

2023

Time - 3 hours

Full Marks - 60

*Answer **all groups** as per instructions.*

Figures in the right hand margin indicate marks.

GROUP - A

1. Answer all questions and fill in the blanks as required. [1 × 8]
- (a) Find out co-ordination number of central metal ion in $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$.
- (b) What is the IUPAC name of $[\text{Pt}(\text{Py})_4][\text{PtCl}_4]$?
- (c) Write two important ores of Mn.
- (d) Give example of linkage isomers.
- (e) What are the geometrical isomers of the complex having formula $[\text{M}(\text{aa})_2\text{b}_2]$ aa : bidentate and b : unidentate ligand.
- (f) Write one function of Haemoglobin.
- (g) $(\text{MnO}_4)^{-1} + 8\text{H}^+ + \underline{\hspace{2cm}} = \text{Mn}^{+2} + 4\text{H}_2\text{O}$. (Fill up the gap.)
- (h) Lanthanum ion does not exist in +4 oxidation state.
(State True / False)

[2]

GROUP - B

2. Answer any eight of the following within two or three sentences each. [1½ × 8

- (a) Find out secondary valency of Cr in $K[Cr(NH_3)_2(C_2O_4)_2]$.
- (b) Give one example of Chelating agent.
- (c) Define Crystal field stabilisation energy.
- (d) Between $[NiCl_4]^{-2}$ and $[Ni(CN)_4]^{-2}$, which one is paramagnetic.
- (e) Indicate the hybridisation of metal ion and geometry of $[Co(NH_3)_6]^{+2}$ ion.
- (f) Why is human blood red in colour ?
- (g) Explain : $1\text{ M } KMnO_4 = 5\text{ N } KMnO_4$ solution in acidic medium.
- (h) Write down toxic effect of Mercury.
- (i) Write down uses of Na/K pump.
- (j) Between $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_3Cl_3]$, which one shows conductivity ?

GROUP - C

3. Answer any eight of the following within 75 words each. [2 × 8

- (a) Discuss the geometry of $[Ni(CN)_4]^{2-}$ ion.

[3]

- (b) $\text{CoCl}_3 \cdot 5\text{NH}_3$ when dissolved in water, two chloride ions are precipitated. Its molar conductivity corresponds to 3. What is the formula of co-ordination compound ? Write its IUPAC name.
- (c) Calculate crystal field stabilisation energy for d^5 high spin octahedral.
- (d) Anhydrous Copper Sulphate is colourless but hydrated Copper Sulphate is blue in colour. Explain.
- (e) Discuss Labile and Inert Complex.
- (f) Write down differences of primary and secondary valency.
- (g) What happens when Sodium oxalate is added to warm solution of acidified potassium permanganate solution ? Write the balanced ionic equation.
- (h) Why is Fe(III) more stable than Co(III) ?
- (i) What are the various oxidation states of Vanadium ?
- (j) Why does Zinc show only 2(+) oxidation state ?

GROUP - D

4. Answer any four questions within 500 words each.

- (a) Write down the basic postulates of valence bond theory. Discuss Inner orbital complex with one example. [6]

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- (b) Discuss Lanthanide contraction. E
- (c) Discuss separation of Lanthanoids by ion-exchange method. E
- (d) Discuss the chemistry of CrO_2 referring to preparation and structure. E
- (e) Discuss the chemistry of +4 oxidation state of Titanium. E
- (f) What is Lanthanide contraction? Discuss its causes and consequences. E
- (g) Write a brief note on Catalytic activity and Catalytic cycle. E

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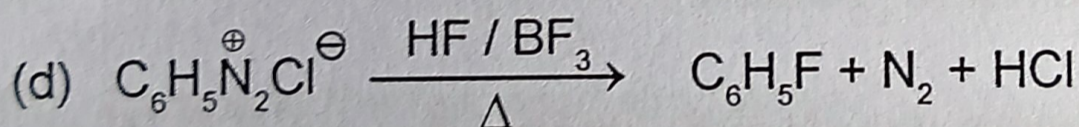
GROUP - A

1. Answer all questions and fill in the blanks as required. [1 × 8]

(a) Primary amine on reaction with nitrous acid forms _____.

(b) Aniline on heating with fuming H_2SO_4 gives _____.

(c) What is a coupling reaction ?



This reaction is known as _____.

(e) How many monosubstituted isomers are possible in Naphthalene ?

(f) Write the structure of Alizarine.

(g) Paal-Knorr synthesis is used for the preparation of _____.

(h) _____ terpenoid is extracted from rose.

