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St Aloysius College (Autonomous)
Mangaluru
Semester I- P.G Examination - M. Sc. Analytical Chemistry
November - 2019

INORGANIC CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **FIVE** sub-divisions of the following: (2x5=10)
- Calculate the number of Zn^{2+} and S^{2-} ions in a unit cell of ZnS.
 - Among CaF & CaO which is more soluble in water? Justify using the concept of lattice energy.
 - Why is magic acid superacid?
 - Electron affinity of S is more than that of O: Justify.
 - Give the STYX number of B_5H_9 .
 - Why is Borazine called inorganic Benzene: Justify.
 - Interhalogens are more reactive than halogens: Justify.
 - Why XeF_6 cannot be stored in glass vessels? Justify with equation.

PART - B

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

UNIT- I

2. a) Explain Ion dipole & ion induced dipole interactions. Justify the order of stability of polyhalide ions X_3^- . (4)
- b) Using a Born-Haber cycle, calculate the lattice energy for NaBr(s), given the following data:
- Sublimation energy for Na(s)=108kJ/mol
 Heat of vaporization for Br_2 =30.91kJ/mol
 First ionization energy for Na(g)=496kJ/mol
 bond energy for $Br_2(g)$ =192.8kJ/mol
 electron affinity for Br(g)=-324kJ/mol
 enthalpy of formation of NaBr(s)=-360kJ/mol (4)
- c) Give reasons:
- AgI_2^- complex is stable but AgF_2^- is not.
 - CH_3F & CHF_3 react to form CH_4 & CF_4 (4)
3. a) Justify the following:
- Ionic radii of coinage metals (4)
 - Zr & Hf, Y & La has same ionic radii (4)
- b) The internuclear distance in KCl is 3.44\AA . Calculate the radii of K^+ & Cl^- ions. (4)
- c) Draw the MO diagram of CO & F_2 (4)

Contd....2

4. a) Give reactions to represent autoionisation reactions of liq NH_3 & liq SO_2 & and give any two advantages of these solvents. (4)
- b) What are Lewis acids & bases? Arrange the following in the order of decreasing strength
 i) NH_3 , PH_3 , SbH_3 ii) NH_3 , NCl_3 , NF_3 iii) Fe^{3+} , Ag^+ , Fe^{2+} (4)
- c) What are leveling and differentiating solvents? Explain with examples. (4)
5. a) Arrange the following in the order of decreasing acid strength and justify the order
 HNO_3 , HAsO_3 , HPO_3
 H_3PO_4 , H_3PO_2 , H_3PO_3
 HBrO_4 , HBrO_2 , HBrO_3
 CH_4 , HF , H_2O , NH_3 (4)
- b) Complete the following equations & identify the acids & bases
 i) $\text{SO}_3 + \text{K}_2\text{O} \longrightarrow$
 ii) $\text{MgO} + \text{Al}_2\text{O}_3 \longrightarrow$
 iii) $\text{CaO} + \text{P}_4\text{O}_{10} \longrightarrow$
 iv) $\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} \longrightarrow$ (4)
- c) By taking ammonia as solvent, explain solvent system concept of acids and bases and explain any two acid base reactions in liquid ammonia. (4)

UNIT- III

6. a) What are silicones? Explain their preparation and applications. (4)
- b) Explain bonding in boranes using MOT. (4)
- c) Classify the following carboranes and write the formula of their respective ionic boranes from which they are derived $\text{C}_4\text{B}_2\text{H}_6$, $\text{C}_3\text{B}_3\text{H}_7$, $\text{C}_2\text{B}_5\text{H}_7$. (4)
7. a) How does the structure of BN differ from that of graphite? Explain. (4)
- b) Explain the structures of closo and Arachnocarboranes with an example for each. (4)
- c) Explain the difference between Pyroxenes and amphiboles. (4)

UNIT- IV

8. a) Explain the structure and preparation of cyclic phosphazine with an example. (4)
- b) Explain the Geometries of XeF_6 and XeO_3 . (4)
- c) Name the hydrides of N & P explain the variation of their properties with respect to i) basic nature ii) reducing character iii) covalent nature iv) bond angle. (4)
9. a) How does Cl_2O_6 react with NaOH and H_2O ? Give Equations. (4)
- b) Discuss the preparation and structure of S_4N_4 (4)
- c) Discuss the structure and preparation of XeOF_4 (4)

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Mangaluru

Semester I – P.G. Examination – M.Sc. Analytical Chemistry
November- 2019

ORGANIC CHEMISTRY

Time: 3 Hours

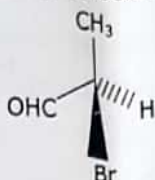
Max. Marks: 70

PART - A

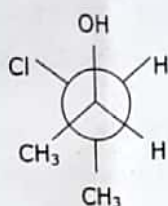
1. Answer any **FIVE** sub divisions of the following: (5x2=10)

- Give reasons: o-nitrophenol is more volatile than p-nitrophenol.
- Compare the acid strengths of benzoic acid and benzene-sulphonic acid.
- What are enamines? Give a synthetic method.
- Which among cyclopropyl methylation and benzylation is more stable? Justify your answer.
- Write the Fischer projection representation of the following and assign R/S configuration for the chiral carbons.

i)



ii)



- Differentiate between stereospecific and stereoselective reactions.
- Give a synthetic method for the ketal derivative of monosaccharides.
- Write the partial structure of chitin and glycogen highlighting the nature of glycosidic linkage.

