SET A

Unique Paper Code : 42177925_OC

Name of the Paper : Chemistry of d-block elements, Quantum Chemistry & Spectroscopy

Name of the Course : B.Sc.(Prog.) Life Sciences/Physical Sciences

Semester : V

Duration : 3 hours

Maximum Marks : 75

Instruction for Candidates

Following details to be written on first page:

University. Roll. No.
Name:
Class:
Course:
Semester:
Paper Name:
Unique paper code:

1. Put page numbers on every page of the answer script.
2. Attempt ***ANY TWO*** questions from each section.
3. Each Question carries equal marks.
4. First part of each question carries 6.75 marks.
5. Remaining parts of each question carry 6 marks.
6. Attempt all parts of a question together.

SECTION-A

Q1.

(a) (i) The complex ion $[CoCl_6]^{3-}$ has a maximum in absorption of visible light at 363 nm. What is the value of CFS for this complex ion, expressed in cm^{-1}.

(ii) Give all possible geometrical and optical isomers of: $[Co(en)Cl_2Br_2]^-$, $[Co(NH_3)_2BrCl]^+$, and $[Pt(NH_3)_2(NO_2)_2]$. If optically active, give reasons to account for it.

(b) (i) Explain why knowledge of magnetic moment is often necessary for a correct assignment of the electron configuration and geometry according to the Valence bond theory.

(ii) $K_4[Cr(NCS)_6]$ has a magnetic moment of 5.0 B. M. while $K_4[Cr(CN)_6]$ has a value of only 3.2 B.M. Using the valence bond treatment for both the complexes, (i)) assign the electronic configuration to the central metal ion, (ii) predict the type of hybridization involved, and (iii) explain the geometry.

(c) (i) Arrange the following complex ions in the order of increasing Δ_0 giving reasons:

$[Co(NH_3)_6]^{3+}$, $[CoF_6]^{4--}$, $[Rh(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$

(ii) What is CFS? In a square planar complex, the CFS of the d-orbital energies of a central ion decrease in the sequence: $d_{x2-y2} > d_{xy} > d_{z2} > d_{xz}, d_{yz}$. Offer an explanation for the decreasing trend in energies.

Q2.

(a) Construct the Latimer diagram for iron in acidic medium. Given the standard reduction potentials in volts at 25°C as follows:

$FeO_4^{2-} + 3e^- \rightarrow Fe^{3+}$	$E°_{red} = 2.20$ V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$E°_{red} = 0.77$ V
$Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$	$E°_{red} = -0.47$ V

Based on the Latimer diagram answer the following:

(i) Is there any tendency of Fe^{2+} to reduce to Fe? Give reasons.
(ii) Is there any state which undergoes disproportionation? Explain
(iii) Calculate skip step emf for $Fe^{3+} \rightarrow Fe$ change.
(iv) Which is the most stable species and which is the most oxidizing species? Give reasons for your choice.

(b) (i) Define Jahn-Teller theorem. (ii) Octahedral Complexes are found to possess distorted structures due to Jahn-Teller Distortions. Rank the following compounds in terms of their degree of distortion from regular octahedral structure. (iii) Explain your reasoning with the help of crystal field splitting diagram.

$[Mn(CN)_6]^{3--}$, $[Co(NH_3)_6]^{3+}$, and $[Cu(OH_2)_6]^{2+}$

(c) For the Mn^{3+}, the electron-pairing energy, P, is about 335 kJ mol^{-1}. Approximate values of CFS, Δ_0 for the complexes $[Mn(H_2O)_6]^{3+}$ and $[Mn(CN)_6]^{3-}$ are 250 kJ mol^{-1} and 460 kJ mol^{-1} respectively. Calculate the crystal field stabilization energy (CFSE) for both high-spin and low-spin states and predict if these complexes have high-spin or low-spin configurations? Give the electron compositions of the t_{2g} and e_g levels for the observed spin states.

Q3. Answer ***ANY THREE*** of the following:

(a) Transition elements (3d series) show variable oxidation states. Explain giving reasons. Which of the following will show greater number of oxidation states: Cr or Mn and why?

(b) Discuss the magnetic behaviour in Lanthanides and actinides as compared to transition elements. Among the lanthanide ions the magnetic moment of only Gd^{3+} is in agreement with the moment calculated from spin only formula. Explain?

(c) Actinides have a greater tendency to form complexes than lanthanides.

(d) How does CFT account for preference for octahedral geometry? Why do metal ions with d^3 and d^8 ions prefer octahedral geometry?

(e) Transition elements and their compounds are good catalysts. Explain giving reasons.

SECTION-B

Q4.

(a) 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.

(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?

(c) For a particle of mass m in a 1-D box of length l, show that Ψ_n forms an orthonormal set of wavefunctions.

Q5.

(a) What are the selection rules for a molecule to show rotational and vibrational spectra. Which of the following molecules will give rise to observable rotational and vibrational spectra CO, O_2, HBr.

(b) Write the properties of an acceptable wavefunction. State which of the following wavefunctions are acceptable over the range:

$x = 0$ to 2π .

(i) tan(x) (ii) cosec(x) (iii) cos (x) + sin(x)

(c) Write the formula for the reduced mass of a diatomic molecule. 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 distance, $r = 121.25$ pm)

Q6.

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

(b) Explain the process of Fluorescence and Phosphorescence with appropriate diagram.

(c) Write short note on the following:
(i) Auxochrome
(ii) Frank-Condon principle
(iii) Photoelectric cell