[2]

GROUP - B

2. Answer any eight of the following within two or three sentences each. [1½ × 8

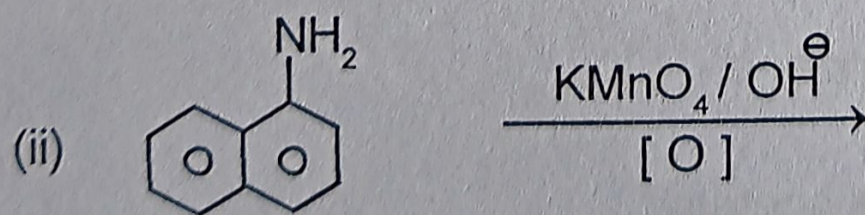
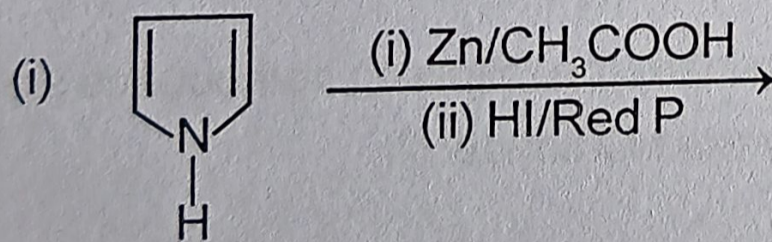
- (a) What is Carbylamine reaction ?
- (b) Arrange the following in the increasing order of their basicity.
p-Toluidine, N, N-Dimethyl-p-toluidine, Aniline, p-Nitro Aniline
- (c) How can you prepare butter yellow dye from BDC ?
- (d) Why excess of HCl is used during diazotisation of Aniline with NaNO_2 and HCl at $0-5^\circ \text{C}$?
- (e) What happens when α -aminonaphthyl amine is oxidised with alkaline KMnO_4 solution ?
- (f) Why naphthalene is more reactive than benzene ?
- (g) Explain why pyrrole is acidic like phenol ?
- (h) Write the structural formula of Imidazole.
- (i) How can you detect an alkaloid if it contains a phenolic $-\text{OH}$ group ?
- (j) What is isoprene rule ?

[3]

GROUP - C

3. Answer any eight of the following within 75 words each. [2 × 8]

- (a) Aniline is a weaker base than cyclohexyl amine. Explain.
- (b) Explain Hoffmann's exhaustive methylation of amine.
- (c) How can you prepare benzoic acid from B.D.C. ?
- (d) Why pH is maintained between 5-7 during the preparation of dye from benzene diazonium chloride with aniline ?
- (e) How can you synthesize α -Naphthoic acid from α -chloro-naphthalene ?
- (f) Describe the formylation of anthracene.
- (g) Explain why pyridine is a stronger base than aniline ?
- (h) Complete the following reactions :



P.T.O.

[4]

- (i) How can you prove the presence of pyridine moiety in Nicotine ?
- (j) Write the structural formula of two geometrical isomers of citral and give their names.

GROUP - D

4. Answer any four questions within 500 words each.

(a) How can you distinguish between 1^o, 2^o and 3^o amines with Hinsberg reagent ? [6]

(b) How can you prepare ethylamine using : [2 × 3]

(i) Curtius degradation method

(ii) Gabriel phthalimide synthesis

(iii) Mannich reaction [6]

(c) How can you prepare the following compounds starting from Benzene Diazonium Chloride ? [2 × 3]

(i) Iodobenzene

(ii) Nitrobenzene

(iii) Phenyl acetate

[5]

- (d) Elucidate the structure of Napthalene. [6]
- (e) Elucidate the structure of Citral. [6]
- (f) Bring out the following conversions : [2 × 3]
- (i) Phenol to Aminocyclohexane
 - (ii) Napthalene to Phthalic acid
 - (iii) Pyridine to 4, 4'-Dipyridyl
- (g) Write short notes on (within 250 words each). [3 × 2]
- (i) Reductive oxidation
 - (ii) Medicinal importance of Morphine

2023

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GROUP - A

1. Fill in the blanks. (all)

[1 × 8

- (a) The relation between specific conductance (K) and equivalent conductance (λ) of an electrolyte is _____.
- (b) Transport number of CH_3COO^- ions is _____ than that of $\text{C}_6\text{H}_5\text{COO}^-$ ions.
- (c) Which among the following is the strongest reducing agent Zn(s), Cr(s), $\text{H}_2(\text{g})$ and $\text{Fe}^{2+}(\text{aq})$?
- (d) According to Debye Huckel theory, the speed of an ion in an electric field is _____.
- (e) The mass of substance deposited by passage of 1 coulomb of charge is called _____.
- (f) In a Galvanic cell, the anode is made up of _____ metal.

