

PGIS-N 1009 B-15
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:

1. Answer **all** the questions
2. All questions carry **equal** marks.

1. Answer any **Eight** questions. (8×2=16)
- a) Explain the significance of radius ratio rules.
 - b) Write the expression for Kapustinskii equation and indicate the terms involved.
 - c) State the eighteen electron rule? Calculate the electron count for $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$.
 - d) Explain why a sigma bond is stronger than pi bond.
 - e) Write the consequences of Schottky and Frenkel defects in crystals.
 - f) Why do tetrahedral complex of the type $[\text{MA}_2\text{B}_2]$ does not show geometrical isomerism.
 - g) Define spin orbit coupling constant.
 - h) Write the requirements for orbital contribution to magnetic moments.
 - i) Explain the Lux-Flood concept with examples.
 - j) Urea is an acid in liquid ammonia but a base in glacial acetic acid. Justify with suitable reaction.

2. a) Discuss Fajan's rule for understanding the existence of covalent character in ionic compounds. (5)
- b) Derive Born-Land's equation and show how the lattice energy of NaCl crystal is determined? (5)
- c) Discuss the VSEPR concept and explain the structures of XeF_4 , IF_7 and PCl_5 . (6)

OR

Draw the molecular orbital diagram for the homo-nuclear diatomic molecule. Calculate the bond order and comment on their magnetic properties.

3. a) What are metal carbonyls? Discuss the methods of preparation, properties and structures of some typical metal carbonyls. (5)
- b) Discuss in detail about the stoichiometric and non-stoichiometric defects in solids. (5)
- c) What are semiconductors? Explain what is meant by n-type and p-type semiconduction? What is the effect of temperature on semiconduction. (6)

OR

- a) Explain the structures and applications of the metal nitrosyl complexes.
- b) Write the preparation of dioxygen complexes.
4. a) Outline a method for the determination of magnetic susceptibility of a paramagnetic sample. (5)
- b) Discuss the stereochemistry of complexes exhibiting coordination number 5 and 7. (5)
- c) Draw the molecular orbital diagram of $[\text{CoF}_6]^{3-}$ and explain the metal ligand bonding and properties of the complex. (6)

OR

What do you understand by optical isomerism? Discuss the optical isomerism of complexes of the type $[\text{M}(\text{aa})_3]$, $[\text{M}(\text{aa})_2\text{bc}]$, $[\text{M}(\text{aa})\text{b}_2\text{c}_2]$, and $[\text{Mabcdef}]$.

5. a) With suitable examples, demonstrate the effect of back strain, front strain and internal strain in the molecules with reference to Lewis character. (5)
- b) Give the classification of hard-soft acids and bases with suitable criteria. (5)
- c) Explain with the examples the types of reaction involved in acetic acid and anhydrous sulphuric acid. (6)

OR

Write a note on

- i) Irving William series and
- ii) Solvent system and levelling effect
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PGIS - N 1013 B-15
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.

Answer any eight sub-questions

(2×8=16)

1.
 - a) Explain the effect of temperature and catalyst on energy of activation. Show them graphically
 - b) What is Salt effect? Calculate 10 ml strength of 0.08 N $K_4Fe(CN)_6$ aqueous solution at room temperature
 - c) What are fast reactions? What is the time scale for fast reactions?
 - d) Explain graft copolymer and random copolymer
 - e) Explain optical isomerism in polymers
 - f) Determine mean ionic activity coefficient of 0.01M $CuSO_4 \cdot 5H_2O$ solution at room temperature.
 - g) Calculate pH of buffer solution containing 0.1M acetic acid and
 - h) Give the significance of entropy of activation 0.01 M sodium acetate. If PKa of acetic acid is 4.75
 - i) Distinguish between orthogonality and normalisation of a wave function.
 - j) Give reasons for photoelectric effect representing as particle nature.
2.
 - a) Explain significance of energy of activation. Can the activation energy of a reaction

be zero or negative? The gaseous first order reaction has activation energy 38Kcal/mole. Calculate the ratio of its rate at 30°C and 40°C (5)

b) Derive the expression $K=A.e^{-E_a/RT}$. The rate constant for a first order reaction is $4.5 \times 10^{15} \times e^{-65000/RT} \text{ sec}^{-1}$. Calculate energy of activation (5)

c) Discuss relaxation method of studying fast reactions. How this method difference from conventional method (6)

OR

c) Explain

i) Lindemann Theory of unimolecular rates

ii) Secondary Salt effect (6)

