Reg. No:

# St Aloysius College (Autonomous)
## Mangaluru
### Semester I – P.G. Examination - M. Sc. Analytical Chemistry
#### February 2021

# INORGANIC CHEMISTRY

Time: 3 Hours

Max. Marks: 70

**Answer any FIVE questions. Each questions carries 2 marks** (5×2=10)

1. a) Justify whether the two iodine-iodine bond lengths in triodide ion are equal.

   b) State radius ratio rule and give any two applications.

   c) Among $AsH_3$ and $H_2Se$, which is a stronger acid? Why?

   d) Explain with one example Drage-Waylend equation.

   e) Write a note on zeolites as molecular sieves.

   f) Assign the STYX number $B_{10}H_{14}$. Mention the types of bonds involved in it.

   g) Which of the following has a higher melting point? NaCl and $AlCl_3$. Give reasons.

   h) Justify that interhalogens are more reactive that the parent halogens.

**Answer any FIVE questions choosing at least one question from each unit.**
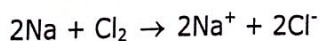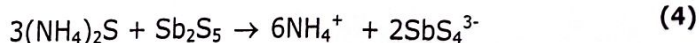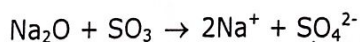
(5×12=60)

## UNIT I

2. a) Construct a molecular orbital diagram for $O_2$ molecule and predict its bond order and magnetic property. Also predict the order of stability of $O_2^+$, $O_2^-$ and $O_2^{2-}$. **(4)**

   b) State and explain Fajan's rules. Identify most covalent and most ionic alkali metal halides. **(4)**

   c) Compare the solubilities of NaCl and KCl. Justify that $BaCl_2$ is soluble in water but $BaSO_4$ is not. **(4)**

### OR

3. a) Derive Borne Landes equation. **(6)**

   b) Calculate the effecrive nuclear charge on a 3d electron of Cu(Z=29) by using Slaters rules. **(3)**

   c) Explain the molecular orbital description for $BeH_2$ molecule. **(3)**

## UNIT II

4. a) Explain solvent system of acids and bases by taking ammonia and acetic acid as solvents. **(4)**

   b) Outline the applications of HSAB concept. **(4)**

   c) Explain Usanovich theory of acids and bases. Based on the theory classify the reactants in the following reaction into acids and bases. Justify.

$$Na_2O + SO_3 \rightarrow 2Na^+ + SO_4^{2-}$$

$$3(NH_4)_2S + Sb_2S_5 \rightarrow 6NH_4^+ + 2SbS_4^{3-}$$

$$2Na + Cl_2 \rightarrow 2Na^+ + 2Cl^-$$

**(4)**

### OR

5. a) Explain leveling and differentiating solvents. **(4)**

b) Outline the complex formation reactions ammonia and sulphur dioxide solvents.

(4)

c) What are super acids? Explain their preparation.

(4)

## UNIT III

6. a) Classify the following boranes by their structural type
   i) $B_3H_3^{-2}$   ii) $B_3H_9$   iii) $B_5H_{11}$   iv) $B_8H_{10}$   v) $B_6H_{14}$

(5)

   b) Discuss the molecular orbital description for the 3 centre 2 electron bonds boranes.

(4)

   c) Give the preparation of linear and cross linked silicone polymers.

(3)

### OR

7. a) What are pyroxenes and amphiboles? Explain their structures.

(4)

   b) Differentiate between borazine and benzene with respect their chemical properties.

(4)

   c) Explain the Wades rules for the classification of boranes and carboranes.

(4)

## UNIT IV

8. a) Explain the geometries of $XeO_3$ and $XeF_4$.

(4)

   b) Explain the structures of $S_4N_4$ and $(SN)_x$.

(4)

   c) Name the allotropic forms of sulphur. Explain the anomalous features exhibited by liquid sulphur.

(4)

### OR

9. a) Comment on the stability and acidic strength of oxoacids of halogens.

(4)

   b) Discuss the structure and preparation of cyclic phosphazine with an example.

(4)

   c) Discuss the following:
   i) Geometry of $I_3^-$
   ii) Any two methods of preparation of metaphosphoric acid.

