

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2016

SECOND YEAR [BATCH 2015-18]

CHEMISTRY [Honours]

Paper : III [Gr – C]

Date : 14/12/2016

Time : 11 am – 1 pm

Full Marks : 25

[Answer one question from each unit]

Unit – I

[13 marks]

1. a) “Disproportionation and comproportionation reactions are actually redox cell reactions”—justify the statement with suitable examples. [4]
b) Predict thermodynamic redox stability of H_2O_2 with the help of free energy calculation and also construct the Frost diagram from the following data : [3]
$$\text{O}_2 \xrightarrow{+0.70\text{ V}} \text{H}_2\text{O}_2 \xrightarrow{+1.76\text{ V}} \text{H}_2\text{O}$$

c) The $\text{p}K_a$ value of HASO_4^{2-} is 11.5. Is this value consistent with the two Pauling's rules? [2]
d) Explain why adding ammonium acetate to either zinc amide(s) in liquid ammonia or, zinc acetate(s) in liquid acetic acid causes the solids to dissolve. Give relevant equations. [2]
e) What do you mean by ‘Levelling effect of Solvents’? [2]
2. a) How is the hardness of a base determined? Why is methyl mercury cation chosen as a standard for this purpose? [2+1]
b) Find out the equivalence point potential during the titration of a 0.1 (M) Fe^{+2} solution with 0.1 (M) Ce^{+4} solution.
Given $E^\circ_{\text{Fe}^{+3}/\text{Fe}^{+2}} = 0.77\text{ V}$; $E^\circ_{\text{Ce}^{+4}/\text{Ce}^{+3}} = 1.57\text{ V}$
Name one suitable indicator for the above titration. [3+1]
c) Define disproportionation and comproportionation reactions. Cu^+ ion in aqueous solution undergoes disproportionation accordingly :
$$2\text{Cu}^+_{(\text{aq})} \rightleftharpoons \text{Cu}^0 + \text{Cu}^{2+}$$
 Given : $\text{Cu}^{2+} \xrightarrow{0.15\text{ V}} \text{Cu}^+ \xrightarrow{0.5\text{ V}} \text{Cu}$
Calculate the disproportionation potential and hence the equilibrium constant for the said reaction. [2+2]
d) What happens when I_2 is added to excess aqueous acidic HClO_3 ? Write half reactions. Predict which net reaction will occur. [2]
Given : $E^\circ_{\text{I}_2/\text{I}^-} = 0.54\text{ V}$; $E^\circ_{\text{ClO}_3^-/\text{ClO}_4^-} = 1.20\text{ V}$.

Unit – II

[12 marks]

3. a) Using MO theory, explain the observations that the bond length in N_2^+ is 0.02 Å greater than that in N_2 , while the bond length in NO^+ is 0.09 Å less than that NO . [2+2]
b) What do you mean by coordination number? Mention the facts that influence coordination number. [3]
c) Write IUPAC nomenclature of following : [2]
i) $[\text{Cr}(\text{en})_3][\text{Co}(\text{CN})_6]$
ii) $\left[(\text{H}_3\text{N})_4\text{Co} \begin{array}{c} \diagup \text{NH}_2 \\ \diagdown \text{O}_2 \end{array} \text{Co}(\text{NH}_3)_4 \right]^{3+}$
d) The complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has two isomeric forms. Suggest a chemical pathway to elucidate the structures of the isomers. [3]

4. a) Mention the conditions for linear combination of atomic orbitals related to the formation of molecular orbitals. [3]
- b) Explain why the conductivity of germanium is enhanced many folds when trace amount of arsenic is added to it. [3]
- c) Write the IUPAC names of [3]
- i) $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$
- ii) $[(\text{NH}_3)_4\text{Co}(\text{OH})(\text{NH}_2)\text{Co}(\text{NH}_3)_4]^{+4}$
- iii) $\text{K}_2[\text{O}_5\text{Cl}_5\text{N}]$
- d) Predict the possible isomers of $\text{Co}(\text{en})_2\text{Cl}_2$ species (en = ethylene-diamine). [3]

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