PART - B

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

UNIT - I

- Identify aromatic/antiaromatic/nonaromatic compounds among the following. Justify your answer. (5)
Cyclobutadiene, [18]-Annulene, cyclooctatetraene, [10]-Annulene.
- Discuss different types of tautomerism involving migration of hydrogen in organic compounds. (4)
- Arrange the following in the order of their acid strength. Justify your answer. (3)
 HCO_2H , ClCH_2COOH , CH_3COOH , $\text{Cl}_3\text{CCO}_2\text{H}$
- With suitable examples, discuss the effect of (nature) hybridisation on base strength of organic compounds. (4)
- Explain cross conjugation and hyperconjugation with suitable examples. (4)

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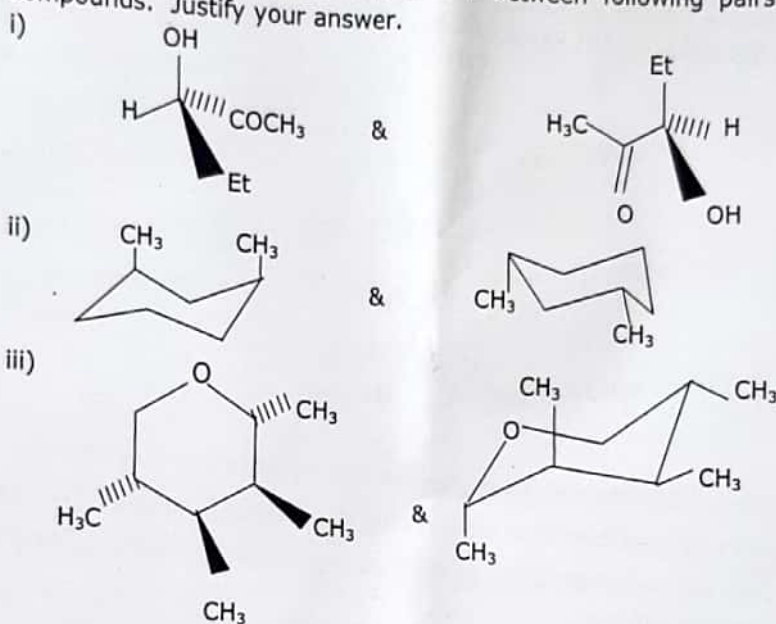
- c) Briefly explain the effects of the solvent on acid and base strength of organic compounds. (4)

UNIT - II

- 4.a) With suitable examples, explain any two important factors affecting the stability of carbocations. (4)
- b) Explain the following methods of determining reaction mechanism.
i) Isotope labelling and ii) Cross-over experiments (5)
- c) Write a note on structure and stability of Ylides. (3)
- 5.a) Give any two methods for the generation of carbenes. Highlight their important reactions. (4)
- b) Discuss the important reactions of nitrenes and arynes. (4)
- c) Illustrate that stereochemical evidences are helpful in determination of reaction mechanism. (4)

UNIT - III

- 6.a) Predict the stereochemical relationship between following pairs of compounds. Justify your answer.



- b) Explain any two methods of resolution of racemic mixtures. (5)
- c) Explain the origin of optical activity on spiro[3, 3] heptane-2, 6-dicarboxylic acid. (4)
- 7.a) Write the stable conformers for cis and trans isomers of the following. Justify your answer. (3)
- i) 1, 2 - Dimethylcyclohexane
- ii) 1, 3 - Dimethylcyclohexane
- b) Discuss the optical activity in biphenyls and allenes. (4)
- c) Explain a method for the determination of configuration of geometrical isomers. (3)

UNIT - IV

- 8.a) Give any two methods each for the synthesis of acetal and amino derivatives on monosaccharides. (5)
- b) Explain the Smiths degradation method. (4)
- c) Discuss the important structural features of cellulose. (3)
- 9.a) Explain carbohydrate epimerization with an example. (4)
- b) Discuss any two methods of structural degradation of polysaccharides. (4)
- c) Explain the ascending sugar series with an example. (4)

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St Aloysius College (Autonomous)

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

November – 2019

PHYSICAL CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **FIVE** sub-divisions of the following: (5x2=10)
- Entropy is not a convenient criterion for the feasibility of a transformation. Justify.
 - The activity of 2.5 moles of a substance changes from 0.05 to 0.35. What would be the changes in its free energy at 29°C?
 - Write the units of the rate constants for a i) zero order ii) $\frac{3}{2}$ order reaction.
 - What are oscillatory reactions?
 - What is catalytic poison. Give an example.
 - Write the Harkin- Jura equation. Why is it used?
 - Calculate the specific conductance and molar conductance of a 0.005M KCl solution.
Given :Resistance is 210 ohm at 25°C, cell constant =0.88 cm⁻¹
 - Give reason: Why smaller ions do not satisfactorily obey Walden's rule if they are solvated?

PART - B

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

UNIT - I

- Determine the absolute entropy of a gas at 25°C under atmospheric pressure using third law of thermodynamics. (4)
 - By deriving suitable mathematical expression, explain the variation of chemical potential with temperature. (4)
 - An aqueous solution containing 0.25g of a solute dissolved in 20g of water froze at -0.42°C. Calculate the molar mass of the solute. Enthalpy of fusion of ice at 0°C is 6024.6 J mol⁻¹. (4)
- How is partial molar volume determined by intercept method? Explain. (4)
 - Derive and explain the significance of Duhem-Margules equation. (4)
 - Formulate any two Maxwell's relations. Explain its significance. (4)

UNIT - II

- Derive the expression for the rate constant based on Transition State theory. (4)
 - Explain the effect of ionic strength on the reaction rates in solution. (4)
 - Discuss the relaxation method for the study of fast reactions. (4)
- Outline the kinetics of the reaction between Hydrogen -Bromine. (4)
 - Discuss the kinetics of parallel reactions. Give an example. (4)
 - Explain Hammett's relationship. What are its limitations? (4)

Contd...2

6. a) Outline Langmuir's unimolecular theory of adsorption and deduce the expression of Langmuir adsorption isotherm. (4)
- b) Discuss the protolytic mechanism of acid-base catalysis. (4)
- c) At 18°C, the surface tension, γ of an aqueous solution of butyric acid is represented by the equation $\gamma = \gamma_0 - 29.8 \log(19.64C_2 + 1)$ where γ_0 , the surface tension of water is 0.073 Nm^{-1} and C_2 is the bulk concentration of the solute. Calculate the surface excess of butyric acid at $C_2 = 0.01 \text{ mol dm}^{-3}$ using Gibb's adsorption isotherm. (4)
7. a) Derive Michaelis-Menten equation for enzyme catalysed reactions. (4)
- b) Explain the activation energies for catalysed reactions forming Arrhenius and Van't Hoff intermediates. (4)
- c) Give an account of semiconductor catalysis. (4)

