10.12.18(M)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 388 **IC**

Unique Paper Code : 42177925

Name of the Paper : Chemistry of d Block Elements, Quantum Chemistry and Spectroscopy

Name of the Course : **B.Sc. (Prog.) Chemistry : DSE-2A**

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 any **three** questions from **Section A** and any **three** from **Section B**.
3. **Section A** and **B** are to be attempted separately in the same sheet.
4. Calculators and log tables may be used.

Section A

Attempt any **three** *questions.*

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

P.T.O.

(i) Transition metals form alloys.

(ii) Cu^{2+} ions are coloured while Zn^{2+} ions are colourless.

(iii) The atomic radii of second and third transition series elements are similar.

(iv) Many transition metals and their compounds act as catalysts.

(v) Low spin tetrahedral complexes are not known.

(vi) The oxides of first transition series elements are acidic in high oxidation state and basic in low oxidation state. (10)

(b) Complexes with empirical formula $Pt(NH_3)_4Cl_2SO_4$ exist in two isomeric forms A & B. Form A yields one mole of $BaSO_4$ when treated with a solution of $BaCl_2$ where as form B yields two moles of AgCl ppt when treated with a solution of $AgNO_3$. Write down the structural formulae of both the forms and name the type of isomerism involved. (2½)

2. (a) Name **any three** ofthe following complexes according to IUPAC system of nomenclature.

(i) $[Co(NH_3)_6]$ $[Co\ F_6]$

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

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

(iv) $[(en)_2Co(NH_2)(O_2)Co(en)_2]$ $(NO_3)_4$ (4½)

(b) Calculate CFSE in terms of Δ_t of a d^7 metal ion placed in a tetrahedral field. Draw the splitting diagram. (4)

(c) Define Jahn Teller theorem. Which of the following high spin complexes would you expect to exhibit Jahn Teller distortion? Give reasons.

$[Cr(NH_3)_6]^{3+}$ or $[MnCl_6]^{3-}$ (4)

3. (a) The complex $[Cr(C_2O_4)_2(NH_3)_2]$ exists in two isomeric forms A & B. A is optically active whereas B is optically inactive. Draw the structures of A & B and explain briefly. (4½)

(b) Write the formulae of **any two** of the following :

(i) Tetraamminedichloridoplatinum(IV) tetrachloridoplatinate(II)

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

(iii) Potassium bis(thiosulphato)argentate (I) (4)

(c) Which will show greater crystal field splitting and why?

(i) $[Co(NH_3)_6]^{2+}$ or $[Co(NH_3)_6]^{3+}$

(ii) $[Cr(NH_3)_6]^{3+}$ or $[Cr(CN)_6]^{3-}$ (4)

4. (a) Explain why the crystal field splitting in tetrahedral complexes is always less than that in octahedral complexes. Calculate Δ_t for $[NiCl_4]^{2-}$, given Δ_o for octahedral $[NiCl_6]^{4-}$ is 7300 cm^{-1}. (4½)

(b) Although $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ have same geometry but they differ in their magnetic behavior. Explain. (4)

(c) Given below is the Latimer diagram for copper

$$Cu^{2+} \underset{}{\overset{+0.15}{\longrightarrow}} Cu^{+} \overset{+0.50}{\longrightarrow} Cu$$

Answer the following questions :

(i) Is there any state which undergoes disproportionation? Explain by showing necessary calculations.

(ii) Calculate skip step emf for Cu^{2+} ------ Cu change.

OR

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

(i) Separation of lanthanides by ion exchange method

(ii) Complex formation tendency of d – block elements

(iii) Variable oxidation states in transition elements. (4)

Section B

Physical constants

Planck's constant, $h = 6.626 \times 10^{-34} Js$

Boltzmann Constant, $k = 1.38 \times 10^{-23} JK^{-1}$

Mass of electron, $m_e = 9.31 \times 10^{-31} kg$

Velocity of light, $c = 3 \times 10^8 \ m \ s^{-1}$

Attempt any **three** *questions.*

1. (a) Write the Schrodinger wave equation and apply it to the particle in a one dimensional box. Obtain expression for energy. (4½)

P.T.O.

(b) What do you understand by the terms singlet state and triplet state? Explain the phenomenon of fluorescence and phosphorescence using jablonskidiagram. (4)

(c) A 0.03 M solution of a substance has an absorbance of 0.75 at 600 nm using a cell of pathlength 1 cm. Calculate molar absorption coefficient and the percent absorption for 0.01 M solution in the same cell. (4)

2. (a) The pure rotational spectrum of the gaseous molecule CN has a series of equally spaced lines separated by 3.79 cm^{-1}. Calculate the internuclear distance of the molecule. The molar mass of C and N are 12.011 and 14.007 g/mol respectively. (4½)

(b) Normalise the function $\psi = a - x$ over the interval $0 \leq x \leq a$. (4)

(c) Explain the terms chromophore and auxochrome giving examples. (4)

3. (a) Calculate the probability of finding a particle between $x = 0.4$ nm and $x = 0.5$ nm in a one dimensional box of length 1nm. (4½)

(b) Discuss the reasons for low and high quantum yield in photochemical reactions. A system absorbs 3×10^8 quanta of light per second. On irradiation for 20 mins, 0.003 moles of reactant was found to have reacted. Calculate the quantum yield for the process. (4)

(c) Define BornOppenheimer approximation. Explain its application in spectroscopy. (4)

4. (a) Show that the function cos ax.cos by. cos cz is an eigenfunction of laplacian operator and determine the eigenvalue. (4½)

(b) What are the essential conditions for a molecule to show microwave spectrum? Which of the following will show Microwave spectrum? Give reason.

(i) CO_2 (ii) H_2O

(iii) O_2 (iv) CO (4)

(c) Write a note on any **two** of following :

(i) Bathochromic and hypsochromic shifts

(ii) Free electron model

(iii) Laws of photochemistry (4)