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(Residential Autonomous College under University of Calcutta)

B.A./B.SC. THIRD SEMESTER EXAMINATION, DECEMBER 2011

SECOND YEAR

Date : 16/12/2011 CHEMISTRY (Honours)

Time : 11 am – 12.30 pm Paper : III Full Marks : 25

Group – C

Unit - I

Answer any one from the following:

9. a) Arrange the following ions with increasing order of acidity and justify

 $\left[\text{Ni}(\text{H}_2\text{O})_6\right]^{+2}, \left[\text{Mn}(\text{H}_2\text{O})_6\right]^{+2}, \left[\text{Sc}(\text{H}_2\text{O})_6\right]^{+3}$ [2]

- What will be the effect on the acidity of the solution when urea is added to liquid ammonia? [1]
- c) Write down the criteria of a redox indicator. What is the mechanism of action of barium diphenyl amine sulfonate indicator? [3]
- d) What are superacids? Give an example. [2]
- e) Which of the following reactions have equilibrium constant value greater than one?
 - i) $R_3PBBr_3 + R_3NBF_3 \rightleftharpoons R_3PBF_3 + R_3NBBr_3$
 - ii) $CH_3HgI + HC1 \rightleftharpoons CH_3HgCl + HI$ [2]

Explain in the light of SHAB concept.

f) Construct the Frost diagram from the following Latimer diagram: [2]

 $O_2 \xrightarrow{0.70 \text{ v}} H_2O_2 \xrightarrow{1.76 \text{ v}} H_2O$

- g) Using Pauling's rules predict the structure of each that is consistent with the pKa value mentioned against each in parenthesis H₃PO₄ (2·12), H₃PO₃ (1·80), H₃AsO₃ (9·2) [3]
- 10. a) What is formal potential? Discuss its importance in the reaction,

$$2\text{Fe}(\text{CN})_6^{4-} + \text{I}_2 \rightleftharpoons 2\text{Fe}(\text{CN})_6^{3-} + 2\text{I}^{-}$$

in presence of ZnSO₄. Given— [3]

 $E^{\circ} Fe(CN)_{6}^{3-} / Fe(CN)_{6}^{4-} = 0.36 v$

$$E^{\circ} \frac{1}{2} I_2 / I^- = 0.54 \text{ v}$$

- b) AlF₃ is insoluble in liquid HF. However, it dissolves if NaF is added to a mixture of AlF₃ and HF but reappears with addition of excess BF₃. Explain giving necessary equations. [3]
- c) Ferric chloride oxidises iodide to iodine but oxidation does not occur in presence of excess fluoride. —Explain [2]
- d) Why does cuprous ion behave differently in water and in aqueous solution of potassium iodide? [2]

Given E° of Cu^{+2} / $Cu^{+} = 0.15 \text{ v}$ E° of Cu^{+} / Cu = 0.52 v

[2]

Solubility product of $CuI = 10^{-12}$

- e) H₂SO₄ may behave as an acid as well as a base— explain [1]
- f) Discuss the feasibility of the reaction

 $MnO_2 + 4HCl (conc) = MnCl_2 + Cl_2 + 2H_2O$

Given E° of $MnO_2 / Mn^{+2} = 1.23 \text{ v}$

$$E^{\circ} \text{ of } \frac{1}{2} \text{ Cl}_2 / \text{Cl}^- = 1.36 \text{ v}$$
 [2]

<u>Unit – II</u>

Answer **any one** from the following:

d) Answer **any one** of the followings:

11.	a)	Explain 'Walsh rule' for linear and bent molecules.	[1]
1	b)	Illustrate the structure of BeH ₂ with the help of Walsh diagram.	[2]
•	c)	Give examples of a binuclear carbonyl hydride and polynuclear carbonyl hydride both with bridged hydrogen atom.	[2]
(d)	Distinguish between extrinsic semiconductor and intrinsic semiconductor.	[2]
(e)	Distinguish between	
		i) ambidentate ligand and flixidentate ligand	
		ii) inert complex and latile complex	[3]
12.	a)	Sketch the molecular orbital energy level diagram of B_2 and suggest its magnetic behaviour.	[3]
1	b)	Write the IUPAC names of $K[PtCl_3(\eta^2C_2H_4)]$ and $\left[(H_3N)_4CO \stackrel{OH}{\swarrow} CO(NH_3)_4\right]^{4+}$.	[2]
	c)	Stability of a chelate complex is greater than that of a non chelate complex— Explain.	[2]

i) From the molecular orbital energy level diagram of carbon monoxide explain its dipole

[3]

moment value.

ii) Give a concise account of 'inner metallic complexes'.

80%(28