

(8)



[This question paper contains 8 printed pages]

Your Roll No. : *2019*

S1. No. of Q. Paper : **2201** **IC**

Unique Paper Code : 32171401

Name of the Course : **B.Sc. (Hons.) Chemistry**

Name of the Paper : Inorganic Chemistry- III,
Coordination Chemistry

Semester : IV

Time : 3 Hours **Maximum Marks : 75**

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
- (b) Attempt **Six** questions in **all**.
- (c) Question **No. 1** is compulsory.

1. Attempt any **five** of the following : **5×3=15**

- (i) In comparison to lanthanoids, actinoids have greater tendency to form complexes. Explain.
- (ii) Metal ions with d^3 and d^8 electronic configuration, prefers octahedral geometry. Justify.

P.T.O.

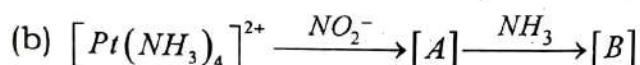
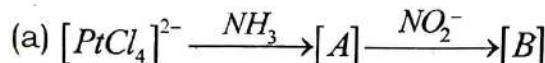
- (iii) Explain the variation of lattice energy of the divalent 3d transition metal halides.
- (iv) When hydrogen peroxide is added to the solution of potassium dichromate in dilute sulphuric acid and the resultant solution is shaken with ether, a blue coloured solution is obtained. Give the relevant chemical equation and the structure of the compound responsible for imparting blue colour in ether.
- (v) What is nephelauxetic effect? How does this effect explain the covalent nature of metal-ligand bonds?
- (vi) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is square planar, while CuCl_4^{2-} is tetrahedral. Give reason.
- (vii) Why do transition metals act as good catalysts?
2. (i) Name the following complexes according to the IUPAC system of nomenclature (attempt any four) : 4
- (a) $[(\text{en})_2\text{Co}(\text{O}_2)(\text{NH}_2)\text{Co}(\text{en})_2](\text{NO}_3)_4$
- (b) $[\text{Co}(\text{CO}_3)(\text{NH}_3)_4]\text{NO}_3$
- (c) $\text{K}_2[\text{OsCl}_5\text{N}]$
- (d) $\text{Na}[\text{Pt Br Cl}(\text{NH}_3)(\text{NO}_2)]$
- (e) $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$
- (ii) Write the formulae of the following complexes (attempt any four) : 4
- (a) Tris(ethylenediamine)cobalt(III) hexacyanidochromate(III).
- (b) Tetraamminechloridonitrit-N-cobalt(III)ion
- (c) Tetrakis(triphenylphosphane)platinum (0)
- (d) Pentaamminethiocyanato-N-chromium (III)tetrachloridozincate(II)
- (e) Potassium tetraazidocobaltate(II)
- (iii) A solution containing 0.319 g of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was passed through cation exchange resin in the acid form and the acid liberated was titrated with a standard solution of NaOH. This required 28.5 mL of 0.125 M NaOH. Determine the correct formula of Cr(III) complex. 4

3. (i) Why Charge transfer transitions give rise to more intense absorptions ? State the nature of transitions responsible for colour in the following species : 4

- (a) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
- (b) KMnO_4
- (c) $[\text{Fe}(\text{dipy})_3]^{2+}$ and
- (d) CrO_4^{2-}

- (ii) The complex $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ exists in two isomeric forms α and β . The α -form reacts with oxalic acid to form $[\text{Pt}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$ whereas β -form gives $[\text{Pt}(\text{NH}_3)_2(\text{C}_2\text{O}_4\text{H})_2]$. Give the structures of α and β forms. Explain what physical method can be used to differentiate between the two forms. 4

- (iii) Based on **Trans effect**, write the products of the following reactions : 4



4. (i) Using the valence bond theory, predict the type of hybridization involved, along with the geometry and the magnetic moment (in Bohr magnetons) for $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{MnF}_6]^{3-}$.