P.T.O.

[2]

- (g) A measure of the electric intensity due to presence of ions in the solutions is called _____.
- (h) Potentiometric titrations are used for _____ type of solutions.

GROUP - B

2. Answer any eight of the following within two or three sentences each. [1½ × 8

- (a) Define molar conductance.
- (b) What are the factors determining conductance of an electrolyte ?
- (c) What is the advantage of transport number ?
- (d) What is the principle of conductometric titrations ?
- (e) What is the effect of dilution on equivalent conductance ?
- (f) In the electrochemical cell, $M/M^+ || X^-/X$, $E_{m^+/m}^0 = 0.44 \text{ V}$ and $E_{X/X^-}^0 = -0.33 \text{ V}$. Calculate the E_{Cell}^0 .
- (g) Explain why KNO_3 is used to make salt bridge ?
- (h) How dipole moments value can be used to predict shapes of molecules ?

[3]

- (i) What is Lorenz-Laurentz equation ?
- (j) State Liquid Junction potential.

GROUP - C

3. Answer any eight of the following within 75 words each. [2 × 8]

- (a) The increase in magnitude of equivalent conductance on dilution is more for weak electrolytes than for strong electrolytes. Explain.
- (b) What is Debye Huckel theory for strong electrolytes ?
- (c) Show that the transport numbers of cation and anion is unity.
- (d) Derive a relation between ionic conductance and transport number.
- (e) Define ionic mobility and ionic conductance. How are they related ?
- (f) Differentiate between cell potential and potential difference ?
- (g) What is a reversible electrode ? Give an example.
- (h) Derive a relationship between free energy and electrical energy.

P.T.O.

[4]

- (i) What is Clausius-Mosotti equation used for ?
- (j) Give a method of measuring dipole moment.

GROUP - D

4. Answer any four questions.

- (a) State Kohlrausch law. Calculate the equivalent conductance at infinite dilution of CH_3COOH from the following data :

[2 + 4

$$\Lambda_{0 \text{ HCl}} = 426.2 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{g} \cdot \text{eq}^{-1},$$

$$\Lambda_{0 \text{ CH}_3 \text{ COONa}} = 91 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{g} \cdot \text{eq}^{-1},$$

$$\Lambda_{0 \text{ NaCl}} = 126.5 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{g} \cdot \text{eq}^{-1}$$

- (b) Derive Debye Huckel Onsager equation for strong electrolytes.

[6

- (c) Write notes on :

[3 × 2

(i) Debye-Falkenhagen effect

(ii) Walden's rule

- (d) Describe moving boundary method for determination of transport number. What is the effect of concentration on transport number ?

[4 + 2

- (e) What is Nernst equation ? Derive Nernst equation for the following reaction : $\text{Mn}^+(\text{aq}) + n\text{e}^- \rightarrow \text{M}(\text{s})$

[2 + 4

- (f) (i) How can you determine equilibrium constant from EMF ? [3]
- (ii) Briefly describe concentration Cell. [3]
- (g) (i) Write a note on single electrode potential. [3]
- (ii) Draw the cell diagram that undergoes the following redox reaction : $\text{Ce}^{4+}(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Ce}^{3+}(\text{aq}) + \text{Fe}^{3+}(\text{aq})$. [3]
- (h) (i) How can you determine ionic product of water from conductance measurement ? [3]
- (ii) Write a brief note on molecular polarizabilities. [3]

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GROUP - A

1. Fill in the blanks. (all)

[1 × 8]

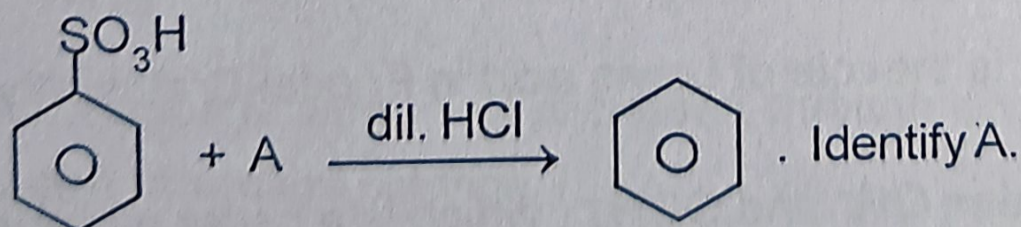
(a) At standard state, the values of pressure and temperature is _____.

