RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SECOND SEMESTER EXAMINATION, JUNE 2022

FIRST YEAR (BATCH 2021-24)

Date : 22/06/2022 **CHEMISTRY (HONOURS)**

Time : 11.00 am – 1.00 pm **Paper : IV [CC4]** Full Marks : 50

[Use a separate Answer Book for **each unit**]

Unit : I

Answer **any one** question: [13 marks]

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's electronegativity of F = 4.0
   c) PbF_4 is stable but PbI_4 is readily disproportionate to PbI_2 and I_2, Explain.
   d) Auride ion is common but Cuprite ion does not exist, comments.
   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 advantages and disadvantage of Mullikan electronegativity scale over Pauling scale?
   c) What is 'inert-pair' effect? Comment on the oxidation state of Bi in sodium bismuthate and also explain why sodium bismuthate is a strong oxidising agent.
   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) Determine the screening constant and effective nuclear charge for a valence electron in Tl and Au atom. [2+2+3+3+3]

Unit : II

Answer **any one** question: [12 marks]

3. a) Explain with example, equivalent and non-equivalent hybrid orbitals.
   b) What is Bent's rule? 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) $ZnO/ZnCO_3$ is yellow when hot but white when cold, explains with the light of crystal defect.
   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+3+3+2+(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

Answer **any one** question: [13 marks]

5. a) With the help of an approximate molecular orbital energy level diagram, explain the following:

   i) High polarity of HF
   ii) CO and N_2 are isoelectronic species but differ greatly in their donor property.

   b) Give reason of the following observations:

   (i) A solution of hexacyano ferate (3-) ion can not oxidize iodide to iodine but it can do so in the presence of zinc ion;

(ii) Chloride ion is oxidized to chlorine by permanganate solution at low pH.

Given E^0 /volts: hexacyano ferate(3-)/hexacyano ferate(4-) = + 0.36; iodine/iodide= +0.54;

Permanganate/manganese(II) = +1.51; Chlorine/chloride = +1.36 [(3+4)+(3+3)]

6. a) 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^0/volts: Fe^{3+}/Fe^{2+} = +0.76 and Ce^{4+}/Ce^{3+} = +1.44)

   Name a most suitable indicator which can be used for accurate end point detection giving reason.

   b) Construct the Latimer diagram from following E^0 data and check whether MnO_4^{2-} would disproportionate in solution:

   E^0 /volts: MnO_4^-/MnO_4^{2-} = +0.56; MnO_4^{2-}/MnO_2 = +1.44 and MnO_2/Mn^{2+} = -0.70

   c) Using the concept of metallic band concept, explain the following: (i) Fermi energy gap (ii) insulator (iii) p-type semiconductor (iv) n-type semiconductor

   d) Predict the magnetic property of B_2 and C_2 from the correct molecular orbital diagrams. [(2+2)+2+4+3]

Unit : IV

Answer **any one** question: [12 marks]

7. a) What do you mean by Flexidentate ligands? Explain with proper example.

   b) Predict the IUPAC nomenclature of the following compounds:
   i) $(NH_4)_3[ZrF_7]$
   ii) $K_3[Al(C_2O_4)_3]$

   c) What happens when gypsum is heated gradually from room temperature to 400˚C in a carbon free environment?

   d) Chloride salt (B) of a white metal (A) on reaction with washing soda produces two colourless gas (C) and (D). One of them is a strong oxidant that produces a sulphate (F) with the sulphide (E) of metal (A). Identify (A) to (F) with proper reactions involved. [2+2+2+6]

8. a) Among1(M) aqueous solution of $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$ which have greater magnitude of depression in freezing point ? Explain with justification.

   b) What would be the oxidation state of Pt in complex cation and complex anion in the complex $[Pt(NH_3)_4Cl_2]$ $[PtCl_4]$.

   c) 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.

   d) What happens when copper sulphate solution gradually treated with excess potassium cyanide solution? Explain with the reactions involved. [2+2+6+2]

———— × ————