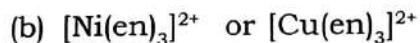
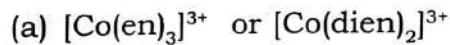
- (ii) Coordinated water molecules in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ can be successively replaced by 2,2'-dipyridyl, finally resulting in the formation of $[\text{Fe}(\text{dipy})_3]^{2+}$. In this process, the third equilibrium constant is observed to be greater than the second one. Explain. 4

- (iii) The magnitude of the crystal field splitting in tetrahedral complexes is considerably less than in octahedral fields. Explain. 4

5. Explain the following :

- (i) Show by means of a diagram, how the pattern of d-orbital splitting changes as an octahedral complex undergoes tetragonal distortion and eventually becomes a square planar complexes. 4

- (ii) Why are chelated complexes more stable in comparison to non-chelated complexes ? Which one of the following is more stable ? Justify your answer : 4



(iii) NiFe_2O_4 is inverse spinel while Mn_3O_4 is a normal spinel. Explain on the basis of CFT.

4

6. (i) Indicate the type of isomerism exhibited by the following pairs of isomers and suggest one method in each set to distinguish them :

4

(a) cis - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and trans - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

(b) $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$

(ii) On the basis of molecular orbital theory, explain the order of Δ_0 for octahedral complexes having the ligands I^- and CO .

(iii) Calculate in kJmol^{-1} , the crystal field stabilization energy attained by Fe^{2+} ion in an octahedral oxide ion environment. Given, Δ_0 for Fe^{2+} in oxide ion environment is 124 kJmol^{-1} . What will be the value of CFSE in a tetrahedral environment of oxide ion.

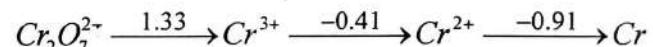
4

7. (i) Explain the effect of temperature on magnetic susceptibility of ferromagnetic and antiferromagnetic materials. 4

(ii) In the electronic spectra of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ single broad peak with maximum at 20300 cm^{-1} is observed. Explain. 4

(iii) What is lanthanoid contraction ? What are the major consequences of lanthanoid contraction ? 4

8. (i) Given below are the Latimer diagram for Cr in acidic medium : 6



Answer the following questions :

(a) Write the half reaction for the conversion of $\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cr}^{3+}$

(b) Is there any tendency of Cr^{2+} to reduce to Cr ? Give reasons.

(c) Calculate the skip step emf for $\text{Cr}^{3+} \longrightarrow \text{Cr}$ change.

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- (ii) A blackish brown coloured solid (A) when fused with alkali metal hydroxides in presence of air produces a dark green compound (B), which on electrolytic oxidation in alkaline medium gives a dark purple coloured solution of compound (C). Acidified aqueous solution of (C) on treatment with oxalic acid gives a colourless species (D). Identify (A), (B), (C) and (D). Also explain the sequence of reactions involved. 6

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[This question paper contains 4 printed pages]

Your Roll No. : 

Sl. No. of Q. Paper : **2202** **IC**

Unique Paper Code : 32171402

Name of the Course : **B.Sc. (Hons.) Chemistry**

Name of the Paper : Organic Chemistry - III

Semester : IV

Time : 3 Hours

Maximum Marks : 75

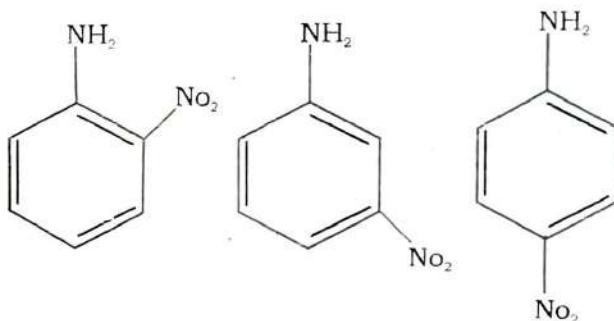
Instructions for Candidates :

- Write your Roll No. on the top immediately on receipt of this question paper.
- Attempt **six** questions in **all**.
- Question **NO.1** is compulsory and carries **15** marks.
- All** other questions are of **12** marks each.