UNIT - IV

8. a) Derive Debye -Huckel -Onsagar equation. How is it validated? (4)
- b) Draw phase diagrams and phase rule for two component systems in which the two components form (4)
- i) a eutectic mixture
- ii) a stable compound with congruent melting point.
- c) Calculate the mean activity coefficient ν_{\pm} of (4)
- i) 0.01M NaCl ii) 0.001M Na_2SO_4 at 25°C.
9. a) How are three components systems studied with the help of phase rule? (4)
Discuss briefly the system $\text{CH}_3\text{CO}_2\text{H}-\text{CHCl}_3-\text{H}_2\text{O}$.
- b) Discuss Bjerrum theory of ion association. (4)
- c) Explain Debye-Huckel theory of strong electrolytes. (4)

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St Aloysius College (Autonomous)

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

November – 2019

PRINCIPLES OF ANALYTICAL CHEMISTRY AND SEPARATION TECHNIQUES

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **SEVEN** sub-divisions of the following:

(7x2=14)

- Mention the significance for 'F' test.
- Explain accuracy and precision.
- What is peptisation in gravimetric titration?
- What is poly protic acids? Give two examples.
- Explain briefly the action of redox indicator.
- What are chelating ligands? Give example.
- Define R_f value. Explain the factor affecting R_f value.
- What are cation & Anion exchange resins? Give examples.
- What is eddy diffusion?

PART - B

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

UNIT - I

- How are 't' & F test used for comparison of analytical data. (4)
 - Discuss the types of impurities in gravimetry. (5)
 - What are the advantages of using organic reagents as precipitating agents in gravimetric analysis? Explain with two examples. (5)
- In ore analysis, the percentage of an element were found to be 65.55, 65.90, 67.85, 66.85, 69.90 and 65.00. The value 69.90 appears to be suspect. Ascertain whether this should be retained or rejected. The Q critical for observation at 90% confidence level is 0.56. (4)
 - What is fractional precipitation? Briefly explain its significance in gravimetric methods of estimation. (4)
 - Explain i) Determinate & Indeterminate errors. (3+3)
ii) Condition for precipitation

UNIT - II

- Explain the important applications of acid base titration. (4)
 - Mention the application of Karl-Fisher reagent in determination of water. (3)

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- c) Discuss the effect of p^H on conditional stability constant in EDTA titration. (3)
- d) A 0.5g bronze sample containing Zn is dissolved in 100ml of acid if an aliquot of 20ml need 10.1ml of 0.011 M EDTA. Calculate the percentage of Zn in bronze sample. (4)
(At.Wt of Zn= 65.38amu)
5. a) Discuss the theories of acid base indicator with example. (4)
- b) Give an account for potentiometric titration & determination of equivalence point. (3)
- c) How do you determine any three metal ion in a mixture by complexometric titration using masking and demasking agent. (4)
- d) Explain the factor affecting the shape of EDTA titration curve. (3)

UNIT - III

6. a) Distinguish between batch & continues solvent extraction process. (5)
- b) Explain briefly the instrumentation of HPLC with schematic representation. (5)
- c) Explain the working of electron capture & flame ionisation detector used in GC. (4)
7. a) Discuss the factors effecting and applications of solvent extraction process. (5)
- b) Write a note on GC/MS technique. (4)
- c) Explain the application of Ion exchange chromatography in preparative, purification and recovery. (5)

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Mangaluru
Semester I- P.G Examination – M. Sc. Analytical Chemistry
November - 2018

INORGANIC CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **FIVE** sub-divisions of the following: (2x5=10)
- Explain Bent's rule.
 - With illustrative examples explain intra molecular and inter molecular hydrogen bond.
 - With suitable examples, explain conjugate acid base concept.
 - Justify that though B and S belong to different groups, they resemble in their properties.
 - Borazine is also known as inorganic benzene. Give reason.
 - Explain the significance of styx number.
 - Justify that liquid sulphur exhibits anomalous properties.
 - What are super acids? Why are they called so? Give examples.

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PART - B

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

UNIT- I

- Construct molecular orbital diagram for O_2 molecule and predict its bond order and magnetic property. Also comment on bond order of O_2^+ , O_2^- and O_2^{2-} . (4)
 - Explain the postulates of Fajans rule and explain how these rules will help in predicting covalent character in ionic bond. (4)
 - Write notes on: i) Slaters rule
ii) Inter molecular forces. (4)
- With illustrative examples, explain the significance of radius ratio rules. Show that the radius ratio for octahedral site is 0.414. (4)
 - Construct the Born-Haber cycle for the preparation of 1 mole NaCl from sodium and chlorine. (4)
 - Predict the structures of molecules using VSEPR theory. I_3^- , SF_4 . (4)

UNIT- II

- Discuss the Arrhenius concept of acids and bases. Write its applications and limitations. (4)

Contd...2

- b) With illustrative examples, explain the Usanovich and solvent system concept of acids and bases. (4)
- c) By giving suitable examples, explain the classification of solvents. (4)
5. a) Explain acid base reactions, precipitation reactions in liquid ammonia and glacial acetic acid. (4)
- b) What is HSAB rule? With example discuss the applications of HSAB concept. (4)
- c) Write notes on : i) Symbiosis ii) Drago-Wayland equation (4)

UNIT- III

6. a) With illustrative examples, explain levelling and differentiating solvents. (4)
- b) Discuss the preparation and applications of linear polyphosphazines. (4)
- c) Explain how wades rules can be used as thumb rule in the classification of boranes (4)
7. a) Give the preparation of $(\text{NPCl}_2)_3$ and discuss its structure. (4)
- b) Explain the structure of H_2SO_4 and justify that it has high viscosity. (4)
- c) Write notes on: i) Silicones ii) Boron nitride. (4)

UNIT- IV

8. a) Explain the structure and bondings in $\text{B}_{10}\text{H}_{14}$ and B_5H_9 . (4)
- b) What are carboranes? Discuss its classifications. (4)
- c) Explain the structure, geometry and hybridization involved in XeF_4 and XeO_3 . (4)
9. a) Explain a method of preparation for H_3PO_4 and explain its structure. (4)
- b) What are inter halogen compounds. With suitable examples, discuss the preparation and structure of AB_3 and AB_5 type compounds. (4)
- c) Write notes on : i) Polyhalide ions (4)
- ii) Sulphur-nitrogen compounds.

