

PGIS-N 1009 B-14
M.Sc. Ist Semester (CBCS) Degree Examination
Chemistry
(Inorganic Chemistry-I)
Paper - HCT-1.1
(New)

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:

- i) Answer all questions
- ii) All questions carry equal marks

1. Answer any eight questions:**(8×2=16)**

- a) Explain Bent's rule.
- b) How are σ , π and δ molecular orbitals formed?
- c) What is synergic bond, how does it correlate to bonding in metal carbonyls?
- d) What are Lewis acids and bases? Explain with example.
- e) Predict the co-ordination number and geometries in $\text{VO}(\text{acac})_2$ and $\text{Zr}(\text{acac})_4$ complexes (acac=acetylacetone).
- f) Calculate the spin-only magnetic moment values for high-spin complexes of cobalt (III) and iron(II).
- g) NaCl do not favour Frenkel defect, while AgCl does it. Why?
- h) Distinguish 'n' and 'P' type semiconductors.
- i) Strong oxidizing agents apparently do not exist in liquid ammonia. Why?
- j) What is symbiosis? Give examples.

- 2.**
- a) Write briefly on the concept of resonance by taking carbonate and thiocyanate as examples. **(5)**
 - b) What is meant by partial ionic character of covalent bonds? How is this related to electronegativity? **(5)**
 - c) Depict a Walsh diagram for AH_2 molecule, based on it explain the shapes of linear and bent triatomic molecule. **(6)**

OR

What are the postulates of VSEPR model? Based on it, explain the shapes of ClF_3 , SF_4 and PF_5 .

3. a) Write briefly on the non-stoichiometric defects in solids. (5)
- b) Outline the preparation and structure of metal nitrosyls. Explain IR spectral studies in the structure of nitrosyls. (5)
- c) Based on band theory, explain how solids can be classified as conductors, semiconductors and insulators. (6)

OR

Discuss briefly on preparation, reactions structure and bonding in metal carbonyls.

4. a) Write briefly on evidences on metal-ligand covalency, and spectro chemical series. (5)
- b) Discuss the Gouy's method for the determination of magnetic susceptibility of metal complexes. (5)
- c) Explain static and dynamic Jahn-Teller effects and discuss distortion in the structure of $[\text{C}_4(\text{H}_2\text{O})_6]^{2+}$ (6)

OR

Draw MO energy level diagram for an octahedral complex involving sigma and pi-bonding. Explain its characteristic features.

5. a) Write briefly on the chemical reactions involved in non-aqueous solvent liquid sulfur dioxide. (5)
- b) Write briefly on the variation in conductance and magnetic properties of solutions of alkali metals in liquid ammonia. (5)
- c) Explain solvent system concept of acids and bases. Discuss the leveling and differentiating solvents with examples. (6)

OR

Discuss briefly on the Pearson's concept of hard and soft acids and bases. Based on it, will Cu^{2+} react more strongly with HO^- or NH_3 ? With O_2^- or S^{2-} ?

PGIS - O 1014 B - 14
M.Sc. Ist Semester (Non-CBCS) Degree Examination
Chemistry
(Physical Chemistry)
Paper : CHEMT 1.33
(Old)

Time : 3 Hours

Maximum Marks : 80

Instructions to Candidates:

- 1) All questions carry **equal** marks
- 2) All questions are **compulsory**

Answer the followings

(8×2=16)

1.
 - a) State and explain Heisenberg uncertainty principle
 - b) Calculate the ionic strength of 0.003M K_2SO_4 Solution
 - c) What do you mean by energy of activation?
 - d) Define activity and activity coefficient
 - e) Explain corrosion
 - f) Give any two thermal properties of ceramics
 - g) Distinguish between ideal and non - ideal solutions
 - h) Define buffer capacity
2.
 - a) Explain black body radiation **(5)**
 - b) Give an account of eigen functions and eigen values. **(5)**
 - c) What are operators? Discuss Linear operator and additive operator **(6)**

