Li_2O$ (4)

c) Explain complexation reactions in liquid ammonia. (4)

UNIT – III

6. a) Give the method of preparation of silicones (3)

b) Explain the similarity and differences between pyroxenes and amphiboles. (3)

c) Classify the following boranes and carboranes and justify

(i) $B_8H_{13}^-$ (ii) $B_7H_{10}^-$ (iii) B_4H_8 (iv) $C_2B_2H_7^-$

(v) $C_2B_9H_{11}$ (vi) $C_2B_4H_{10}$ (6)

7. a) Explain the similarity and differences between benzene and borazine. (4)

b) What are Zeolites? Outline their applications. (4)

c) Explain the molecular orbital concept of 3 centre 2 electron bonds in boranes. (4)

UNIT – IV

8. a) Discuss the geometry of I_3^- (3)

b) Explain the preparation and structure of S_4N_4.How is it converted to Polythiazyl? (5)

c) Discuss the geometries of XeF_6 and XeO_3. (4)

9. a) Give the order of oxidizing power of oxyacid's of chlorine? Justify the observed trend (3)

b) Write a short note on:

(i)Polyhalide ions (ii)Linear Polyphosphazenes (5)

c) Discuss the preparation and applications of condensed phosphates. (4)

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Semester I – P.G. Examination - M.Sc. Analytical Chemistry
February – 2022
ORGANIC CHEMISTRY

Time: 3 Hours **Max. Marks: 70**

PART - A

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

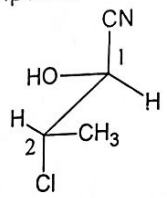
a) What are crown ethers? Give any application of the crown ethers.

b) State whether the following statement is true or false. Justify your answer. In case of 2-bromocyclohexanone, the axial form is more polar than the equatorial form.

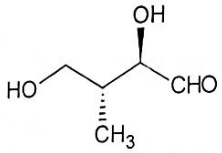
c) What are enamines? Give a method for the preparation of enamines.

d) $:CH_2$ is a triplet carbene whereas $:CCl_2$ is a singlet carbene – why?

e) Assign R/S configuration at the chiral carbons (C1 & C2) in the following compound



f) Write the Fischer and Newman projections of the following stereoisomer.



g) What are deoxysugars? Give example.

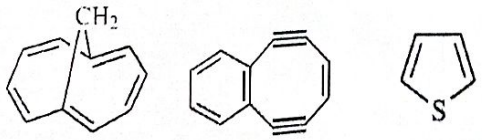
h) Define Chichibabin reaction with example.

PART - B

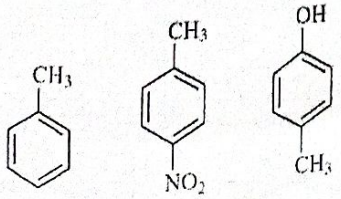
Answer any FIVE of the following choosing at least one full question from each unit: **(5x12=60)**

UNIT - I

2. a) Discuss the aromatic character of following compounds



b) Assign the correct dipole moment values of 1.57, 0.43 and 4.39 to the following molecules. Justify your answer.



Contd...2

c) Explain any two factors affecting the acid strength of organic compounds.

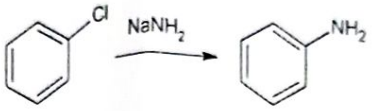
(6+3+3)

3. a) Explain the following with suitable examples.
   i) Homoaromaticity ii) Hyperconjugation
   b) Discuss the different types of proton shift tautomerism in organic compounds.
   c) Arrange following in the order of their base strength. Justify your answer.
   Pyridine, Aniline, Pyrrole.

(5+4+3)

UNIT - II

4. a) Discuss the structure and stability of sulfur and phosphorous ylides.
   b) Explain the stereochemical features of reactions involving carbene intermediates.
   c) How the mechanism of the following reaction is determined using labelling experiments?



(5+4+3)

5. a) Give any two methods for the generation of nitrenes.
   b) What are kinetic studies? Explain their significance in the determination of reaction mechanism.
   c) Explain any two reactions of Aryne.