(4)

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### February 2021
# ORGANIC CHEMISTRY

Time: 3 Hours

Max. Marks: 70

## PART - A

(5x2=10)

1. **Answer any FIVE sub divisions of the following:**

a) What are bifurcated hydrogen bonds? Give an example.

b) Comment on the aromaticity of 1,6-methano[10]annulene.

c) What are non-classical carbocations? Give an example.

d) How the mechanism of the following reaction can be determined using labelling experiments?
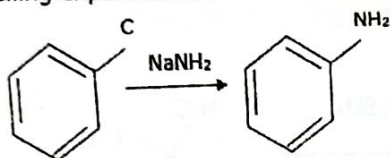
e) Assign the stereochemical relationship between following set of compounds (A, B and C).
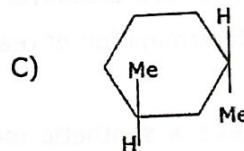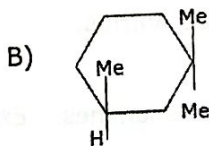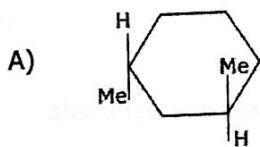


f) What are atropisomers? Give an example.

g) What is muta rotation? Give an example.

h) Give a method to convert glucose into glucaric acid.

## 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 structural factors favoring the enol form in keto-enol tautomers. (4)

b) What are super acids? How are they prepared? Give any two synthetic applications of super acids. (4)

c) Comment on the aromaticity of following compounds (4)



Contd...2
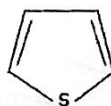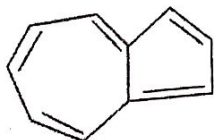
3.a) Arrange the following compounds in the increasing order of their acid strength. Justify your answer.

Phenol, p-Nitrophenol, p-Cresol, m-Chlorophenol                                      (4)

b) Explain the following with suitable examples.

i) Hyper-conjugation                ii) Anti-aromatic compounds.                       (4)
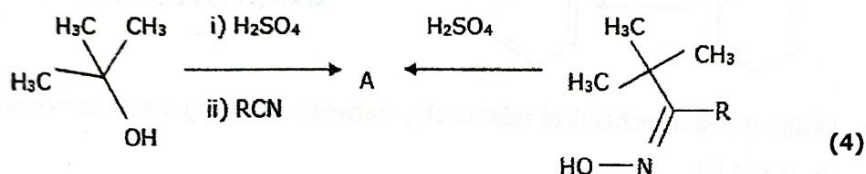
c) Arrange the following oxyanions in the increasing order of the base strength. Justify your answer.

$CH_3O^-$, $CH_3CO_2^-$, $PhO^-$, $(CH_3)_3CO^-$                                      (4)

## UNIT - II

4.a) Differentiate between singlet and triplet carbenes in terms of their structure and stability.                                                          (4)

b) Following two reactions give the same product (A), why? Write the structure of A and reaction mechanisms.



(4)

c) What are crossover experiments? Illustrate their application in the determination of reaction mechanisms.                                           (4)

5.a) Give a synthetic method for enamines. Explain any one synthetic application of enamines.                                                         (4)

b) Give any two methods for the preparation of nitrenes and illustrate their reactivity.                                                            (4)

c) Explain how the stereochemical evidences can be utilized to predict $S_N1$ and $S_N2$ mechanisms.                                               (4)

## UNIT - III

6.a) Write the Newman and Fischer representations of D-erythrose and L-threose.                                                                    (4)

b) Explain the optical activity in biphenyl derivatives.                             (4)

c) Explain the general methods for the determination of configuration of geometrical isomers.                                                       (4)

7.a) Write the Fischer projection formula of the following and assign R/S configuration at the chiral carbons.



(3)

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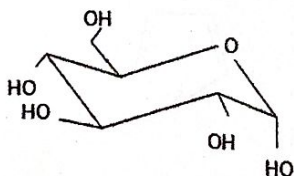
b) Explain any two methods of resolution of racemic mixtures. (5)

c) What is asymmetric synthesis? Explain the chiral auxiliary methods of asymmetric synthesis. (4)

## UNIT - IV

8.a) Write a note on acetal derivatives of monosaccharides. (4)

b) Briefly explain the structural elucidation of lactose. (4)

c) Explain Smith degradation of polysaccharides. (4)

9.a) Discuss ascending sugar series with a suitable example. (4)

b) Outline the conversion of D(+) glucose into D(+) mannose. (4)

c) Briefly explain the structure of cellulose. (4)

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### Semester I – P.G. Examination – M.Sc. Analytical Chemistry
#### February 2021
## PHYSICAL CHEMISTRY

Max. Marks: 70

Time: 3 Hours

### PART - A                                (5x2=10)

1. Answer any **FIVE** sub divisions of the following:

a) Under what special circumstances does $\Delta S = \Delta H/T$?

b) Why is third law of thermodynamics useful?

c) What is a pseudo-first-order rate constant? How do its dimensions differ from those of a second-order rate constant?

d) Why are chain mechanisms so common when species with unpaired electrons (such as H, Br, $CH_3$) are generated in an initiation step?

e) How does chemisorption differ from physisorption?

f) What is the effect of temperature on enzyme calaysed reaction?

g) Calculate the eutectic temperature and eutectic composition for a binary solid-liquid system if $\Delta H_{fus,A}$ =500 cal $mol^{-1}$ , $\Delta H_{fus,B}$ =1000 cal $mol^{-1}$ and the melting points of pure A and B are 400°C and 600°C respectively.

h) Calculate the mean ionic activity coefficient of NaCl at a molality of 0.01 in aqueous solution at 25°C.

