[This question paper contains 6 printed pages.]

Sr. No. of Question Paper : 86 **G** **Your Roll No.....**

Unique Paper Code : 217561

Name of the Paper : CHPT – 505 : CHEMISTRY – V Chemistry of d block Elements Quantum Chemistry & Spectroscopy

Name of the Course : **B.Sc. Programme Life Science / Physical Science / Applied Life Science (Agrochemical & Pest Management) / Applied Physical Science (Analytical Chemistry / Industrial Chemistry)**

Semester : V

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on the receipt of this question paper.
2. Attempt **3** questions from **Section A** and 3 questions 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.
5. Calculators and log tables may be used.

SECTION A

Attempt any **3** *questions.*

1. (a) Give brief reasons for **any 3** of the following :

   (i) Ti(III) compounds are coloured while Ti(IV) compounds are colourless

(ii) Octahedral complexes of Fe(II) may be of inner and outer orbital types but those of Ni(II) are only outer orbital.

(iii) The densities of the elements of the third transition series are much higher than those of the corresponding elements of the second transition series.

(iv) Transition metals form a large number of complexes.

(v) Strong field ligands prefer Co(III) to Co(II).

(b) $[Co\ Br(NH_3)_5]^{2+}$ undergoes ligand substitution reaction when treated with $NaNO_2$ to give two isomeric pentaammine ions depending upon the experimental conditions. Deduce the structures of these. What is this type of isomerism called ? How can you distinguish between the two isomers ?(9,3½)

2. (a) An octahedral complex of Cu(II) is generally distorted and two bonds are longer than the other four. Explain and draw the splitting diagram. What is the driving force towards this distortion ?

(b) Give the IUPAC names of **any 3** of the following :

(i) $K_3[Ag(S_2O_3)_2]$

(ii) $[Cr(NH_3)_6][Cu(CN)_5]$

(iii) $Li[Mn(CO)_5]$

(iv) $[(en)_2Co(O_2)Co(en)_2](OH)_4$

(c) Using VBT predict the hybridisation, geometry and magnetic behaviour of **any 2** of the following :

(i) $[Ni(CO)_4]$

(ii) $Ca_2[Fe(CN)_6]$

(iii) $K_2[NiCl_4]$ (5,4½,3)

3. (a) Write the formulae of **any 3** of the following :

(i) Caesium tetrafluorooxochromate (III)

(ii) Pentaamminesulphatorhodium(III) perchlorate

(iii) Zinc tetrabromoiodate(III)

(iv) Tetraaquapalladium(II) amminetrichloropalladate(II)

(b) Calculate the CFSE of Fe^{2+} ion placed in an octahedral weak field environment. Draw the splitting diagram. What will be the CFSE in a tetrahedral field ? Comment on the difference in splitting pattern in both the fields.

(c) Indicate the type of isomerism in the following pairs :

(i) $[Co\ Cl(NH_3)_5]\ SO_4$ and $[CoSO_4(NH_3)_5]\ Cl$

(ii) $[Co(NH_3)_6]\ [Cr(ox)_3]$ and $[Cr(NH_3)_6]\ [Co(ox)_3]$

(iii) $[Fe(NH_3)_3(NO_2)_3]$ and $[Fe(NH_3)_6]\ [Fe(NO_2)_6]$

(d) What phenomenon is responsible for the intense colour of potassium permanganate and potassium dichromate ? (4½,4,3,1)

4. (a) Changing the ligand may alter the geometry and magnetic behaviour of a four coordinate Ni(II) complex. Explain using VBT.

(b) Indicate the appropriate choice and give brief reasons :

(i) Greater value of Δ_0 $[Co(NH_3)_6]^{3+}$or $[Co(H_2O)_6]^{3+}$

(ii) Good oxidizing agent Sm(II) or Ce(IV)

(iii) Optically active cis or trans $[CrCl_2(en)_2]^+$

(c) Construct the Latimer diagram of iron in acidic medium from the following data :

$FeO_4^{2-} \longrightarrow Fe^{3+}$ $\quad E^0 = 2.20V$

$Fe^{3+} \longrightarrow Fe^{2+}$ $\quad E^0 = 0.77\ V$

$Fe^{2+} \longrightarrow Fe$ $\quad E^0 = -0.47\ V$

Calculate E^0 for $FeO_4^{2-} | Fe^{2+}$. Identify the species which is highly oxidizing and give reasons for your choice. Will any Species undergo disproportionation ?

OR

Write short notes on **any 2** of the following :

(i) Lanthanide contraction and 2 consequences.

(ii) Geometrical Isomerism in complexes of coordination number 4.

(iii) Catalytic properties of 3d metals and their compounds. (3,4½,5)

SECTION B

Attempt any **3** *questions.*

Physical Constants

Planck's constant 6.626×10^{-34} J s

Velocity of light 3×10^8m s^{-1}

Avogadro's number 6.023×10^{23} mol^1

Atomic mass unit 1.661×10^{-27}kg

Mass of electron 9.109×10^{-31} kg

$\pi = 3.142$

5. (a) Write the mathematical expressions for the position operator x and the kinetic energy operator T_x.

(b) Which of the following are eigenfunction is of the operator d^2/dx^2: ?

(i) sin nx; (ii) 3 exp(−5x)

Give the eigenvalues wherever appropriate.

(c) A molecule XY is studied by microwave spectroscopy under the rigid rotator approximation. Draw the schematic stick line spectrum. What is the structural information that can be obtained from this spectrum ?

(d) The linear N_2O molecule shows three fundamental vibrational frequencies in the IR spectrum. Suggest a molecular structure for this molecule. Justify briefly. (2,3,3½,4)

6. (a) Calculate the percentage change in the energy of a particle of mass m in a one dimensional box of edge length L when, the edge length is decreased by 10%

(b) A diatomic molecule AB undergoes vibrational motion according to the harmonic oscillator model. Write the mathematical expression for the Hamiltonian, Schrodinger's equation and the vibrational energy E_{vib} associated with this system.

(c) The fundamental stretching vibration for $^1H^{35}Cl$ is observed at 2886 cm^{-1}.

(i) Draw an energy diagram indicating the vibrational energy levels.

(ii) Calculate the force constant and the zero point energy. (4,4½,4)

7. (a) Calculate the transmittance, absorbance and the extinction coefficient of a solution which absorbs 90% of a certain wavelength of light when the beam passes through a 1 cm cell which contains a solution of molarity 0.25 M.

(b) Consider the Free Electron Molecular Orbital (FEMO) description of the linear molecule hexatriene. What is the minimum excitation energy, given that the average C-C bond distance is 140 pm ?

(c) Define quantum yield. What are the reasons for high and low values of quantum yield ? (4½,4,4)

8. (a) Write short notes on **any three** of the following :

(i) Effect of hydrogen bonding on vibrational frequencies

(ii) Laws of photochemistry

(iii) Fluorescence and phosphorescence

(iv) Born Oppenheimer approximation

(b) Define the unit "Einstein". (3½×3,2)