# RAMAKRISHNA MISSION VIDYAMANDIRA

**(Residential Autonomous College affiliated to University of Calcutta)**

**B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2019**

**SECOND YEAR (BATCH 2018-21)**

Date : 13/12/2019 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm **Paper : III (Gr. B)** Full Marks : 35

**(Use one Answer Book for Unit-I and another Answer Book for Unit II,III,IV)**

**[Attempt one question from each unit]**

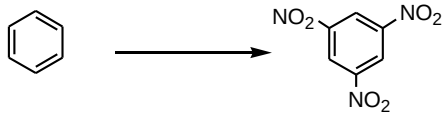
## Unit-I

[10 marks]

1. a) For the synthesis of salicylic acid, Kolbe-Schmidt reaction of sodium phenolate is useful and not potassium phenolate. Explain. [2]

   b) The 2,6-deuterated fluorobenzene and 2,6-deuterated bromobenzene derivatives react differently with $KNH_2$ in liq. $NH_3$. Write the product(s) in each case with justification. [2]

   c) Carry out the following transformations: [2 × 3]

   i) 


   ii) p-Benzoquinone ⟶ Dichlorodicyanoquinone

   iii) N,N-dimethylaniline ⟶ Para-N,N-dimethylaminobenzaldehyde

2. a) Explain the relative rate of aromatic nucleophilic and electrophilic substitution of the following halobenzene with proper explanation.
   Flurobenzene, Chlorobenzene, Bromobenzene and Iodobenzene [2+2]

   b) Account for the following observations:

   i) 1,3-Dichloro-2,5-dinitrobenzene on treatment with methanolic NaOMe produces only 1,3-dichloro-2-methoxy-5-nitrobenzene.

   ii) Phenol and Salicylic acid give identical product upon bromination. [2+2]

   c) Convert: Phenol ⟶ Paracetamol [2]

## Unit-II

[8 marks]

3. a) What are the theories behind hard-hard and soft-soft interactions of acids and bases? [3]

   b) Why $SF_6$ inert towards hydrolysis while $TeF_6$ undergoes rapid hydrolysis? Give balanced equation of the hydrolysis reaction. [3]

   c) What happens when dimethyl glyoxime is added to $Ni^{+2}$ (aq) in ammonical medium? Draw the structure of the compound formed showing all the bonds. [2]

4. a) Comment on the change in acidity by adding (i) BiN in liquid $NH_3$ (ii) $CuSO_4$ in aqueous solution of $(NH_4)_2SO_4$. [2]

   b) Whether different formulation for $H_3PO_3$ and $H_3BO_3$ are necessary? Justify your answer. [2]

   c) Explain your choice of acid-base indicator from the given data for the acid base neutralisation of a 10 ml aqueous solution of 0.05N HCl with 0.025N $NH_3$ (aq.). [Given

pKa for $NH_4^+$ = 9.2; pH (transition) for (i) Methyl yellow: 2.9-4.0 (ii) Methyl red: 4.4-6.2 (iii) Phenolphthalein: 8-10] [2]

d) Write IUPAC names of $[Cr(NH_3)_6][Co(NO_2)_6]$ and $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$ [2]

## Unit-III [8 marks]

5. a) Zimmermann-Reinhardt solution is used in the titration of $Fe^{2+}$ with $KMnO_4$ solution in HCl medium — Explain. [2]

b) "Oxidation of Ag to $Ag_2S$ in damp air in the presence of $H_2S$ is thermodynamically feasible" — Justify this statement using the given data.

[Given: $E^o_{Ag^+/Ag} = 0.80$ V; $E^o_{o_2/H_2O} = 1.23$ V; $pK_1$ of $H_2S$ = 7.1; $pK_2$ of $H_2S$ = 15; Solubility of $H_2S$ at ordinary condition is 0.1 mol $dm^{-3}$; $K_{sp}$ of $Ag_2S = 10^{-49}$] [3]

c) Calculate the pK value for the reaction $HFe(CN)_6^{3-} = H^+ + Fe(CN)_6^{3-}$. [Given $E^0_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} = .365\,V$ ; $E^0_{Fe(CN)_6^{3-}/HFe(CN)_6^{3-}} = +0.619$ V ]. [3]

6. a) Construct the Frost diagram from the Latimer diagram:

$Te^{+3}$ —1.25— $Te^{+1}$ —(–0.34)— Te

(0.72)

Show the calculations for evaluation of coordinates of each point of the plot. [3]

b) A solution of $K_3[Fe(CN)_6]$ cannot oxidise iodide to iodine but it can do so in presence of zinc ion – explain.

[Given: standard Reduction Potential values:

$[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{4-} = 0.36\,v$; $\frac{1}{2}I_2/I^{\ominus} = 0.54\ v$ ] [3]

c) From Li to Na, the ionisation energy value decreases but still Li is a strong reducing agent than Na. Justify or contradict. [2]

## Unit-IV [9 marks]

7. a) Compare the large difference in dipole moment value between HF (1.91 debye) and HI molecule (0.42 debye) in the light of M.O. theory. [4]

b) In $[Fe(CN)_6]^{4-}$ structure, the Fe(II) is bonded through the C-end of $CN^-$ ion. Justify. [2]

c) What are intrinsic and extrinsic semiconductors? Indicate the type of semiconduction (n or p) expected in the followings: (i) As doped Ge (ii) B doped Si. [3]

8. a) What is 'Walsh diagram'. Based on this diagram, give molecular orbital configuration of $H_2O$. [3]

b) Ionization energy of $O_2$ is smaller than atomic oxygen while that of $N_2$ is greater than atomic nitrogen. Explain using molecular orbital energy level diagram. [3]

c) $CuSO_4$, $5H_2O$ loses four water molecules at relatively lower temperature but the fifth water molecule eliminates with decomposition of the compound. Explain the fact using the concept of hydrogen bonding. [3]

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