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St Aloysius College (Autonomous)

Mangaluru

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

November- 2018

ORGANIC CHEMISTRY

Time: 3 Hours

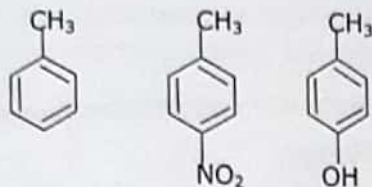
Max. Marks: 70

PART - A

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

(5x2=10)

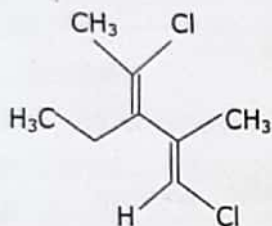
a) Arrange the following in increasing order of dipole moment.

b) Which among CH_3COOH and CF_3COOH is stronger acid? Justify your answer.

c) Why tropylium ion is more stable than trilyl cation.

d) What are singlet and triplet carbenes? Write the structure of some typical carbenes.

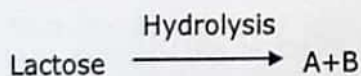
e) Designate the configuration of the double bonds in the following Diene and write the structure of Diene with opposite configuration.



f) What are Stereospecific Reactions and Stereo Selective Reactions?

g) Account for the change in optical rotation from dextro to levo during hydrolysis of sucrose.

h) Give structures of Reactant and Products in the following Reactions



PART - B

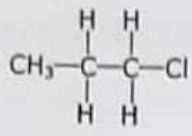
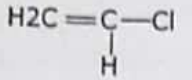
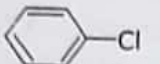
Answer any **FIVE** of the following choosing at least one (5x12=60)

full question from each unit:

UNIT - I

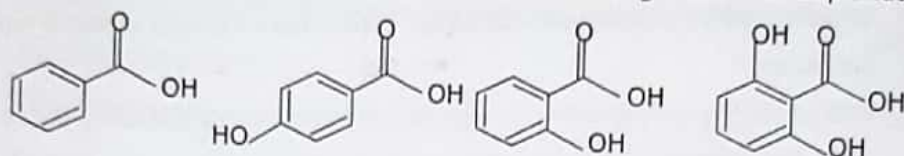
2.a) Account for variations in the C-Cl bond length and dipole moments in the following compounds.

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	C-Cl (\AA)	Dipole moment
	1.77	2.10
	1.69	1.44
	1.69	1.73

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- (5)
- b) Differentiate between Ethylacetoacetate and acetylacetonone in terms of their strength with proper justification. (4)
- c) What is cross conjugation? Explain with example. (3)
- 3.a) Assign pka values of 2.3, 2.9, 4.2 & 4.6 to following acids with explanation. (5)



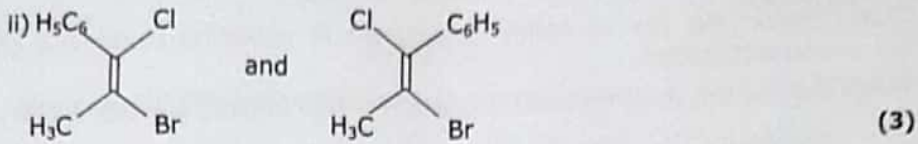
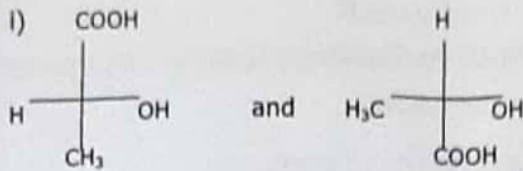
- (4)
- b) Explain the following with suitable example. (4)
- Homo aromaticity
 - Bis Homoaromaticity
- c) Explain different types of tautomerisation present in organic molecules. (4)

UNIT - II

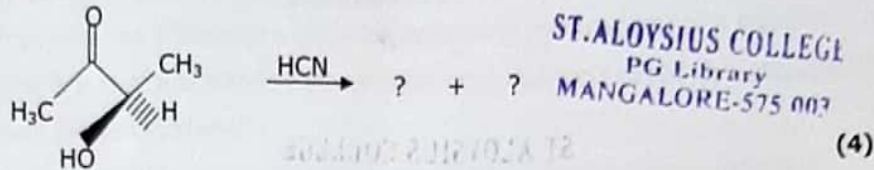
- 4.a) Explain generation, stability and reactivity of carbocations. (4)
- b) Give any two methods for the generation of nitrenes. Comment on general reaction of nitrenes. (4)
- c) Discuss the application of kinetic isotopic effect in determining the reaction mechanism for elimination reaction of isopropyl bromide using sodium ethoxide. (4)
- 5.a) Explain the following aspects of Fries rearrangement with suitable examples. (4)
- Kinetic and thermodynamic control
 - Cross over product formation
- b) What are carbenes? Suggest two methods for their generation and illustrate their reactivity. (4)
- c) Discuss structure and stability of free radicals. (4)

UNIT - III

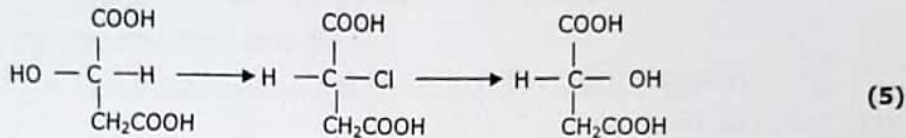
- 6.a) Designate the following pairs as Enantiomer/Diastereomers/identical compounds with suitable explanation. (4)



- b) Give the structures of stereo isomeric products formed in the following reaction. Predict the major stereo isomer and justify your answer.



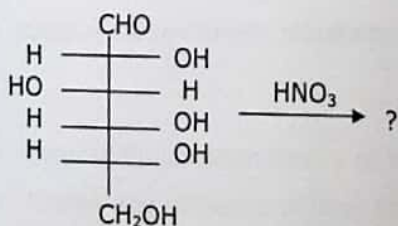
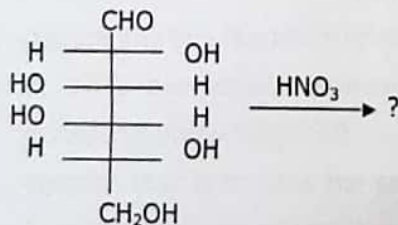
- c) Designate the stereo isomers I, II and III as R/S, use suitable reagents to account for their formation. Account for changes in configuration.