3. a) Discuss viscosity method of determining polymer molecular weight. For a polymer solution in chloroform Mark-Houwink constants 'K' and 'a' are 3.5×10^{-6} and 0.75 units respectively. If the Intrinsic viscosity of a polymer is $175 \text{ cm}^3/\text{g}$. Calculate molecular wt of polymer (5)

b) Discuss the osmotic pressure method of determining molecular weight of a polymer. In an osmotic pressure experiment plot of ' π/c ' vs ' c ' gives a straight line with slope 0.675×10^{-4} . Calculate the molecular mass of a polymer (Interup is 3.1×10^{-3}) (5)

c) Explain

i) Polydispersity index

ii) Glass transition temperature and melt temperature

iii) Theta temperature and theta solvent (6)

OR

c) Give an account of

i) Commercial importance of polymer

ii) Significance of polymer molecular weight (6)

4. a) i) Explain the effect of dilution conductance and specific conductance

ii) State the laws of Debye-Huckel limiting law for conductance of strong electrolytes. (5)

b) Derive Handerson-Hassalback equation. Explain the use of this equation in preparation of buffer solutions (5)

c) i) What are Maxwell's relations? Derive any two of them

ii) Derive the expression

$$\Delta A = RT \ln f_2 / f_1 \quad (6)$$

OR

c) Show that $\Delta A = \Delta E + T \left(\frac{\partial}{\partial t} (\Delta A) \right)$. Give the significance of this equation (6)

5. a) Represent molecular energy level diagram for N_2 and O_2 molecules (5)

b) State the postulates of quantitative mechanics and define schrodinger wave equation. (5)

c) Give the characteristics of σ , σ^* , π and π^* molecular orbitals (6)

OR

c) Represent resonance and overlap integrals for H_2 and give their explanations (6)

PGIS-N 1016 B-15
M.Sc. Ist Semester (CBCS) Degree Examination
Chemistry
(Analytical Chemistry-I)
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. (8×2=16)
- a) Differentiate between precision and accuracy.
 - b) What is detection limit? Give its significance.
 - c) Mention the role of Quality control in analytical laboratories.
 - d) What is meant by peptization in gravimetric analysis? Explain.
 - e) Write the structure of phenolphthalein. Why two indicators are used in the determination of carbonates and bicarbonates?
 - f) A 10.0 mL of waste water sample containing calcium consumed 15.0 mL 0.05 MEDTA solution during the titration. Calculate the amount of calcium in the water sample.
 - g) List the factors affecting the shape of precipitation titration curves.
 - h) Distinguish between stepwise and overall formation constants.
 - i) Define in exchange capacity of a resin. List the factors affecting exchange capacity of a resin.
 - j) What is synergistic extraction? Explain with example.
2. a) What are errors? How they can be minimized in the analytical laboratory? Explain. (5)

- b) A steel sample was analyzed for iron using a newly developed method and obtained the following results. 45.8; 53.2; 47.6; 51.7 and 49.4 mg. The new method was compared with standard method and obtained following results : 47.7; 48.3; 48.9; 47.4; and 48.1 mg. Find whether the new method is significantly different from standard method at 95% confidence level. (Given F-value at 95% confidence level = 6.39). (5)
- c) What is sampling process? Explain the sampling procedure for solids, liquids and gaseous samples. (6)

OR

Describe the application of linear least squares in constructing a best straight line for a set of measurements.

3. a) Construct the titration curve for the titration of 0.1N NaOH with 50 mL 0.1N H_2SO_4 . (5)
- b) With the help of chemical reactions, discuss the determination of nitrogen in a given sample by using acid-base titration. (5)
- c) Briefly describe the merits of precipitation from homogeneous solution and explain the gravimetric procedure for the determination of nickel as dimethyl glyoximate. (6)

OR

What are non-aqueous solvents? Briefly describe the procedure for the determination of phenols by non-aqueous acid-base titrations.

4. a) Explain the application of different types of indicators in precipitation titrations. (5)
- b) What are metal-ion indicators? Write the structure of Eriochrome Black-T and discuss the mechanism of color change at the end point of complexometric titration. (5)
- c) Write a note on different types of titration methods employing EDTA titrant in complexometric titrations. (6)

OR

- i) Briefly describe the application of EDTA titration in determination of hardness of water.
- ii) Describe the titration of chloride with Hg^{2+} by complexometric titration.

