[This question paper contains 4 printed pages.]

Sr. No. of Question Paper : 6815 **D** **Your Roll No.....**

Unique Paper Code : 217561

Name of the Course : **B.Sc. (Programme) Physcial Science / Life Science**

Name of the Paper : CHPT–505 : CHEMISTRY – V

Semester : V

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **3** questions from **Section A** and **3** from **Section B.**
3. Sections A and B are to be attempted in separate portions of the same answer sheet.
4. Please indicate the section you are attempting at the appropriate place and do not intermix the sections. The questions should be numbered in accordance to the number in the question paper.

SECTION A

Attempt any **3** *questions.*

1. (a) Give brief reasons of the following :

   (i) Transition elements usually exhibit higher oxidation states in their fluorides than in carbon monoxide.

   (ii) The radii of the elements of third transition series are very similar to those of second transition series.

   (iii) Cu^{2+} ions are colored and paramagnetic while Zn^{2+} ions are colorless diamagnetic. Explain.

   (iv) Transition metals and their compounds act as good catalysis.

   (v) Low-spin tetrahedral complexes are not known.

P.T.O.

(b) Complex with empirical formula $Co(NH_3)_3(H_2O)_2Br_2Cl$ exists in two isomeric forms A and B. Form A Yield two moles of AgBr when treated with solution of $AgNO_3$ whereas B form yields only one mole of AgBr. Write down the structural formula of the both forms. What are these isomers called ? (10,2½)

2. (a) Chromium(II)fluoride and manganese(II)fluoride, both have a central metal ion surrounded by six Fluoride ligands. All the Mn-F bond lengths are equal, but two of the Cr-F bond lengths are shorter than the remaining four. Explain.

(b) Give the IUPAC names of the following complexes :

(i) $[(CH_3)_4N][PtCl_3.C_2H_4]$

(ii) $[Co(NH_2)_2(NH_3)_4]Br$

(iii) $[Co(en)_2Br(ONO)]^+$

(iv) $K_3[Cl_3TlCl_3TlCl_3]$

(v) $[Co(NH_3)_6]\ [CoF_6]$

(c) Write down all the possible isomers of $[Cr(en)_2(NCS)_2]Br$. (3,5,4½)

3. (a) Write the formulae for the following :

(i) Diamminesilver(I)tetracyanoplatinate(II)

(ii) μ-amido-μ-peroxobis{tetraamminecobalt(III)}phosphate

(iii) Potassiumcarbonylpentacyanoferrate(II).

(b) Given below are the Latimer diagrams for Fe in acidic media :

$$FeO_4^{2-} \xrightarrow{2.20} Fe^{3+} \xrightarrow{0.77} Fe^{+2} \xrightarrow{-0.47} Fe$$

Answers the following questions :

(i) Why is FeO_4^{2-} a strong oxidizing agent ?

(ii) Are there any states which undergo disproportionation ?

(iii) Calculate E° value of FeO_4^{2-} / Fe^{2+}.

(c) Work out the number of unpaired electrons in the following ions :

Sm^{3+} (At. No. 62); Er^{3+} (At. No. 68)

(d) $[Co(NH_3)_6]^{2+}$ complex can be easily oxidize to $[Co(NH_3)_6]^{3+}$ why ? Explain on the basis of VB theory. (3,4½,3,2)

4. (a) Which of the following complexes will have higher Δ_0 and why ?

(i) $[Co(H_2O)_6]^{2+}$ or $[Co(H_2O)_6]^{3+}$

(ii) $[NiCl_4]^{2-}$ or $[PdCl_4]^{2-}$

(iii) $[Cr(OX)_3]^{3-}$ or $[Cr(bipy)_3]^{3+}$

(b) For Mn^{3+} ion, the electron pairing energy, P is 28000 cm^{-1}, Δ_0 values for the complexes $[Mn(H_2O)_6]^{3+}$ and $[Mn(CN)_6]^{3-}$ are 21000 cm^{-1} and 38500 cm^{-1}, respectively. Do these complexes have low spin or high spin configurations ? Also write down the configurations corresponding to these states.

(c) Although $[NiCl_4]^{2-}$ and $Ni(CO)_4$ have same geometry but they differ in their magnetic behavior. Explain.

(d) Oxocations MO^{2+} is formed by U, Pu, Np and Am only whereas heavier actinides not form such oxocation why ? (3,4,3,2½)

SECTION B

Attempt any **3** *question.*

1. (a) Attempt any three parts.

(i) Why is n=0 not permitted in the equation

$$E_n = \frac{n^2h^2}{8ml^2}$$

(ii) Explain the process of Fluorescence.

(iii) State Stark - Einstein law of photochemical equivalence.

(iv) Zero point energy need not be equal to zero. Comment.

(b) Show that $\psi = 3\cos 2x$ is an eigenfunction of the operator

$$\frac{-h^2}{4\pi^2}\frac{d^2}{dx^2}$$

What is the eigenvalue ? (9,3½)

2. (a) Write the selection rules for IR spectra and microwave spectra.

(b) Which of the following molecules will give rise to observable rotational and vibrational spectra HCl, N_2, CO, H_2O ?

(c) What important aspect is signified by the property of commutation ? Find whether the operators $A = \frac{d}{dx}$ and $B = x$ commute with each other.

(2,4,6½)

3. (a) Define the term 'Quantum Efficiency'. Justify the statement that the quantum efficiency of a primary process is always one.

(b) How do you account for the fact that the quantum yield of the photochemical reaction

$H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$ is low (–0.01), while that of the reaction

$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ Is very high (10^5) ?

(c) Write the Hamiltonian for hydrogen atom. (4½,6,2)

4. (a) Write short note on any **three** :

(i) Auxochrome

(ii) Frank-Condon principle

(iii) Photoelectric cell

(iv) Chemilumisence

(b) For HCl molecule calculate energy of the rotational state with J = 1. ($m_H = 1.673 \times 10^{-27}$ kg $m_{Cl} = 58.06 \times 10^{-27}$ kg and equilibrium internuclear distance is 121.25 pm). (9,3½)

(4500)