OR

 - c) Write a note on quantum number **(6)**
3.
 - a) State the assumption of Debye-Huckel theory **(5)**
 - b) Explain use of Handerson -Hassalbalch equation in the preparation of buffer solutions **(5)**
 - c) Write a note on importance of buffer's in biological systems **(6)**

OR

 - c) Give an account of corrosion control and prevention **(6)**
4.
 - a) Derive Gibb's - Helmholtz equation. **(5)**
 - b) What are partial molar quantities. Discuss the determination of partial molar volume. **(5)**
 - c) Explain the classification of composites & give their general characteristics **(6)**

OR

 - c) Give the comparison between Collision theory and transition state theory **(6)**

5. a) Derive the rate expression on the basis of transition state theory. (5) ;
b) What is salt effect? Discuss secondary salt effect (5) .
c) Discuss the characteristics and classification of Spinel materials (6)

OR

- c) Explain Fluorescence and Phosphorescence. (6)
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PGIS-O 1010 B-14
M.Sc. Ist Semester (Non CBCS) Degree Examination
Chemistry
(Inorganic Chemistry)
Paper - CHEMT-1.11
(Old)

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:

- i) Answer **all** the questions
- ii) All questions carry **equal** marks

1. Answer the following: (8×2=16)
- a) Ionization potential of nitrogen is more than that of oxygen. Give reason.
 - b) Though KCl and CaO are isostructural, the latter has a larger lattice energy than the former. Explain.
 - c) Boiling point of H₂O is more than that of HF. Define the statement.
 - d) What is digestion of a precipitate? Give its importance in a gravimetric analysis?
 - e) What are complexometric titrations? Which titrant do you use for the determination of hardness of water?
 - f) Give the name and structure of an organic reagent which could be employed as chromogenic spraying agent for obtaining detectable chromatogram of metals.
 - g) What is a delta bond? Explain with a suitable example.
 - h) Write the basic principle on which the volumetric analysis is based.
2. a) Solve the following.
- i) Calculate the enthalpy of formation of BeCl₂, given: Electronegativities of chlorine and beryllium are 3.0 and 1.5 respectively, (5)
 - ii) Calculate the bond distance C-O, Given : Electro negativities of carbon and oxygen are 2.5 and 3.5 respectively covalent radii of carbon and oxygen are 0.77 and 0.74 Å° respectively. (5)
 - b) Pi-bonding through p-orbitals is quite common in lighter p-block elements but is rare in heavier p-block elements. Explain the observation with suitable examples. (5)
 - c) Write a note on biological applications of complexes of Mg⁺⁺, Fe⁺⁺ and Co⁺⁺ (6)

OR

How would you account the following:

- i) Compounds of s and p-block elements are generally colourless but those of

transition metals are generally coloured.

ii) Electrode potentials of transition metals are higher than that of hydrogen still these metals do not displace hydrogen from acid solutions.

3. a) Derive the limiting radius ratio for a trigonal site and provide the geometry. if the limiting radius ratio is between 0.414 and 0.732. (5)
- b) Derive Born-Landé equation for the lattice energy of an ionic compound. (5)
- c) What are Fajans rules? Explain how do they explain the presence of covalency in ionic bonding. (6)

OR

Account for the following

i) Ionic compounds do not conduct electricity in solid state but do conduct in molten or dissolved state.

ii) Ionic compounds are soluble in polar solvents but insoluble in organic solvents.

4. a) Based on molecular orbital theory, explain the π -acid character of carbon monoxide. Comment on the bond order and magnetic properties of this molecule. (5)
- b) Account for equal carbon-oxygen and nitrogen-oxygen bond lengths in CO_3^{2-} and NO_3^- ions respectively. (5)
- c) Write a note on hydrogen bonding and its consequences (6)

OR

Using the principle of LCAO for the wave function of H_2^+ , obtain the normalised wave functions for bonding molecular orbital and antibonding molecular orbital.