5. a) Write the synthetic procedure for cation and anion exchange resins. (5)
- b) What is the principle of solvent extraction? A 25 mL aqueous solution of 0.15M butyric acid shaken with 10 mL ether. After layers separated, it was found by titration that 0.6 mmol of butyric acid remain in aqueous layer. Calculate the percent extracted and distribution ratio for the given sample. (5)
- c) Discuss the application of ion-exchangers in separation of lanthanides and actinides. (6)

OR

What are extraction reagents? Describe the procedure for the determination of iron as 8-hydroxy quinolate.

PGIS-N 1011 B-15
M.Sc. Ist Semester (CBCS) Degree Examination
Chemistry/Organic Chemistry
(Organic Chemistry-I)
Paper : HCT - 1.2
(New)

Time : 3 Hours

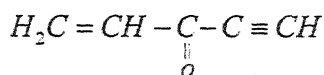
Maximum Marks : 80

Instructions to Candidates:

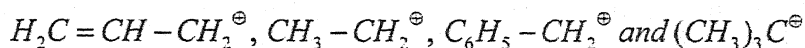
- 1) Answer **ALL** the questions
- 2) All questions carry **equal** marks

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

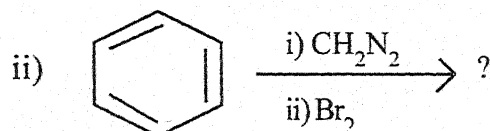
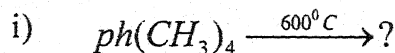
- a) Explain the bonding in EDA complex between ethylene and silver ions
- b) Indicate the type of hybridization and bond angle in each of the carbon atoms in the following compound.



- c) Write the following carbocations in the decreasing order of their stability.

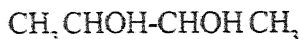


- d) How do you differentiate between singlet and triplet carbenes?
- e) Write the formula of the carbon intermediate formed during the following reactions.

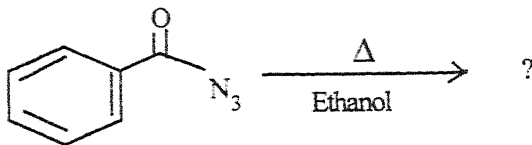


- f) Explain the difference between configuration and conformation?

- g) Draw the possible stereo isomers of the following (Fischer projection) and indicate them as optically active, inactive or meso.



- h) Benzamide undergoes Hofmann rearrangement but N-methyl benzamide does not? Explain.
- i) Formulate the product(s) in the following and give suitable explanation.



- j) Give the mechanism of Fries rearrangement.

2. a) State Huckel's rule. Explain the aromaticity of the following giving reason.



- b) Explain the utility of the following with suitable examples.

- i) Crown ethers
- ii) Cyclodextrins

- c) Write an account of hydrogen bonding. How it contributes for the abnormal behaviour of water?

(OR)

- c) With examples, Explain the following

- i) Delocalized chemical bonding.
- ii) Bonding in Fullerenes

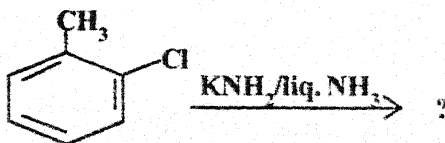
(5+5+6=16)

3. a) What is isotopic labelling? Describe the application of this technique in the determination of reaction mechanism.
- b) Describe different methods for the formation of carbenes and discuss their insertion reactions.
- c) How are free radicals generated? Discuss briefly the reactions of free radicals.

(OR)

- c) Formulate the structures of product(s) in the following reaction and suggest suitable mechanism

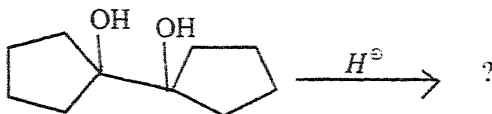
(5+5+6=16)



4. a) Describe the procedure for assigning R and S of chiral compounds. (5+5+6=16)
 b) Discuss the relationship between optical activity and elements of symmetry.
 c) Write an account of Curtin-Hammett principle relating the products to energies of the transition states.

(OR)

- c) Draw the potential energy diagram of different conformations of butane and discuss their relative stability.
 5. a) Discuss the mechanism of wittig reaction and give its synthetic applications.
 b) Formulate the product(S) and describe the mechanism in the following.



- c) Describe the mechanism in the following
 i) Beckman rearrangement
 ii) Benzylic acid rearrangement current.

(OR)

- c) Write the product(s) and describe the mechanism :

(5+5+6=16)

