

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2015

SECOND YEAR [BATCH 2014-17]

CHEMISTRY [Hons]

Paper : III [Group – C]

Date : 17/12/2015

Time : 11 am – 1 pm

Full Marks : 25

[Answer one question from each unit]

Unit - I

1. a) State the theory by which the reaction $6\text{CaO} + \text{P}_4\text{O}_{10} \rightarrow 2\text{Ca}_3(\text{PO}_4)_2$ may be regarded as an acid-base reaction. [2]
b) Calculate the solubility of CaF_2 in a solution of 0.1M $\text{Ca}(\text{NO}_3)_2$, $K = 4.9 \times 10^{-11}$. [3]
c) Explain the solubility of all the four halides of silver and Lithium by a proper acid base concept. [3]
d) $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$; $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15\text{V}$, $E^\circ_{\text{Cu}^+/\text{Cu}} = 0.52\text{V}$, $E^\circ_{\text{I}_2/2\text{I}^-} = 0.54\text{V}$;
 K_{sp} of $\text{CuI} = 1 \times 10^{-12}$.
From the following data justify the oxidising properties of copper sulphate solution when it is treated with a 1N KI solution and also explain the formation cuprous iodide not to metallic copper. [3]
e) $\text{Mg}(\text{OH})_2$ is insoluble in water but soluble in presence of NH_4Cl . Explain. [2]
2. a) What are superacids? Explain with examples. [2]
b) From the following standard reduction potential diagram
 $\text{MnO}_4^- \xrightarrow{0.90\text{V}} \text{MnO}_4^{2-} \xrightarrow{2.09\text{V}} \text{MnO}_2 \xrightarrow{1.23\text{V}} \text{Mn}^{+2}$.
Calculate E° value for $\text{MnO}_4^- / \text{Mn}^{+2}$ redox system and hence its formal potential at $\text{pH} = 4$. [3]
c) Arrange and explain the acidity of the following aqua ions $[\text{Na}(\text{H}_2\text{O})_n]^+$, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. [2]
d) $E^\circ_{\text{Co}^{3+}/\text{Co}^{2+}} = 1.82\text{V}$; $E^\circ_{\text{Methylene blue (OX) / Methylene blue (Red)}} = 0.52\text{V}$. $K_{\text{stability}}$ of $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{4-}$ are 1×10^{64} and 1×10^{19} . [Given colour of the methylene blue in oxidised and reduced form is blue and colourless] so justify the colour of the indicator in a solution of Co^{3+} and Co^{2+} and in presence of sufficient cyanide ions. [Methylene blue is indicator] [3]
e) Can XeF_6 behave both as a Lewis acid and base? Explain with equations. [1.5]
f) Balance with ion electron method when KMnO_4 reacts with oxalic acid. [1.5]

Unit - II

3. a) The photoelectron spectrum of water molecule shows four bands at around 12eV , 13.7eV , 17.2eV and 36eV . Explain the spectrum by constructing MO energy level diagram of water molecule. [3+2]
b) Show how acetylacetonate form chelate complexes with Co^{+3} . Why chelated complexes are more stable than unchelated complexes. [3]
c) Predict the possible isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (en = ethylene diamine) [2]
d) Which is the likely structure of the complex $[(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)\text{Pd}(\text{SCN})_2]$? Explain. (Ph = phenyl, Me = Methyl) [2]
4. a) The energy necessary to dissociate one oxygen atom from dioxygen species are reported as (kJ mol^{-1}): 623 , 494 , 351 and 205 . Correlate these terms with the species O_2^+ , O_2 , O_2^- and O_2^{2-} . Explain. [4]

- b) A compound $\text{Co(en)}_2(\text{NO}_2)_2\text{Cl}$ has been prepared in three isomeric forms A, B, and C. A undergoes no reaction with AgNO_3 or en and is optically inactive. B reacts with AgNO_3 but not with en and is optically inactive. C is optically active and reacts with both AgNO_3 and en. Identify A, B and C. Explain. [en = ethylene diamine]. [3]
- c) Write IUPAC nomenclature of the following : [1+1]
- i) $[\text{Cr(en)}_3][\text{Co(CN)}_6]$
- ii) $\left[(\text{H}_3\text{N})_4\text{Co} \begin{array}{c} \diagup \text{NH}_2 \\ \diagdown \text{O}_2 \end{array} \diagup \text{Co(NH}_3)_4 \right]$
- d) Mention the differences between the perfect and imperfect complexes with suitable example. [2]
- e) Mention the use of an organic reagent that is applied for the detection of metal ion. [1]

_____ × _____