5. a) Write a note on co-precipitation and post-precipitation. (5)
- b) Explain the factors influencing the particle size of a precipitate in a gravimetric analysis (5)
- c) Solve the following
- i) How would you prepare 250ml of 2.0M HCl from the commercial concentrated acid. According to the label on the bottle, reagent is 36.8% HCl and has a density of 1.16g/mL.
- ii) A solution of KMnO_4 was standardised by titrating against a standard solution of oxalic acid -obtained by dissolving 1.562 g of oxalic acid (Formula weight=126) in 100mL solution. 20mL of this solution require 9.5mL of KMnO_4 for complete titration. What is the molarity of KMnO_4 . (6)

OR

Explain the following

- i) Phenolphthalein is not a suitable indicator for titrating a weak base against a strong acid.
- ii) Methyl orange is not a suitable indicator for titrating a weak acid against a strong base.

PGIS - N 1013 B - 14
M.Sc. Ist Semester (CBCS) Degree Examination
Chemistry
(Physical Chemistry - I)
Paper : HCT 1.3
(New)

Time : 3 Hours

Maximum Marks : 80

Instructions to Candidates:

- 1) All questions are **compulsory**
- 2) All questions carry **equal** marks

1. Answer any **eight** sub-questions (2×8=16)
 - a) What are eigen functions and eigen values?
 - b) What is an operator? Explain
 - c) Calculate the mean ionic activity Coefficient of 0.01M $BaCl_2$ solution at room temperature
 - d) What do you mean by a buffer action? Explain
 - e) What are polymers? Give their applications
 - f) Explain radius of gyration and mean end-to-end distance of a polymer
 - g) Calculate \bar{M}_w for polyethylene, if the degree of polymerization is 8,000
 - h) Calculate the ionic strength of 0.002 M $AlCl_3$ aqueous solution
 - i) Most of the reactions takes place in solution phase as compared to gas and solid phases. Comment
 - j) Calculate the thickness of ionic atmosphere for 1 : 1 electrolyte KCl when concentration is 0.03 M
 2.
 - a) Explain photoelectric effect and de - Broglie's hypothesis (5)
 - b) Explain the terms : (5)
 - i) Zero point energy
 - ii) Hybrid orbitals
 - iii) Compton effect
 - c) Define linear operator and commutative operators. Show that d/dx is a linear operator where $\hat{A} = d/dx$, $f(x) = ax^m$; $g(x) = bx^n$ (6)
- OR**
- c) Show that eigen values of a Hermitian operators are real (6)

3. a) Explain the laboratory method of preparation of acidic and basic buffer solutions. Calculate the ratio of lactic acid and lactate in a buffer system whose PH is 3.5 and PKa of an lactic acid is 3.20 (5)
- b) Derive Gibb's - Helmholtz equation. Give it's significance in thermodynamics (5)
- c) State the assumptions of Debye-Huckel law. Derive the expression for thickness of ionic atmosphere (6)

OR

- c) Give an account of thermodynamics of ideal and non - ideal solutions. (6)
4. a) Explain the difference between Sedimentation velocity and sedimentation equilibrium methods. If the diffusion coefficient and sedimentation coefficient of alcohol dehydro genease are $6.38 \times 10^{-5} \text{ cm}^2/\text{s}$ and 4.98 s respectively. Calculate molecular mass. The density of water is 0.988 g/cm^3 and volume of enzyme is $0.758 \text{ cm}^3/\text{g}$. (5)
- b) Discuss the Osmotic pressure technique of determining polymer molecular weight (5)
- c) Explain \bar{M}_n , \bar{M}_w and \bar{M}_v concepts. Equal numbers of molecules with molecular weight 10,000 and 15,000 are mixed calculate \bar{M}_n (6)

OR

- c) Give an account of polydispersity and molecular weight distribution. (6)
5. a) Derive the rate expression for a bimolecular reaction based on thermodynamic concept of transition state theory. (5)
- b) What are fast reactions? Discuss the Kinetics and mechanism of studying fast reaction by flash photolysis method. (5)
- c) What is salt effect? Discuss the secondary salt effect (6)

OR

- c) i) Define the terms :
 - 1) Rate constant
 - 2) Order & reaction
 - 3) Relaxation time
- ii) The energy of activation for a particular reaction is 25.4 Kcal/mole and rate constant is $2.02 \times 10^{-5} \text{ sec}^{-1}$ at 40°C . Calculate Arrhenius frequency factor (3+3=6)

