RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SECOND SEMESTER EXAMINATION, AUGUST 2021

FIRST YEAR [BATCH 2020-23]

Date : 12/08/2021 **CHEMISTRY (HONOURS)**

Time : 11 am – 1 pm **Paper : IV [CC4]** Full Marks : 50

[Attempt <u>one</u> from <u>each unit</u>]

Unit : I

[1×12]

1. a) Reduction of Fe^{3+}, the electron can enter either 3d or 4s. Explain with the reason.

   b) Calculate Pauling's electronegativity of hydrogen atom from the following data : Bond energies (KJ $mole^{-1}$):): H_2 (458), F_2 (155), HF (565) and Pauling'selectronegativity of F = 4.0

   c) PbF_4 is stable but PbI_4 is readily disproportionate to PbI_2 and I_2, Explain.

   d) Arrange the following ions with increasing ionic radii, give reasons.

   H^-, Cl^-, I^-, Br^-, F^-.

   e) Electronegativity is not inherent property, comment. [3+3+3+2+2]

2. a) The electronegativity value of Ga is higher than Al.

   b) What are the disadvantages and disadvantage of Allred-Rochow electronegativity scale?

   c) What is 'inert-pair' effect? Comment on the oxidation state of Bi in sodium bismuthate and also explain its chemical nature.

   d) Rationalize the trends in the specific atomic properties in the following atoms.

	C	N	O
First electron affinity (eV) :	1·263	–0·070	1·461

   e) The interatomic distance in chlorine molecule is 1·98Å. Calculate the Allred-Rochow electronegativity using Slater rules. [2+2+3+3+3]

Unit : II

[1×12]

3. a) Explain with example, equivalent and non-equivalent hybrid orbitals.

   b) In SF_4 molecule equatorial F-S-F bond angle is 101^0, explain this large variation of bond angel from idealised bond angle (120^0).

   c) Explain how the presence of 'Non-stoichiometric Defects' in solids influence the properties of the solid with at least one representative example.

   d) Explain the position of fluorine in PCl_3F_2, using Slater's rule.

   e) Using VSEPR theory determines the shape of I_3^- and XeF_2. [2+2+3+3+(1+1)]

4. a) Define with example Schottky defect and Frenkel defect. Mention the differences between Schottky defect and Frenkel defect.

   b) XeF_6 is distorted octahedral but $SbCl_6^{3-}$ is regular octahedral, explain.

c) What happen, if Na-vapour is passing through NaCl crystal?

d) What are the limitations of VBT, using VSEPR theory determine the shape of XeO_2F_2, XeF_6(S), and BrF_4^-. [3+3+2+(1+1+1+1)]

Unit : III

[1×13]

5. a) Write the advantages of 'Molecular orbital theory' over 'Valence bond theory'.

b) Draw the molecular orbital diagram for CN^- and discuss about its bond order and magnetic property.

c) Latimer diagram of Chlorine in acidic medium is given below.

At pH=0

$$ClO_4^- \xrightarrow{+1.20V} ClO_3^- \xrightarrow{+1.18V} HClO_2 \xrightarrow{+1.60V} HClO \xrightarrow{1.67V} Cl_2 \xrightarrow{1.36V} Cl^-$$

Calculate $E^0_{ClO4-/Cl-}$;

d) Also calculate the equilibrium constant for

$$ClO_3^- + 5Cl^- + 6H^+ = 3Cl_2 + H_2O$$

e) What will result when Si is doped with B? [2+(2+1+1)+3+3+1]

6. a) Write a short note on band theory explaining the difference among conductor, semiconductor and insulator.

b) The Latimer diagram for manganese in acidic solution at 25^0 C is shown below. Calculate the standard reduction potential for the reduction of MnO_4^{2-} to Mn^{2+}.

$$\underset{(+7)}{MnO_4^-} \xrightarrow{0.558} \underset{(+6)}{MnO_4^{2-}} \xrightarrow{2.26} \underset{(+4)}{MnO_2} \xrightarrow{0.95} \underset{(+3)}{Mn^{3+}} \xrightarrow{1.542} \underset{(+2)}{Mn^{2+}} \xrightarrow{-1.185} \underset{(0)}{Mn(s)}$$

c) Discuss from the above Latimer diagram whether MnO_2 will undergo disproportionation or not.

d) What do you mean by sp interaction? Explain with an example.

e) Explain the geometry of water molecule taking the help of 'Walsh diagram'. [3+3+2+2+3]

Unit : IV

[1×12]

7. a) What are the primary and secondary valencies in the complex $[Co(NH_3)_5Cl]Cl_2$ respectively?

b) Among 1M aqueous solution of $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$ which have the greater magnitude of depression in freezing point ?

c) Predict the formula of the following compounds:

i) Hexaammine cobalt (III) tetrachlorodiammine chromate (III)
ii) Ammonium heptafluorozirconate (IV)
iii) Trans- bis- (2-aminoethnethiolato)nickel (II)

d) When a white substance (A) was treated with dilute HCl a colorless gas (B) was evolved which turned moist litmus paper red. On bubbling (B) through lime water a precipitate (C) was formed but passage of further gas resulted in a clear solution (D). A small sample of (A) was moistened with conc. HCl, placed on a platinum wire and introduced into a Bunsen burner flame where it caused a green flame coloration. When 1.973g of (A) was heated strongly it decomposes and gave 1.533g of (E) which turned red litmus paper blue. Identify the substance (A) to (E) and give equation for all the reactions.

e) In the process of extraction of gold:

Roasted ore + NaCN + H_2O → [X]
[X] + Zn → [Y] + Au

Identify the complexes [X] and [Y]

f) What happens when potassium ferrocyanide is added to a solution containing Cu^{2+} ion.

[1+1+3+4+2+1]

8. a) What is the coordination number of Ce^{4+} in the compound $[Ce(NO_3)_6]^{2-}$ and denticity of the ligands ?

b) Which species have the greater molar conductance among 1M aqueous solution of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_3Cl_3]$

c) Predict the IUPAC nomenclature of the following compounds:

i) $K_3[Al(C_2O_4)_3]$ ii) $Fe_4[Fe(CN)_6]_3$ iii) $[Cr(NH_3)_6][CoF_6]$

d) When a white colored hygroscopic sulphate salt of a transition metal (A) was dissolved in water and reacted with KCN a white colored precipitate (B) formed at the beginning. Upon addition of excess KCN it is dissolved by formation of a complex compound (C). This complex (C) can react with H_2S to produce a yellow precipitate (D) which is soluble in HNO_3. Identify the substance (A) to (D) and give equations for all the reactions.

e) Why electron affinity of Zn is much lower than Cu?

f) What happens when zinc chloride reacts with excess NaOH solution? [1+1+3+4+2+1]

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