(4+4+4)

UNIT - III

6. a) Discuss the optical activity in allenes and spiranes.
   b) What is asymmetric synthesis? Illustrate any one method of asymmetric synthesis.
   c) Explain Cram's rule with an example.

(4+4+4)

7. a) Explain any two methods of resolution of racemic mixtures.
   b) Differentiate between stereoselective and stereospecific reactions with suitable examples.
   c) Write a note on conformational analysis of decalins.

(5+4+3)

UNIT - IV

8. a) Briefly explain the following
   i) Amino sugars ii) Ketals
   b) Write a note on
   i) Wittig Reaction – Mitsunobu reaction
   ii) Cannizaro reaction
   c) Explain Buchener reaction with mechanism.

(4+4+4)

9. a) Briefly explain the following
   i) Stork Enamine reactions ii) Ullmann Reaction
   b) Explain Duff reaction with mechanism.
   c) Explain sharpless asymmetric epoxidation.

(4+4+4)

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St Aloysius College (Autonomous)
Mangaluru

Semester I – P.G. Examination - M.Sc. Analytical Chemistry

February - 2022

PHYSICAL CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

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

a) A sample containing 2.25 moles of He (1 bar, 298 K) is mixed with 3 mol of Ne (1 bar, 298K) and 1.75 mol of Ar (1 bar, 298 K). Calculate Gibbs free energy of mixing.

b) Write combined form of First and Second law of thermodynamics. Give its significance.

c) What is consecutive reaction? Give an example.

d) Depict the effect of ionic strength on rate of ionic reaction.

e) Give any two differences between enzyme catalysis and general heterogeneous catalysis.

f) Write Herkin-Jura equation. Why is it used?

g) If concentration of $Al_2(SO_4)_3$ is x mol kg^{-1}, then what will be the ionic strength of the solution?

h) Determine the number of components, number of phases and degrees of freedom for $H_2O_{(s)} \leftrightarrow H_2O_{(l)} \leftrightarrow H_2O_{(g)}$.

PART - B

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

UNIT - I

2. a) Deduce the expression of Gibbs-Helmholtz equation **(4)**

b) Derive Duhem-Margules equation **(4)**

c) Discuss the determination of third law of entropies. **(4)**

3. a) Explain the thermodynamics of depression in freezing point and deduce the expression of molar depression constant. **(6)**

b) Give detailed account on activity, activity coefficient and choice of standard states **(6)**

UNIT - II

4. a) Obtain an expression for rate constant for a reaction in which a first order reaction is opposed by first order in terms of equilibrium concentrations. **(4)**

b) Explain the effect of solvent on rate of ionic reaction. **(4)**

Contd...2

c) Write a note on collision theory. (4)

5. a) Discuss the Hammett relationship and derive Hammett equation. (6)

b) Outline the kinetics of branched chain reaction. Explain upper and lower explosion limits. (6)

UNIT - III

6. a) What are general and specific acid-base catalysis. Discuss protolytic and prototropic mechanism of acid-base catalysis. (8)

b) Discuss Langmuir's unimolecular theory of adsorption and deduce the expression of Langmuir adsorption isotherm. (4)

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

b) Explain the activation energies for catalysed reactions forming Arrhenius and van't Hoff intermediates. (4)

UNIT - IV

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

b) Draw and discuss the phase diagram for a three-component system consisting of two solids A, B and water. (4)

9. a) Discuss Bjerrum theory of ion association. (4)

b) Give an account of the Debye-Huckel theory of strong electrolytes. (4)

c) Draw and discuss the phase diagram of Ag/Pb system (4)

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

February - 2022

PRINCIPLES OF ANALYTICAL CHEMISTRY & SEPARATION TECHNIQUES

Time: 3 Hours **Max. Marks: 70**

PART - A

1. **Answer any SEVEN sub-divisions of the following:** **(7x2=14)**

a) Differentiate between absolute and relative error.

b) What are the advantages of using organic precipitants in inorganic analysis?

c) Mention the significance of Q-test.

d) Write the correct order for the following stepwise formation constants and justify your answer.