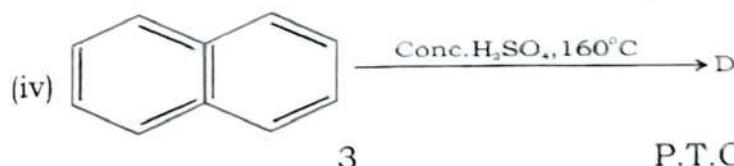
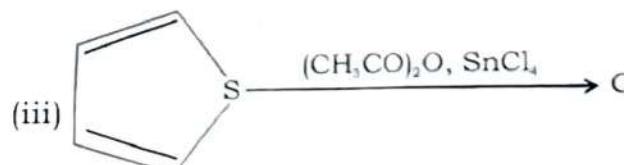
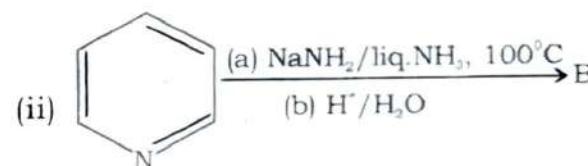
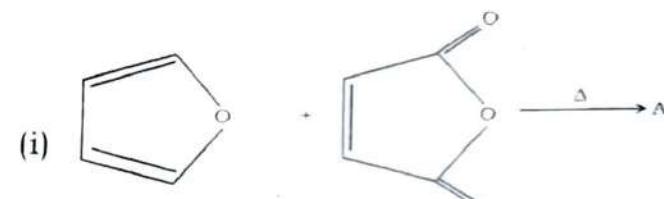
- 1.** (a) Amine 'A' (C_7H_9N) reacts with benzoyl chloride in the presence of sodium hydroxide to give compound 'B' ($C_{14}H_{13}NO$). 'A' reacts with benzene sulphonyl chloride in potassium hydroxide solution to give water insoluble precipitate of compound 'C'. Identify compound A and give equation for its conversion into the compound B and C. Name the reaction involved in the conversion of A to B with mechanism. 6

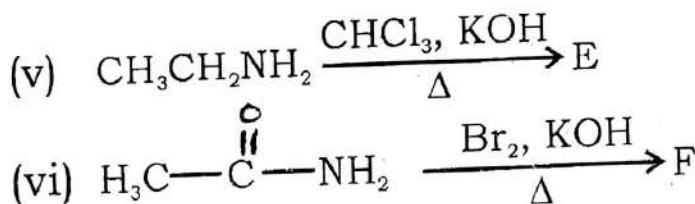
P.T.O.

- (b) Anthracene undergoes electrophilic substitution reactions at 9-position. Explain. 3
- (c) How will you distinguish between 1° , 2° and 3° amines using Hinsberg test. 3
- (d) Suggest a best reagent for the conversion of pyrrole to (i) 2-nitropyrrole, (ii) Pyrrole-2-sulphonic acid, and (iii) Pyrrole-2-aldehyde. $1 \times 3 = 3$
2. Carry out the following conversions using the necessary reagents : $3 \times 4 = 12$
- Nitrobenzene to p-nitrophenol
 - Aniline to p-nitrobenzoic acid
 - Naphthalene to o-aminobenzoic acid
 - Pyridine to 2-pyridylacetic acid
3. (a) Arrange the following nitroanilines in the order of decreasing basicity with suitable explanation : 3



- (b) Give the order of reactivity of 5-membered heteroaromatic compounds with suitable explanation. 3
- (c) Pyridine undergoes nucleophilic substitution mainly at position-2. Explain. 3
- (d) Pyrrole does not undergo Diels-Alder reaction while N-acetyl pyrrole undergoes Diels-Alder reactions. Explain. 3
4. Complete the following and write the name of reaction involved in each case : $2 \times 6 = 12$





5. (a) Explain the reactions which indicate the position of linkage between pyridine and N-methylpyrrolidine in nicotine. 6
- (b) How will you distinguish between nitriles and isonitriles ? Explain giving reactions involved. 3
- (c) What is isoprene rule ? Indicate the isoprene units in the structure of citral. 3
6. (a) Give the synthesis of nicotine from nicotinonitrile. 6
- (b) What happens when : $2 \times 3 = 6$
- (i) Citral is treated with aq. K_2CO_3
 - (ii) Nicotine is treated with $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$
 - (iii) Phenanthrene is subjected to ozonolysis.
7. Write short note on the following (any **three**) :

 $4 \times 3 = 12$

- (a) Gabriel phthalimide synthesis
- (b) Skraup Quinoline synthesis
- (c) Fischer Indole synthesis
- (d) Hoffmann bromamide degradation



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[This question paper contains 8 printed pages]

Your Roll No. : 2019

Sl. No. of Q. Paper : **2203** **IC**

Unique Paper Code : 32171403

Name of the Course : **B.Sc. (Hons.) Chemistry**

Name of the Paper : Physical Chemistry-IV

Semester : IV

Time : 3 Hours **Maximum Marks : 75**

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
- (b) Attempt **six** questions in all.
- (c) Question **No.1** is compulsory.
- (d) Attempt at least **one** question from each **Section**.
- (e) Use of scientific calculator is permitted.