(b) The relation between K_p and K_c of the equation
 $2 \text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ is _____.

(c) Ionic product of water is _____ to temperature.

(d) For precipitation to take place, solubility product must be _____ than ionic product.

(e) In the reaction :



(f) The electrophile used in nitration of benzene is _____.

[2]

- (g) What is the product formed when benzene diazonium chloride is treated with cuprous chloride ?
- (h) t-butyl alcohol can be prepared by reacting methyl magnesium bromide with _____.

GROUP - B

2. Answer any eight of the following within two or three sentences each. [1½ × 8

- (a) Define standard enthalpy of formation.
- (b) State bond dissociation energy.
- (c) What is Le-Chatelier's principle ?
- (d) Name two factors affecting degree of ionisation.
- (e) Blue litmus paper turns red in copper sulphate solution. Explain.
- (f) Why dil. HCl is added first followed by passing H₂S gas for detection of Gr II radicals in qualitative analysis ?
- (g) What is the role of Lewis acid in Friedel-Craft's alkylation ?
- (h) Between OH⁻ and OCH₃⁻, which is a better nucleophile and why ?

[3]

- (i) Like alkyl halide, why aryl halide does not undergo nucleophilic substitution reaction easily ?
- (j) How can you convert phenol to salicylic acid ?

GROUP - C

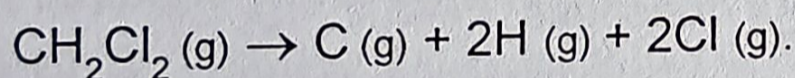
3. Answer any eight of the following within 75 words each. [2 × 8]

- (a) Calculate ΔH^0 for the reaction :



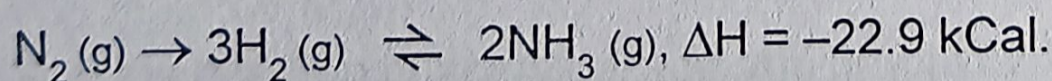
Given that the enthalpies of formation of CH_4 , CF_4 and HF are -75 kJ , -680 kJ and -269 kJ respectively.

- (b) Calculate ΔH of the reaction :



Bond energies of C–H bond and C–Cl bond are $99.28 \text{ kCal mol}^{-1}$ and $77.99 \text{ kCal mole}^{-1}$ respectively.

- (c) What is the effect of temperature and pressure on the following equilibrium :



- (d) What happens when HCl is passed through concentrated solution of sodium chloride ?

- (e) Calculate the pH of 0.0001 M NaOH .

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[4]

(f) Convert : Phenol to O-Cresol

(g) How can you prepare $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{OCH}_3$ from $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Br}$?

Propose a mechanism for the reaction.

- (h) What happens when ethylalcohol is treated with conc. HCl in presence of anhydrous ZnCl_2 ?
- (i) Starting from aniline, how can you prepare phenol ?
- (j) Explain why aldehydes and ketones react with derivatives of ammonia in presence of dil. HCl.

GROUP - D

4. Answer any four questions.

(a) Write short notes on :

[3 × 2

(i) Kirchoff's equation

(ii) Thermochemistry

(b) Derive a relationship between K_p and K_c for the following reaction :



[6

(c) Define solubility of a solute in a given solvent. Calculate the solubility of HgSO_4 . (K_{sp} for HgSO_4 is 6.4×10^{-5}) [2 + 4

[5]

(d) (i) Write a note on electrophilic substitution reaction of benzene. [3]

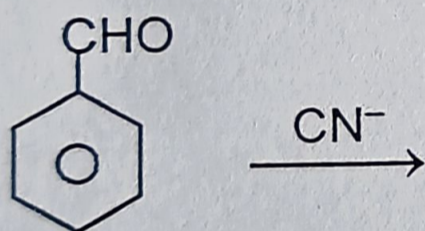
(ii) State Williamson's synthesis. Give its mechanism. [3]

(e) Write short notes on : [3 × 2]

(i) Pinacol-Pinacolone rearrangement

(ii) Oxidation of diols

(f) Complete the reaction giving a suitable mechanism :



What happens when the product obtained is oxidised with conc. HNO_3 ? [2+2+2]

(g) (i) What happens when chlorobenzene reacts with ammonia in presence of potassium amide. [2]

(ii) By the help of a chemical reaction, distinguish between propan-1-ol and propan-2-ol. [2]

(iii) Give the reaction of acetaldehyde and propionaldehyde with dil NaOH . [2]