K_1, K_2, K_3, K_4

e) What is the mechanism behind the colour change of phenolphthalein indicator?

f) Draw a titration curve for Metal-EDTA titrations and explain.

g) How does the pH affect the process of solvent extraction?

h) Compare and contrast GSC and GLC.

i) Define i) selectivity factor ii) column resolution

PART – B

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

UNIT- I

2. a) State 't' test. What are its practical advantages? Discuss the scope and limitations of 't' in the presentation of data. **(5)**

b) What are determinate and indeterminate errors? How can they be minimized? **(5)**

c) Explain the concept of 'precipitation from homogeneous solution' with an example. **(4)**

3. a) Outline the different methods involved in the sampling of solids and liquids. **(5)**

b) Analyses of a sample of ore gave the percentage of iron as 7.08, 7.21, 7.12, 7.09, 7.16, 7.14. Calculate the mean, standard deviation and coefficient of variation of the values. **(5)**

c) Explain the terms 'co-precipitation' and 'post-precipitation'. **(4)**

Contd...2

UNIT- II

4. a) Give an account of factors affecting the shape of redox titration curves. How is the feasibility of redox titration predicted? **(5)**

   b) Justify using suitable examples that the complexes formed from chelating ligands are more stable than non-chelating ligands. **(5)**

   c) Discuss the theory of metal ion indicators in 1:1 complexometric titration. **(4)**

5. a) What are masking and demasking agents? Discuss their importance in quantitative estimation with illustrative examples. **(5)**

   b) Explain the titration curve for acetic acid with sodium hydroxide. Why methyl orange cannot be used as an internal indicator for the above titration? **(5)**

   c) Define redox titration. Discuss the mechanism behind the color change of ferroin indicator in the titration of Fe^{2+} against Ce^{4+}. **(4)**

UNIT- III

6. a) Describe the application of ion exchange chromatography techniques in the following

      i) Separation of lanthanides.

      ii) Softening of hard water. **(5)**

   b) Sketch the block diagram of GC instrument and explain its mode of working. **(5)**

   c) Explain in detail the factors affecting the solvent extraction. **(4)**

7. a) Write a note on principle and applications of LC-MS. **(5)**

   b) How do you develop a method for separation of components in column chromatography? Explain in detail. **(5)**

   c) Discuss the principle and working of thermal conductivity detectors used in gas chromatography. **(4)**

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

February - 2022

RESEARCH METHODOLOGY

Time: 3 Hours **Max. Marks: 70**

PART - A

1. **Answer any SEVEN sub-divisions of the following:** **(7x2=14)**

a) Mention any 2 objectives of research.

b) What is "Impact Factor"?

c) Define "Ontology".

d) What is compressed gas? Give an example.

e) Briefly explain incineration of chemical waste.

f) What is corrosive chemical waste? Give an example.

g) Define ethics and describe why it is important in research methodology.

h) What are intellectual properties? Provide any two examples in the field of science.

i) What is an erratum? What is the significance of erratum?

PART – B

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

UNIT- I

2. a) What is the significance of digital search engines used in Literature Review? **(4)**

b) Define the term "Research Problem"? What are the sources of research problem? **(5)**

c) Explain the types of Research. **(5)**

3. a) What are the factors to be considered while selecting a research problem? **(4)**

b) What is literature review? What are the characteristics of a good quality literature review? **(4)**

c) Explain the types of theory building. **(6)**

UNIT- II

4. a) Write a note on MSDS. **(4)**

b) Describe the recovery, recycling and reuse of laboratory chemicals. **(4)**

Contd...2

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c) Explain the procedure for the laboratory disposal of the explosives. (6)

5. a) Give the guidelines for safe storage and use of hazardous chemicals. (5)

b) Describe the protective apparel used for safe handling of chemicals. (4)

c) What are the first aid procedures to be followed in case of laboratory emergencies? (5)

UNIT- III

6. a) How can we differentiate morality and ethics? (5)

b) Describe factors leading to the unethical conduct of research. (5)

c) What are ethical responsibilities of a researcher? (4)

7. a) What are the major differences between falsification and fabrication? Explain how they are different from plagiarism. (5)

b) What are the rationales for protecting intellectual property rights? (4)

c) Define and compare the 5 different forms of intellectual properties on the basis of duration of protection of rights, their renewal and the ruies/acts behind their implementation. (5)

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