PGIS-N 1016 B-14**M.Sc. Ist Semester (CBCS) Degree Examination****Chemistry****(Analytical chemistry Treatment of Quantitative Results, Gravimetry,
Titrimetry Ion-Exchange and Solvent Extraction)****Paper - SCT:1.1****(New)**

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:*Answer all the questions*

1. Answer any eight of the following (8x2=16)
- a) Explain the term peptization in the method of gravimetric analysis
 - b) What is students t- test? Give its significance
 - c) Distinguish between precision and accuracy
 - d) In the titration of a weak acid with a strong base, which indicator is used? Give reasons
 - e) Distinguish between co-precipitation and post precipitation
 - f) Enumerate the factors affecting the titration curve shape in the complexometric titrations
 - g) Distinguish between chelating and non-checking agents
 - h) What is meant by capacity of ion-exchange resins?
 - i) Listout the factors affecting solvent extraction
 - j) What are specific and non-specific indicators?

2. a) From the following titre values, calculate the mean range, standard deviation, median and coefficient of variation (5)
12.26, 12.28, 12.25, 12.0, 12.29 and 12.27ml
- b) What are random errors? Distinguish between absolute and reactive errors (5)
- c) explain the significance of the following (6)
- i) Quality control
- ii) quality assurance

Or

Which test has to be followed to compare the precisions of two sets of data?
Explain with an example

3. a) Explain the factors that influence the solubility of the precipitates in gravimetry (5)
- b) What type of solvents used for non-aqueous titrations and how is the end point detected in these titrations (5)
- c) what are acid-base indicators? Explain the mechanism of colour change during the acid-base titration with suitable example (6)

Or

Explain the role of acid-base titrations in the determination of nitrates and air pollutants like SO_2

4. a) Discuss the volhard method of precipitation titrations (5)
- b) Explain the titrations of cyanide with Ag^+ (5)
- c) Explain the role of EDTA titrations in the determination of hardness of water and manganese and zinc in a mixture (6)

Or

Explain the role of masking and demasking agents in EDTA titrations

5. a) Discuss the ion exchange method for the separation of lanthanides and actinides (5)
- b) What are solvent extraction techniques? Discuss the factors affecting the solvent extraction (5)
- c) What are ion-exchangers? How are they classified? Discuss their applications in the separation of amino acids and hydrometallurgy (6)

Or

Discuss the following methods

- i) Determination of lead by dithiazone and
- ii) Determination of molybdenum by thiocynate
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PGIS-N 1011 B-14
M.Sc. Ist Semester (CBCS) Degree Examination
Chemistry
(Organic Chemistry - I)
Paper - HCT : 1.2
(New)

Time : 3 Hours

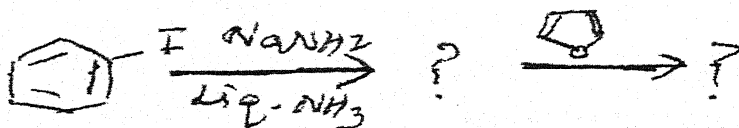
Maximum Marks : 80

Instructions to candidates:

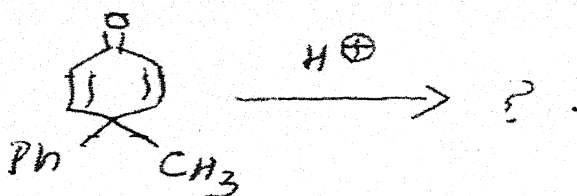
All questions are compulsory and carry equal marks

1. Answer any **eight** of the following (8×2=16)

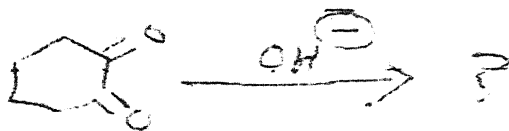
- a) What are alternant and non alternant hydro carbons? Give examples.
- b) Benzamide undergoes Hofmann reaction while N-methyl - benzamide does not. Give reason
- c) Allyl bromide undergoes nucleophilic substitution reaction by SN^1 mechanism. Where as Vinyl bromide does not undergo either SN^1 or SN^2 reaction. Explain.
- d) The 1H NMR spectrum of [18] annulene shows two signals at δ 1.9 and 5.1 with relative intensity of 1:2. Account for
- e) Predict the product in the following