1. Explain any **five** of the following : 5×3

- (a) Larger the activation energy, greater is the effect of temperature rise on rate constant.
- (b) The molar conductivity of Li^+ ion is less than that of Cs^+ ion in aqueous medium.

P.T.O.

- (c) Walden's Rule is not applicable to cations of small size.
- (d) Rate of a photochemical reaction is independent of the initial concentration of the reactants.
- (e) Quantum efficiency of fluorescence decreases with the concentration of the solution.
- (f) Beer's law fails in case of aqueous dilute $K_2Cr_2O_7$ solution.
- (g) It is rare for a reaction to have molecularity more than three.

Section - A

2. (a) Discuss the asymmetry effect and electrophoretic effect in Debye Huckel Onsager theory. 4
- (b) Explain using Grotthus mechanism, how H^+ ion and OH^- ions have abnormally high conductance values. 3
- (c) The conductivity of a saturated solution of $[Co_2Fe(CN)_6]$ is $3.00 \times 10^{-6} \Omega^{-1} cm^{-1}$ and that of water used is $4.1 \times 10^{-7} \Omega^{-1} cm^{-1}$. The ionic molar conductivities of Co^{2+} and $Fe(CN)_6^{4-}$ are $87 \Omega^{-1} cm^2 mol^{-1}$ and $444 \Omega^{-1} cm^2 mol^{-1}$ respectively. Calculate the solubility and solubility product of $[Co_2Fe(CN)_6]$ in water at $25^\circ C$. 5

3. (a) What is transference number ?

Derive the expression $t \propto v$ for an ion where t is the transference number and v is the absolute velocity of the ion. 5

- (b) Explain Wien effect. 3

- (c) A potential of 5.60 V is applied to two electrodes placed 11 cm apart; how far is an ammonium ion expected to move in 2 hours in a dilute solution of ammonium salt at $25^\circ C$? (Given : $\lambda(NH_4^+) = 73.4 \Omega^{-1} cm^2 mol^{-1}$) 4

4. (a) Calculate the transport numbers of H^+ ion and Cl^- ion from the following data obtained from the moving boundary method using cadmium chloride as the indicator electrolyte.

(Given : Atomic mass of Ag = $108 g mol^{-1}$)

Concentration of HCl solution = 0.100 N

Mass of silver deposited in the coulometer

= $0.1209 g$

Movement of the boundary = $7.50 cm$

Cross – section of the tube = $1.24 cm^2$

- (b) Discuss the titration curves obtained in the conductometric titrations of : 4
- HCl versus NaOH solutions
 - CH_3COOH versus NaOH solutions
- (c) Molar conductivity of 0.01 M solution of MgCl_2 is $195 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at 25°C . A cell with electrodes that are 1.80 cm^2 in surface area and 0.50 cm apart is filled with 0.01 M MgCl_2 solution. How much current will flow when the potential difference between the two electrodes is 5.0 V ? 4

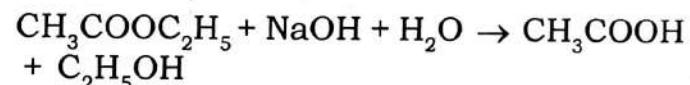
Section - B

5. (a) For the given **second** order reaction



- Write down its differential rate law and deduce the integrated rate law.
- Show that the half-life of such a reaction is inversely proportional to the initial concentration of A. 4
- Write down the differences between order and molecularity. 3

- (c) The following results were obtained from the saponification of ethyl acetate



using equal concentrations of ester and alkali.

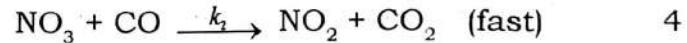
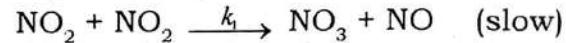
Time/ min	0	4.89	10.07	23.66	∞
Vol. of acid/ml	47.65	38.92	32.63	22.58	11.84

Show that the reaction follows second order kinetics. 5

6. (a) Using Steady State Approximation, derive the differential rate law for the reaction between NO_2 and CO at low temperature.



