RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. THIRD SEMESTER EXAMINATION, DECEMBER 2013

SECOND YEAR

Date : 16/12/2013 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm Paper : III Full Marks : 25

Group - C

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

Unit - I

1. a) What do you mean by buffer capacity of a buffer? [1]

   b) 25ml of 0·1(N) CH_3COOH solution is titrated with 0·1(N) NaOH solution. Calculate pH values of the solutions when volumes of NaOH solution added are 0ml, 24·0 ml, 24·9 ml, 25·0 ml, 25·1 ml and 26·0 ml. Draw the titration curve and from the nature of the curve give your choice of indicator. [4]

   c) Construct the Frost diagram from the following Latimer diagram.

   $$O_2 \xrightarrow{0.70\,V} H_2O_2 \xrightarrow{1{\cdot}76\,V} H_2O \ .$$ [3]

   d) Predict the direction of the following reactions giving reason—

   i) $2CH_3MgF + HgF_2 \rightleftharpoons (H_3C)_2Hg + 2MgF_2$

   ii) $La_2(CO_3)_3 + Tl_2S_3 \rightleftharpoons La_2S_3 + Tl_2(CO_3)_3$ [3]

   e) What happens when sodium bismuthate is added in $MnSO_4$ in the presence of acid? Give equation using ion-electron method. [2]

2. a) What are 'superacids'? Explain with an example. [2]

   b) β_6 of $[Fe(CN)_6]^{4-}$ ion is 10^{35}. Calculate β_6 of $[Fe(CN)_6]^{3-}$ ion. Given : $E^o_{Fe^{3+}/Fe^{2+}} = +0{\cdot}77V$, $E^o_{[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}} = +0{\cdot}36V$ [2]

   c) AlF_3 is insoluble in liquid HF. However, it dissolves if NaF is added to a mixture of AlF_3 and HF but reappears with the addition of excess BF_3. Explain giving necessary equations. [3]

   d) The reduction potential (E^o) of $MnO_4^-/Mn^{2+} = +1{\cdot}51V$ that of each chloride, bromide and iodide to free halogens (E^O = +1·36V, + 1·07 V and +0·54 V) respectively. Discuss the possibility of oxidation of these halides at pH 3·0. [3]

   e) Write the products of the following reactions with the help of suitable acid-base theory. Support your answer with reasoning.

   i) $Na_2S_2O_7 + TiO_2 \xrightarrow{800°C}$

   ii) $(OC)_5MnCl + SnCl_3^- \rightarrow$ [3]

Unit - II

3. a) Draw MO diagram of CO and explain its ligating behaviour to transition elements. Can CN^- show comparable ligation? [3+1]

   b) Mention the differences between intrinsic and extrinsic semiconductors. [2]

   c) Give diagramatic representation of the orbital overlap with reference to bonding, non-bonding and antibonding MOs (considering x-axis as the bond axis).

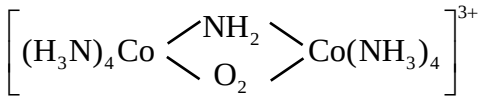
   i) s vs. d_{xy} ii) p_z vs. d_{xz} iii) $d_{x^2-y^2}$ vs. $d_{x^2-y^2}$ [3]

   d) Distinguish between—

   i) ambidentate and flexidentate ligand

ii) Perfect and imperfect complexes. [3]

4. a) Write the IUPAC nomenclature of the following :

i) $[Cr(en)_3][CO(CN)_6]$ ii)  [2]

b) Why does HF show greater heat of vaporization than that of H_2O while boiling point trend is just the reverse. [2]

c) Explain 'Walsh rule' for linear and bent molecules. [3]

d) Show the possible isomers of the complex, $[Co(en)(NH_3)_2Cl_2]^+$ [2]

e) A chromium complex $CrCl_3.6H_2O$ (blue) dissolved in aqueous solution shows molar conductivity of about 430 $ohm^{-1}cm^2$. In contrast $CrCl_3.5H_2O$ is green and has a lower molar conductivity in solution. If the green complex is allowed to stand for several hours in dilute acidic solution, it turns blue again. Interpret the observations in the light of Werner's theory. [3]