[This question paper contains 8 printed pages.] 4/12/18 M (E)

Your Roll No.....

Sr. No. of Question Paper : 339 **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 - IA**

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 **any five** of the following :

(i) Transition metals usually show variable oxidation states.

(ii) $CuSO_4.5\ H_2O$ is coloured but anhydrous $CuSO_4$ is colourless.

(iii) Densities of third transition series elements are almost double the respective elements of second transition series.

(iv) Transition metals form interstitial compounds.

(v) Many transition metals and their compounds act as catalyst.

(vi) The radii of first transition series elements decrease from left to right but the decrease is not as prominent as in s & p block elements. (10)

(b) Complexes with empirical formula $CoBr(NH_3)_5SO_4$ exist in two isomeric forms A & B. Form A yields one mole of $BaSO_4$ when treated with a solution of $BaCl_2$ whereas form B yields one mole of AgBr when treated with a solution of $AgNO_3$. Write down the structural formulae of both the forms. What are these isomers called? (2½)

2. (a) Give the IUPAC names of **any three** of the following complexes :

(i) $[Cr(NH_3)_6]\ [Cu(CN)_5]$

(ii) $Na\ [Mn(CO)_5]$

(iii) $[Cr\ CO_3(NH_3)_5]\ NO_3$

(iv) $[(en)_2Co(NH)(OH)Co(en)_2]\ Cl_3$ (4½)

(b) Calculate CFSE in terms of Δ_t of a d^6 metal ion placed in a tetrahedral field. Draw the splitting diagram. (4)

(c) State Jahn Teller theorem. Giving suitable reason, explain which of the following complexes will be distorted :

$[Fe(H_2O)_6]^{3+}$ or $[Cr(H_2O)_6]^{2+}$ (4)

3. (a) The complex $[Co(en)_2Cl_2]$ exists in two isomeric forms A & B. A is optically active but B is not. Explain the reason briefly and draw the structures of A & B. (4½)

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

(i) Potassium carbonylpentacyanidoferrate (II)

(ii) μ-amido-μ- superoxidotetrakis(ethylene diamine)dicobalt(III) nitrate

(iii) Caesium tetrafluoridooxidochromate (III) (4)

(c) Which will show greater value of Δ_o and why?

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

(ii) $[Fe(H_2O)_6]^{2+}$ or $[Fe(H_2O)_6]^{3+}$ (4)

4. (a) For Mn^{3+} ion, the electron pairing energy is 336 KJ $mole^{-1}$. The crystal field splitting energy for $[Mn(H_2O)_6]^{3+}$ ion is 250 KJ $mole^{-1}$. Will the complex ion have a high spin or a low spin configuration? Calculate CFSE for both the configurations to justify your answer. (4½)

(b) $[Ni(CO)_4]$ has tetrahedral geometry but $[Ni(CN)_4]^{2-}$ is square planer. Explain with the help of VBT. (4)

(c) Given below is the latimer diagram for Fe in acidic medium :

$Fe\ O_4^{2-}$ 2.20 Fe^{3+} 0.77 Fe^{2+} −0.47 Fe

Answer the following questions :

(i) Is there any state which undergoes disproportionation? Explain.

(ii) Calculate skip step emf for Fe^{3+} ------ Fe change

(iii) Is there any tendency of Fe^{2+} to reduce to Fe? Give reason for your answer.

OR

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

(i) Separation of lanthanides by ion exchange method

(ii) Inner and outer orbital complexes

(iii) Geometrical isomerism in square planer complexes (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, $m_e = 9.31 \times 10^{\times -31} kg$

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

Attempt **three** *questions.*

1. (a) Is the function $e^{-\frac{x^2}{2}}$ an eigen function of the operator $\frac{d^2}{dx^2}$? Give reason.

   (b) Define Lambert – Beer's Law. What are its limitations? Give one application of this law.

   (c) The wave number of J=2 rotational state of $^1H^{35}Cl$ is 120 cm^{-1}. Calculate moment of inertia and the bond length of the molecule.

   (d) Phosphorescence is a slow phenomenon. Explain. (3,3,4,2.5)

2. (a) Normalize the function $\psi = x(a-x)$ over the interval $0 \leq x \leq a$.

   (b) What is Stark – Einstein law of photochemical equivalence? What are the reasons for breakdown of this law?

   (c) The absorption band in IR spectrum of $^{12}C^{16}O$ is at 2150 cm^{-1}. Calculate the force constant of CO bond and the zero-point energy of the molecule.

   (d) At room temperature several rotational levels are populated but only the lowest vibrational level is populated. Explain. (3,3,4,2.5)

3. (a) Calculate the transmittance, absorbance and molar extinction coefficient of a solution which absorbs 80% of light of wavelength 250 nm passed through a cell of path length 1cm containing a solution of concentration 0.25 M.

   (b) Explain the terms inter system crossover, internal conversion and primary process.

   (c) Calculate the energy required for excitation of π electron in Butadiene using free electron model. Average C – C bond length is 140 pm.

   (d) IR signal for stretching of C – C bond is at a lower frequency than for C = C bond. Explain. (3,3,4,2.5)

4. (a) What is Bohr's Principle of Correspondence? Explain it taking example of particle in a box.

P.T.O.

(b) What is the essential condition for a molecule to show IR spectrum? Will CO_2 show a spectrum in IR? Give reason.

(c) In photochemical synthesis of HBr, the quantum efficiency was found to be 0.2 with light of wavelength 280nm. How many moles of HBr will be produced per Joule of energy absorbed?

(d) Rotational spectra are observed in microwave region but vibrational spectra are observed in IR region of electromagnetic radiation. Explain.

(3,3,4,2.5)