- f) Formulate the product in the following



- g) PhCHClCOCH_3 and $\text{PhCH}_2\text{COCH}_2\text{Cl}$ gave the same product on treating with NaOEt . Account for
- h) Predict the product in the following



- i) Formulate a method for the generation of singlet carbene.
- j) Describe the mechanism of Smiles rearrangement
2. a) What is Huckel's rule? Explain the difference between non-aromatic, antiaromatic and homo aromatic systems (5)
- b) Write briefly on tautomerism and valence tautomerism (5)
- c) Explain the significance of hyper conjugation in predicting the stability of carbonium ions

Or

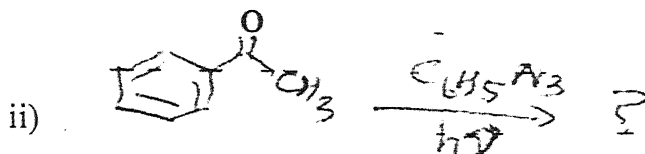
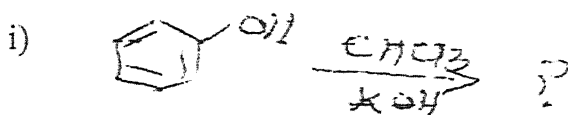
Write short note on :

- i) Addition compounds
- ii) Inclusion compounds (6)
3. a) Explain the utility of cross over experiments in identifying the mechanism of reactions with suitable examples (5)
- b) What are non-classical carbonium ions? Give evidence for the existence of electron sufficient non-classical carbonium ions (5)
- c) Explain briefly the structure of the substrate and nucleophile on SN^1 and SN^2 reaction mechanism

Or

Predict the products and propose mechanisms in the following

(6)



4. a) What is curtain-Hammett principle? Explain its application to the dehydro halogenation of chloro cyclohexane (5)

b) Write the projection formulae for the following compounds

i) 2S, 2R-Tartaric acid

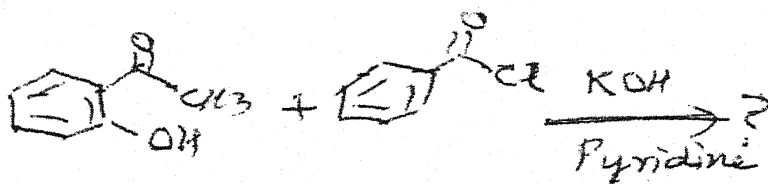
ii) 1R,3S-cyclohexane-1,3-diol (5)

c) How is the configuration of geometrical isomers determined? Describe any two methods

Or

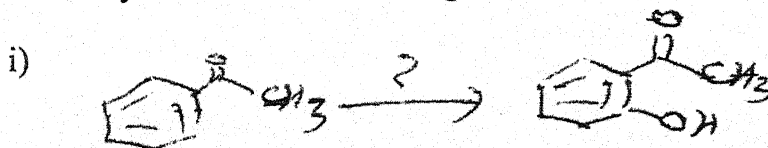
Describe the relationship between elements of symmetry and optical activity with suitable examples (6)

5. a) Predict the product and propose mechanism (5)



b) What are the common features in Hofmann, Curtius and Lossen rearrangements? Explain with suitable example (5)

c) How do you achieve the following transformations?



ii) p - Nitrophenoxy acetamide $\xrightarrow{?}$ N -p-nitrophenyl hydroxy acetamide

Or

Write the synthetic applications of the following

i) Sommelet-Hauser rearrangement

ii) Neber rearrangement

(6)

PGIS-O 1012 B-14
M.Sc. Ist Semester (Non-CBCS) Degree Examination
Chemistry
(Organic Chemistry-I)
Paper - CHEMT-1.22
(Old)