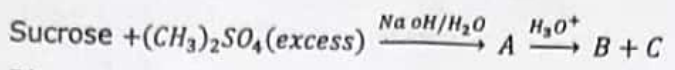
- 7.a) Write the Fisher projection for the meso-2,3-dibromo butane and convert it to newman and sawhorse structure. (3)
- b) Draw all the conformational structures of 1,2, 1,3 and 1,4 cyclohexane diols, provide suitable explanation for the most stable conformation in each case. (4)
- c) Explain the different methods of resolution with example. (5)

UNIT - IV

- 8.a) Give the products of HNO_3 oxidation of the following aldohexoses, comment on their optical activity/inactivity.



- b) Give structures of A, B, C in the following sequence. Account for their formation. (4)



- c) Discuss epimerization with suitable examples. (4)
- 9.a) Explain the use of Smith degradation in structural elucidation of polysaccharides. (4)
- b) Outline the steps involved in the conversion of D(+) glucose to D(+) mannose. (4)
- c) Discuss ascending sugar series with suitable examples. (4)

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Mangaluru**

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

November – 2018

PHYSICAL CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **FIVE** sub-divisions of the following: (5x2=10)
- Entropy is a measure of unavailable energy. Justify.
 - For a chemical reaction, $\Delta H = 16.8 \text{ kJmol}^{-1}$ and $\Delta S = 56.0 \text{ Jk}^{-1}$. At what temperature the reaction exists at equilibrium?
 - Write any two differences between order and molecularity of a reaction.
 - What are fast reactions? Why conventional methods cannot be employed to study these reactions?
 - Give an example each for Homogeneous and Heterogeneous catalysis.
 - What is the effect of temperature on enzyme catalyzed reactions?
 - Explain why KCl-NaCl-H₂O system is a three component system where as KCl-NaBr-H₂O system is regarded as a four component system.
 - Calculate the ionic strength of
 - 0.25 M K₂SO₄ solution and
 - 0.25 M Al₂(SO₄)₃ solution.

PART - B

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

UNIT - I

- Show that the entropy of mixing of gases is always positive. (4)
 - Derive the two thermodynamic equations of state. What is the thermodynamic condition for ideal gas behaviour? (4)
 - State Nernst heat theorem. What are its implications and applications? (4)
- Deduce any two Maxwell's relations. Explain their significance. (4)
 - At 37°C, the osmotic pressure of blood is 7.65 atm. How much glucose (Mol.wt=180g/mol) should be used per litre for an intravenous injection that is to have the same osmotic pressure as blood. (Given $R=0.0821 \text{ dm}^3 \text{ atm K}^{-1}\text{mol}^{-1}$). (4)
 - Obtain Gibbs-Duhem equation. Explain its significance. (4)

UNIT - II

- Discuss the collision theory of bimolecular gaseous reactions. (4)
 - Explain the influence of ionic strength on the rates of ionic reactions. (4)

Contd...2

PH 543.1

- c) Discuss in detail the kinetics of parallel reactions. (4)
5. a) Outline the continuous flow method for study of fast reactions. (4)
- b) Discuss the kinetics of branched chain reactions. Obtain the condition for explosion limits. (4)
- c) Write a comparative note on photochemical hydrogen-halogen reactions. (4)

UNIT - III

6. a) Describe in detail the influence of pH on enzyme catalyzed reactions. (4)
- b) Give a detailed account of bimolecular surface reactions. (4)
- c) Write a note on equilibrium treatment of catalyzed reactions. (4)
7. a) What are the postulates of B.E.T. adsorption isotherm? Explain the application of this isotherm in determination of surface area. (8)
- b) Discuss the activation energies for catalyzed reactions forming Arrhenius and Van't Hoff intermediates. (4)

UNIT - IV

8. a) Explain the variation of molar conductance of strong and weak electrolytes with dilution. (4)
- b) Discuss the phase diagram of three component liquid-liquid-liquid system by taking a suitable example. (4)
- c) Explain Debye-Huckel-Onsager equation. How is it validated? (4)
9. a) Give an account of the effect of viscosity of the liquid on molar ionic conductance. (4)
- b) Calculate the mean ionic activity coefficient of (γ_{\pm}) of 0.001M Na_2SO_4 solution in water at 25°C . Given the constant A for water at 25°C is 0.509. (4)
- c) Outline the application of phase rule to eutectic systems. (4)

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St Aloysius College (Autonomous)**Mangaluru****Semester I – P.G. Examination - M.Sc. Analytical Chemistry****November – 2018****PRINCIPLES OF ANALYTICAL CHEMISTRY AND SEPARATION TECHNIQUES**

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **SEVEN** sub-divisions of the following: (7x2=14)
- Precision always accompanies accuracy, but a high degree of precision does not imply accuracy. Justify.
 - Write significance of Q-test.
 - Write importance of nucleation step in precipitation.
 - Write indicator action of Phenolphthalein.
 - Justify that Eriochrome Black 'T' cannot be used as an acid-base indicator.
 - Mention the factors which influence the shape of redox titration curves.
 - Distinguish between partition co-efficient and distribution ratio.
 - Write the role of modifiers in solvent extraction process.
 - List various types of detector systems used in 'HPLC'.