### PART - B

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

### UNIT – I

2.a) Explain the variation of free energy with temperature and pressure by deriving suitable mathematical expressions.                    (6)

b) One mole of solid gold is raised from 25°C to 100°C at constant pressure. Cp (J/K mol) = 23.7 + 0.00519T. Calculate $\Delta S$ for the transformation.                    (3)

c) Derive the thermodynamic equations of state.                    (3)

3.a) Give detailed account on Maxwell's relations.                    (6)

b) Deduce the expression of Gibbs-Helmholtz equation. Discuss its two applications.                    (6)

### UNIT – II

4.a) Discuss the kinetics of reversible reaction with an example.                    (6)

b) Explain the effect of ionic strength on the reaction rates in solutions.                    (6)

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5.a) Give the comparisons between collisions theory and activated complex theory. (4)

b) Derive the equation for primary salt effect. (4)

c) Explain how flow methods useful to study fast reactions. (4)

## UNIT – III

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

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

7.a) State 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 catalyzed reactions forming Arrhenius and Van't Hoff intermediates. (4)

## UNIT – IV

8.a) Discuss the Debye-Huckel limiting law for strong electrolytes. (6)

b) Derive Debye-Huckel-Onsagar equation. (6)

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

b) Describe the effect of viscosity of the liquid on molar ionic conductance. (4)

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

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# St Aloysius College (Autonomous)
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### Semester I – P.G. Examination - M. Sc. Analytical Chemistry
### February 2021

## PRINCIPLES OF ANALYTICAL CHEMISTRY AND SEPARATION TECHNIQUES

Time: 3 Hours                                                     Max. Marks: 70

1. Answer any **SEVEN** subdivision of the following          $(7 \times 2 = 14)$

    a) Explain the significance of Q-Test.

    b) Mention the importance of nucleation step in precipitation.

    c) Mention the classification of chromatographic methods.

    d) What are chelating ligand? Give examples.

    e) Distinguish direct and displacement titration.

    f) A 50ml sample of drinking water was buffered at pH 10.0 and after the addition of an EBT indicator titrated with 16.5ml of 0.01M EDTA solution. Calculate the hardness of water as ppm $CaCO_3$ (mol.wt of $CaCO_3 = 100$

    g) Explain the principle of gas chromatography.

    h) What is redox titration? Give example.

    i) What are masking and demasking agents in complexometric titration.

Answer any **FOUR** questions choosing at least one question from each unit.          $(4 \times 14 = 56)$

### UNIT I

2. a) Explain the different methods of minimizing the determinate error.          **(4)**

    b) An analyst has reported the following percentage of FeO in a sample. 16.65, 16.70, 16.68, 16.60, 16.58, and 16.63 for set of results. Calculate mean, median, range, average and standard deviation.          **(5)**

    c) Explain the condition for precipitation.          **(5)**

3. a) Discuss normal error distribution curve and explain the salient features.          **(5)**

    b) Discuss the advantages of organic precipitants in inorganic ion analysis.          **(5)**

    c) Mention the significance of fractional precipitation in gravimetric analysis.          **(4)**

### UNIT II

4. a) Explain the quinanoid theory of acid base indicator. Explain the changes in color that occurs when disodium salt of phenolphthalein becomes trisodium salt.          **(5)**

    b) What is Karl fisher reagent? Illustrate the application in the determine the traces of water in organic solvent.          **(5)**

    c) Why EDTA titration are called complexometric titration? Explain the indicator action of metallochromic indicator.          **(4)**

5. a) Discuss the application of acid-base titration in non- aqueous solvents with respect of carboxylic acids and amines.          (4)

   b) Discuss the theory of redox indicators. Describe the indicators action of diphenylamine with relevant structural chemistry.          (5)

   c) Discuss the application of EDTA titration in the determining of Zn, Mg and Pb in the mixture.          (5)

## UNIT III

6. a) Classify the chromatographic technique based on the mechanism of separation and explain their principle.          (5)

   b) Discuss how pH, oxidation states and modifiers affect the extraction process.          (4)

   c) Describe the application of ion exchange chromatography in a purification process.          (5)

7. a) With a neat schematic diagram, explain the principle and working of HPLC.          (4)

   b) Explain the working of electron capture and flame ionization detector used in GC.          (4)

   c) What is rf value? Explain the factor affecting rf-value.          (3)

   d) Mention the factor affecting solvent extraction.          (3)

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