Time : 3 Hours

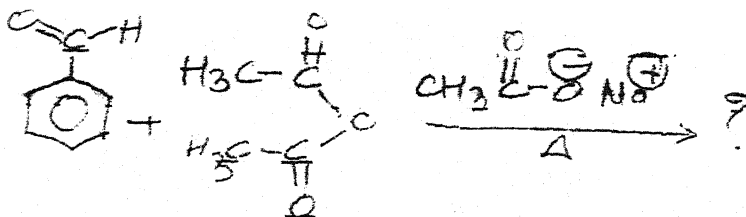
Maximum Marks : 80

Instructions to candidates:

- i) *All the questions are compulsory*
- ii) *All questions carry equal marks*

1. Answer any eight of the following (8×2=16)

- a) What are cryptands? Give two examples
- b) Differentiate between alternant and non-alternant hydrocarbons using appropriate examples
- c) Draw the structures of singlet and triplet carbenes
- d) Predict the product(s) in the following reaction and name the reaction



- e) What are threo and erythro isomers? Explain with examples.
- f) Draw sawhorse formulae for (+) tartaric acid, (-)- tartaric acid and meso-tartaric acid.
- g) Write the structures of purine and pyrimidine bases present in DNA

h) Why is sucrose non-reducing sugar, while maltose is reducing sugar (8×2=16)

2. a) With the help of molecular orbital diagram, explain the aromaticity of cyclic ions taking one example from cyclic cation and one example from cyclic anion
- b) Explain hybridization of carbon atom in ethane and ethene and comment on their geometry
- c) Differentiate between aromatic, antiaromatic and non-aromatic compounds using suitable examples justify your answer

Or

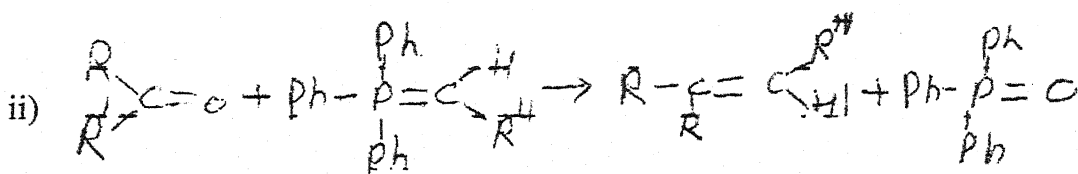
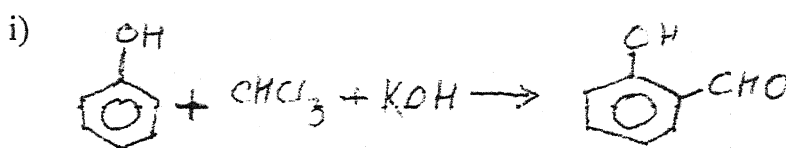
Write notes on the following

i) Crown ethers

ii) Bonding in fullerene

(5+5+6=16)

3. a) What are carbocations? How are they generated? Discuss the reactions of carbocations
- b) The reaction between cis-2-butene with diazomethane in presence of light given exclusively cis product in gaseous medium where as forms a mixture of cis and trans products in liquid medium explain this observative giving reasons
- c) Name the following reactions and illustrate their mechanism



Or

- i) Point out the similarities and differences between Hoffmann and Schmidt rearrangements

- ii) Why does 3-chlorotoluene gives mixture of 3-aminotoluene and 4-aminotoluene on reaction with ammonia in presence of strong base. (5+5+6=16)

4. a) Discuss different elements of symmetry
b) Describe optical activity exhibited by allenes and spiranes
c) Explain one physical method and two chemical methods to determine the configuration of geometrical isomers

Or

Write notes on the following

- i) Optical activity exhibited by - tartaric acid
ii) Conformational analysis of - cyclohexane (5+5+6=16)

5. a) Enumerate the evidences that led to the structure of sucrose.
b) With a neat labeled diagram describe the double helical structure of DNA.
c) Discuss the role of blocking agents in peptide synthesis with appropriate examples.

Or

Discuss the role of r-RNA, m-RNA and t-RNA in the process of - translation.