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PART - B

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

UNIT - I

- Discuss methods of elimination of systematic errors. (4)
 - Analyst of a sample of iron ore gave the following percentage values for the iron content: 7.08, 7.21, 7.12, 7.09, 7.16, 7.14, 7.07, 7.14, 7.18, 7.11. Calculate the mean, standard deviation and co-efficient of variation for the values. (5)
 - Discuss advantages of organic precipitants in inorganic ions analysis. (5)
- Write the significance of students t-test and F-test. (4)
 - Write a note on gas sampling. (3)
 - Explain the concept of 'precipitation from homogeneous solution' with an example. (4)
 - Write a note on random errors. (3)

UNIT - II

- Discuss the titration curves for the neutralization of a strong acid with a weak base. (4)
 - Explain working of diphenylamine indicator in redox titration. (3)

Contd...2

PS 544.1

- c) Explain the role of buffer solution in complexometric titration. (3)
- d) Discuss industrial applications of complexometric titrations. (4)
5. a) Explain titration curves obtained when H_3PO_4 titrated by KOH. (5)
- b) Discuss theory and principle of iodometric estimation. (5)
- c) Explain the importance of masking technique in complexometric titration. (4)

UNIT - III

6. a) Explain the following statement in the process of extraction: The extracting solvent should be used in parts instead of using the whole liquid in one lot. (3)
- b) Write a short note on column packing in HPLC. (3)
- c) Discuss the applications of gas chromatography in quantitative analysis. (4)
- d) Discuss the characteristics of ion exchange resins. Explain Anionic and cationic resins. (4)
7. a) Write differences of batch and continuous extraction. (3)
- b) Explain the plate theory of chromatography. (4)
- c) Discuss the application of ion exchange chromatography in softening of hard water. (3)
- d) Explain the principles of working of Flame Ionisation Detector (FID) and Thermal conductivity detectors used in gas chromatography. (4)

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St Aloysius College (Autonomous)
Mangaluru

Semester I – P.G. Examination – M.Sc. Analytical Chemistry
November- 2017

INORGANIC CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **FIVE** sub divisions of the following: (5x2=10)
- Arrange the group 16 & 17 elements in the order of increasing of electron affinities and justify your answer.
 - Give the geometry of ClF_3 molecule using VSEPR theory and justify the geometry.
 - Among the trihalides of boron, which is more acidic and why?
 - Using the concept of HSAB theory, predict which way, LEFT or RIGHT, that the following reactions will tend to proceed:
 - $\text{AlI}_3 + \text{AgF} \rightleftharpoons \text{AlF}_3 + 3\text{AgI}$
 - $\text{HgO} + \text{H}_2\text{S} \rightleftharpoons \text{HgS} + \text{H}_2\text{O}$
 - Classify the following boranes and carboranes according to Wade's rule: $\text{C}_2\text{B}_9\text{H}_{12}^-$, $\text{B}_{10}\text{H}_{15}^-$, $\text{B}_{11}\text{H}_{13}^{-2}$ & B_2H_7^-
 - Borazine is called inorganic benzene. Justify.
 - Give any evidences for the electropositive nature of I_3^- .
 - Why XeF_6 cannot be stored in glass vessels? Justify with equation.

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PART - B

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

UNIT - I

- Explain the structure of NaCl & calculate the number of Na^+ & Cl^- in a unit cell of it. (4)
 - What are the factors affecting ionic radii. (4)
 - Construct molecular orbital diagram for CO and calculate its bond order. (4)
- Identify the intermolecular forces that will occur between the solute and solvent compounds when dissolved.
 - KBr dissolved in water
 - HBr dissolved in propanol
 - Butanol dissolved in water (4)
 - Benzene dissolved in acetic acid
 - Derive Born Lande's Equation. (5)

Contd...2

PH 541.1

- c) For gaseous reaction $K + F \rightarrow K^+F^-$, $\Delta H = 19 \text{ kcal mol}^{-1}$, under conditions where cation is prevented by electrostatic separation from combining with each other. The I.E. of K = 4.3 eV. Calculate the electron affinity of Flourine in kcal mol^{-1} (1 eV = 23.06 kcal mol^{-1}) (3)

UNIT - II

- 4.a) Give reactions to represent autoionisation reactions of liq NH_3 & Liq SO_2 . Give any two advantages of these solvents. (4)
- b) What are Lewis acids & bases? Arrange the following in the order of decreasing basic strength. (4)
- i) $\text{NH}_3, \text{PH}_3, \text{SbH}_3$ ii) $\text{NH}_3, \text{NCl}_3, \text{NF}_3$
- c) What are levelling and differentiating solvents? Explain with examples. (4)
- 5.a) Arrange perchloric acid, chloric acid, Chlorous acid & hypochlorous acid in the order of increasing acidic strength and justify. (4)
- b) Arrange the following in the order of decreasing acid strength and justify the order. (4)
- $\text{HNO}_3, \text{HAsO}_3, \text{HPO}_3$
 $\text{H}_3\text{PO}_4, \text{H}_3\text{PO}_2, \text{H}_3\text{PO}_3$
- c) Explain the terms i) Super acid ii) Symbiosys (4)

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UNIT - III

- 6.a) Explain the preparation of different types of silicones. (4)
- b) Explain the concept of 3 centre 2 electron bond in boranes using molecular orbital theory. (4)
- c) Give structure of boranes having STYX number 4120 & 4220. (4)
- 7.a) Give the structure of boron nitride. How does it differ from graphite? (4)
- b) What are closo, nido, arachno and klado boranes? Give one example for each. (4)
- c) What are pyroxenes and amphiboles? Give their structure. (4)

UNIT - IV

- 8.a) Explain the structure and preparation of cyclic phosphazine with an example. (4)
- b) Explain the geometries of XeF_6 and XeO_3 . (4)
- c) Explain the preparation and structure of S_4N_4 . (4)
- 9.a) How does Cl_2O react with N_2O_5 and F_2 ? Give Equations. (4)
- b) In what order oxidizing power of oxoacids of chlorine increase and why? (4)
- c) Discuss the geometry of ICl_4^- and I_3^- (4)

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Semester I- P.G. Examination - M. Sc. Analytical Chemistry
November - 2017

ORGANIC CHEMISTRY

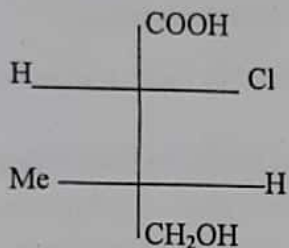
Time: 3 Hours

Max. Marks: 70

PART - A

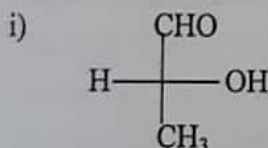
1. Answer any **FIVE** sub-divisions of the following: (2x5=10)

- Cyclohexylamine is a stronger base than aniline, while p-nitroaniline is a weaker base than aniline. Justify.
- What are alternant and non-alternant hydrocarbons? Give examples.
- Give a chemical reaction involving carbene as a reaction intermediate.
- Write down the most stable and least stable free radicals from the following and justify your choice
 $Me\dot{e}$, $Me_3\dot{C}$, $Ph\dot{C}H_2$, $Me\dot{C}H_2$, $Ph_3\dot{C}$
- Convert the following Fischer Projection formula into Newmann and Sawhorse projection formulae.