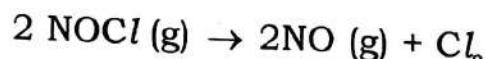
The proposed reaction mechanism is :



- (b) Compare the rate constants as given by Arrhenius equation and the Collision theory and show that : 4

$$E_a = E_0 + \frac{RT}{2}$$

- (c) For the reaction :



The rate constant is $2.8 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $7.0 \times 10^{-1} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 300 K and 400 K respectively. What is the energy of activation for the reaction ? 4

7. (a) Kinetics of enzyme catalysed reactions is studied by Michaelis - Menten mechanism. Using the Steady State approximation, relate enzyme and substrate concentration to rate of the reaction. Also discuss when Michaelis Menten constant \gg substrate concentration, how the rate variation takes place. 4

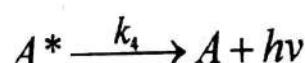
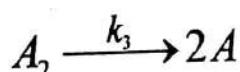
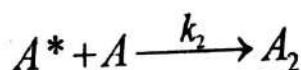
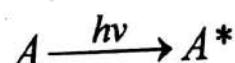
- (b) Outline any **two** methods which are employed for determination of order of a reaction. 4

- (c) At 380°C , the half life period for the **first** order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1} . Calculate the time required for 75% decomposition at 450°C . 4

Section - C

8. (a) Derive Stern -Volmer Equation. What is its significance ? 5
- (b) What is Quantum yield or quantum efficiency ? Write down the reasons for high and low quantum yield. 3
- (c) In the photochemical combination of $\text{H}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ a quantum efficiency of about 1×10^6 is obtained with a wavelength of 480 nm . What amount of HCl will be produced under these conditions if one calorie of radiant energy is absorbed ? 4

9. (a) The mechanism of photochemical dimerisation of Anthracene (A) is given below :



Derive the expression for the rate of formation of dimer, A_2 . 4

- (b) Write the differences between fluorescence and phosphorescence. 3
- (c) Write short notes on any **two** : 2×2.5
- (i) Kohlrausch's law of independent migration of ions
 - (ii) Chemiluminescence
 - (iii) Pseudo-unimolecular reactions

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Your Roll No. _____

Sl. No.: 7) P.P. 3566

2019

Unique Paper Code : 217401

Name of the Course : **B.Sc. (H) CHEMISTRY**

Name of the Paper : Inorganic Chemistry - III (Paper - CHET 408)

Semester : IV

Duration : 3 Hours

Maximum Marks : 75



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Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper
2. Attempt any **FIVE** questions.
3. All questions carry equal marks.

1. Explain any **Five** of the following, giving suitable reasons:

- a) Silicones are inert and water repellent.
- b) $PbCl_2$ is more stable than $PbCl_4$.
- c) Boric acid acts as a strong acid in presence of cis-diols.
- d) Beryllium shows anomalous behaviour in its group.
- e) Solubility of noble gases in water increases on moving down the group.
- f) The solubility of alkaline earth metal sulphates decreases down the group.

(3x5)

2. a) What are silicates ? Discuss the structures of pyro silicates, chain silicates and cyclic silicates.,
- b) What is allotropy ? Explain the various allotropic forms of phosphorus.
- c) Write the names of oxy acids of chlorine in various oxidation states and arrange them in order of increasing acid strength giving justification. (5,5,5)

3. a) What do you understand by diagonal relationship? Explain this relationship between Li and Mg.

b) How will you prepare XeF_2 and XeF_4 . Draw the molecular orbital diagram of XeF_2 .

c) What are interhalogen compounds ? Why are they more reactive as compared to halogens ? Using VSEPR theory discuss the structures of ClF_3 .

(5,5,5)

4. a) Draw the structure of i) Basic Beryllium acetate and ii) XeO_3 .

b) Give the preparation of Borazine. Why is it called Inorganic Benzene? Draw its structure.

c) What are hydrides? How are they classified? State a brief account of ionic hydrides.

(5,5,5)

5. a) Give the preparation and structure of Caro's acid. Give its reaction with i) H_2O_2 and ii) KI.

b) How will you prepare $(\text{NPCl}_2)_3$? Explain the structure and bonding of $(\text{NPCl}_2)_3$. What are the potential uses of these compounds?

c) What is inert pair effect? Explain the inert pair effect by taking example of group 14 elements.

(5,5,5)

6. Write short notes on any Three of the following:

a) Silicones

b) Complexometric Titrations

c) Unusual Oxidation States

d) Pseudohalogens

(5x3)