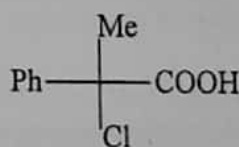


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f) Assign R/S configuration to the following:



ii)



- Write down the chemical structure of heparin.
- Illustrate the terms: anomers and epimers with suitable examples.

PART - B

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

UNIT- I

- What is hyperconjugation effect? Explain how is it useful in explaining the stability of carbocations. (4)
 - Describe the concept of resonance. State the rules of resonance taking suitable examples. (4)
 - Describe briefly the relative strengths of acids based on inductive and mesomeric effects. (4)

Contd...2

- 3. a) Discuss about the types and applications of hydrogen bonds in organic molecules. (4)
- b) Write a note on intermolecular forces. (4)
- c) Comment on the aromaticity of annulenes. (4)

UNIT- II

- 4. a) What are nitrenes? How are they generated? Describe any two important reactions of nitrenes. (4)
- b) Compare the relative stabilities of carbanions and free radicals. (3)
- c) How are the following non-kinetic methods useful in determining reaction mechanisms? (5)
 - i) Detection of intermediates
 - ii) Stereochemical evidences
- 5. a) Give a brief account of structure and stability of carbocations. (4)
- b) Explain the important methods of generation and structure of arynes. (4)
- c) Describe the use of isotopic labelling studies in the determination of reaction mechanisms. (4)

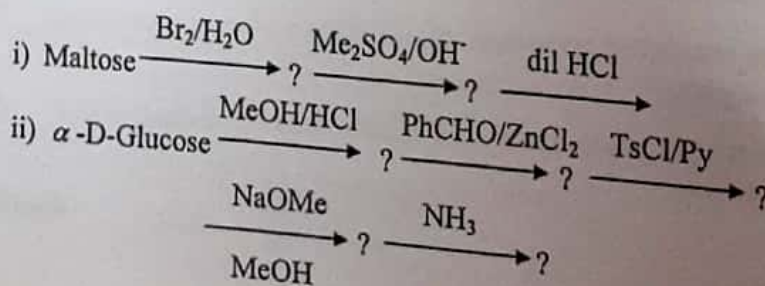
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UNIT- III

- 6. a) What is meant by resolution of a racemic mixture? Describe any two important methods of resolution. (4)
- b) Explain Cram's and Prelog's rules with suitable examples. (4)
- c) Write a note on optical isomerism exhibited by lactic acid and tartaric acid. (4)
- 7. a) Discuss the optical activity in the absence of chiral carbon taking biphenyls as examples. (4)
- b) Write a brief account of conformational analysis of cyclohexane. (4)
- c) Describe any two methods employed for the determination of configuration of geometrical isomers. (4)

UNIT- IV

- 8. a) How is the chemical structure of fructose arrived at? (4)
- b) Write a short note on the chemistry of ether and ketal derivatives of monosaccharides. (4)
- c) Discuss the use of Smith degradation and alkaline degradation techniques in the structural degradation of polysaccharides. (4)
- 9. a) Write a note on the chemistry of deoxysugars. (4)
- b) Elucidate the chemical structure of cellobiose. (4)
- c) Complete the following reactions. (4)



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Semester I – P.G. Examination – M.Sc. Analytical Chemistry
November- 2017
PHYSICAL CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **FIVE** sub divisions of the following: (5x2=10)
- The activity of 2.5 moles of a substance changes from 0.05 to 0.35. What would be the change in its free energy at 27°C?
 - State Nernst heat theorem. Give its significance.
 - Write Taft equation. Why is it used?
 - The rate constant of a second-order reaction is $5.70 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C and $1.64 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 40°C. Calculate the activation energy.
 - What is the effect of pH on enzyme catalyzed reactions?
 - How does chemisorption differ from physisorption?
 - Explain Eutectic point.
 - Walden's rule is more applicable to larger ions than the smaller one. Justify.

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PART - B

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

UNIT - I

- Explain how the absolute entropy of a substance is determined with the help of third law of thermodynamics. (4)
 - Derive any two Maxwell relations. Explain their significance. (4)
 - Define partial molar volume. How is it determined by intercept method? (4)
- Derive Raoult's law for vapor pressure lowering. How is it used for determining the molar mass of a nonvolatile compound? (4)
 - Discuss the effect of temperature and pressure on equilibrium constant by deriving related equation. (4)
 - Derive Duhem-Margules equation. Mention its physical significance. (4)

UNIT - II

- Explain lower and upper explosion limits by deducing the general rate expression of branched chain reaction. (4)
- Hammelt's relations called the linear free energy relations. Explain. (4)
- Discuss in detail the kinetics of consecutive first order reaction, $A \rightarrow B \rightarrow C$. (4)

Contd...2

- 5.a) Comment on the effect of solvent on the rate of chemical reaction by deducing the related expression for an ionic reaction. (4)
- b) Discuss the stopped flow technique for the study of kinetics of fast reactions. (4)
- c) Discuss activated complex theory of bimolecular reactions. (4)

UNIT - III

- 6.a) Derive Gibbs adsorption isotherm for solutions. (4)
- b) Give an account of semiconductor catalysis. (4)
- c) Discuss the kinetics of acid-base catalysed reactions. (4)
- 7.a) Discuss briefly BET theory of multilayer adsorption. (7)
- b) Explain the concept of equilibrium and steady state approximations. (5)

UNIT - IV

- 8.a) Discuss the Debye-Huckel theory of strong electrolytes. (4)
- b) Describe the phenomenon of equivalent conductance minima. (4)
- c) Briefly discuss the Bjerrum theory of ion association. (4)
- 9.a) Discuss the application of phase rule to Ag/Pb systems. (4)
- b) Derive Debye-Huckel-Onsager equation. (4)
- c) Explain the phase rule for 3 component system. Give an example. (4)

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

November - 2017

**PRINCIPLES OF ANALYTICAL CHEMISTRY AND
SEPARATION TECHNIQUES**

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **SEVEN** sub divisions of the following: (7x2=14)
- Write any two differences between post precipitation and co-precipitation.
 - What are the criteria involved while selecting washing liquid in gravimetric precipitation.
 - The following is the data obtained by ISRO on analysis of Cr content in lunar rocks by Chandrayana mission. Is there any value listed below by neutron activation analysis that can be rejected?
0.227, 0.260, 0.248, 0.243, 0.281, 0.262 and 0.345. Tabulated Q-value is 0.5.
 - Why is it impossible to titrate all three protons of phosphoric acid in aqueous medium?
 - Multidentate ligands are preferred to unidentate ligands in complexometric titrations. Justify.
 - What is formal potential? In what respects it differs from Nernst potential?
 - What are masking agents? How are they used in the solvent extraction?
 - What is meant by normal phase and reverse phase HPLC?
 - Sketch two separate chromatograms for the analysis of a mixture containing 4 hydrocarbons and chlorobenzene using i) flame ionisation detector and ii) electron capture detector. Assume the column used for the separation resolves all 5 compounds with baseline separation.

PART - B

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

UNIT - I

- Hydrous oxides of Fe (III) and Al are preferred to precipitate by homogeneous precipitation from solution by hydrolysis of urea at 100°C than by direct method, Give reason. (3)
- Discuss optimum conditions of precipitation based on Weimarn's ratio. (3)
- In BARC Mumbai, detailed records are kept of the quantity of Plutonium received, transported and used. Each shipment of Plutonium pellets received from Canada is carefully analysed to check that the purity and hence the total quantity is as the supplier country's claims. A particular shipment is analyzed with the following results: 99.3, 99.87, 99.9 and 99.86%. The listed purity as received from the supplier is 99.91%. Is the shipment acceptable? (4)

Contd...2

PS 544.1

- d) What are organic precipitants? Mention the advantages and disadvantages. (4)
- 3.a) Analysis of a sample of Iron ore gave the following percentage values for the iron content: 7.08, 7.21, 7.12, 7.09, 7.16, 7.14, 7.18, and 7.11. Calculate mean, standard deviation and coefficient of variation for the values. (3)
- b) Discuss any two methods of sampling used for solids. (3)
- c) A blood sample was sent to Fr Muller's Hospital and KMC Hospital laboratories in Mangalore to be analyzed for blood cholesterol. The results obtained for the concentration (mg/dL) were
- | | |
|----------------------|--------------|
| Fr Muller's Hospital | KMC Hospital |
| Mean = 313 | Mean = 323 |
| $s_1 = 0.13$ | $s_2 = 0.15$ |
| $n_1 = 10$ | $n_2 = 10$ |
- i) Are the standard deviations significantly different at the 95% level? Tabulated F value = 7.56. (4)
- ii) Are the two means significantly different at confidence levels. Tabulated F value for 90%-1.38 and 95%-1.83. i) 90% and ii) 95% (4)
- d) What are systematic method errors? Describe any four ways of identifying and compensating for method errors. (4)

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UNIT - II

- 4.a) Calculate the H⁺ ion concentration in aqueous acetic acid solution if 0.01 M solution has pH=2.5 ($k_a=1.8 \times 10^{-5}$). (3)
- b) What is conditional stability constant? How is it related to concentration? (3)
- c) Discuss the theory of acid base indicators. What factors can shift the pH range of an indicator? (4)
- d) Explain the theory of metal ion indicators. (4)
- 5.a) Name any three interferences in Karl fisher titrations. How are they eliminated? (3)
- b) Discuss the factors that influence the titration curve in redox titrations. (3)
- c) Calculate the cell potentials at various stages in the titration of 50.0 cm³ 0.01 M Fe²⁺ with following volumes of 0.1 M Ce⁴⁺ solution in acedic medium. 0.0, 25.0, 49.9, 50.0 and 50.1, the cell being constructed by dipping platinum electrode and saturated calome electrode. (formal potentials of Fe and Ce are 0.7 and 1.4 V respectively. Saturated calomel electrode potential = 0.2422 V) (4)
- d) Discuss the selectivity and the sensitivity of the applications of redox titrations with suitable examples. (4)

UNIT - III

- 6.a) Write a note on factors affecting solvent extraction. (3)
- b) Draw the block diagram for the HPLC instrument. Explain the functioning of the reciprocating pump. What precaution will you take while selecting solvent for HPLC system while using UV detector. (3)
- c) Write a note on the synthesis of ion exchange resins. Explain the factors affecting ion exchange equilibria. (4)
- d) i) Elaborate the terms WCOT and SCOT as used in gas chromatography. (4)
 ii) How does the resolution vary with (ii.i) Length of the column
 (ii.ii) Diameter of the column.
 iii) Explain the functioning of electron capture detector. (4)
- 7.a) Explain the principle and instrumentation of Ion-Exchange chromatography. (3)
- b) Under what circumstance temperature programming is performed in GC? How does the change in temperature moves the peaks? (3)
- c) The organic compounds dimethyl ether (CH_3OCH_3) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) have the same molecular formula, the same molar mass but different structural formulae. A sample containing both ethanol and dimethyl ether is analysed by GLC with a polar stationary phase and a flame ionization detector. Will the two compounds produce peaks with the same retention time? Explain your answer.
- i) A student runs a sample of hexane through a gas chromatogram at 95°C . The cyclohexane produces a peak after 4.6 minutes. The student then injects a mixture of unknown organic substances into the same column at the same temperature. There are peaks after 3.0, 4.6 and 7.8 minutes. From this information, it can be concluded that (identify the most appropriate statement among the four choices and give explanation)
- i) The mixture has at least three components, one of which must be cyclohexane.
- ii) The mixture has three components, one of which must be cyclohexane.
- iii) The mixture has three components, but cyclohexane is not one of them.
- iv) The mixture has at least three components, one of which might be cyclohexane. (4)
- d) Explain the functioning of GC - MS (You may explain (i) the interfacing of GC and MS, (ii) Quadrupole ion filter (4)
