Unique Paper Code: 42177925

Name of the Paper: DSE: Chemistry of d-block Elements, Quantum Chemistry and spectroscopy

Name of the Course: B.Sc. Prog.

Semester: V

Duration: 3 hours Maximum Marks: 75

Instruction for Candidates

1. Following details to be written on first page:
   University. Roll. No.
   Name:
   Class:
   Course:
   Semester:
   Paper Name:
   Unique paper code:
2. Put page numbers on every page of the answer script
3. Attempt **any two** questions from each section.
4. Each Question carries equal marks.
5. First part of each question carries 0.75 marks.
6. Remaining parts of each question carry 6 marks
7. Attempt all parts of a question together.

SECTION A

Q1.

(a) The relation between Δ_t and Δ_O is ……...

(b) Explain with reasons any three:
(i) Transition elements are good catalyst
(ii) Fe^{3+} is more stable than Fe^{2+}.
(iii)$KMnO_4$ is a strong oxidizing agent whereas MnO is weak reducing agent.
(iv)NH_3 readily form complexes but NH_4^+ does not

(c) Write the IUPAC name of the following (any six):

(i) $[Cr(NH_3)_6][CoF_6]$
(ii) $[Co(NH_3)_4(NO_2)Cl]NO_3$
(iii)$[(NH_3)_5 Cr OH Cr(NH_3)_4(H_2O)]^{5+}$
(iv)$(NH_3)_4[Pt(NCS)_6]$
(v) $Na_3[Fe(C_2O_4)_3]$
(vi)$[Cr(H_2O)_4Cl_2]NO_3$
(vii) $[Mn_3(CO)_{12}]$

(d) Why ions of d- block elements are coloured? How is colour of ions of d-block elements related with magnetic properties? Explain

Q2.

(a) $[Cu(NH_3)_4]^{2+}$ has ……..geometry.

(b) Why don't we come across geometrical isomers in tetrahedral complexes? Name the type of isomerism shown by the following isomers

(i) $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$
(ii) $[Pt(NH_3)_4][PtCl_6]$ and $[Pt(NH_3)_4Cl_2][PtCl_4]$
(iii)$[Co(NH_3)_5(ONO)Cl_2$ and $[Co(NH_3)_5(NO_2)Cl_2$

(c) How does Valance Bond Theory explain the following complexes (Z for Ni=28):

(i) $[Ni(CN)_4]^{2-}$ is diamagnetic and square planar
(ii) $[NiCl_4]^{2-}$ is paramagnetic and tetrahedral
(iii)$[Ni(CO)_4]$ is diamagnetic and tetrahedral

(d) Discuss magnetic properties in tetrahedral complexes on the basis of crystal field theory. Calculate spin magnetic moment of the following complexes according to V.B. theory as well as C.F. theory

(i) $[Cr(H_2O)_6]^{3+}$
(ii) $[Fe(NH_3)_6]^{3+}$

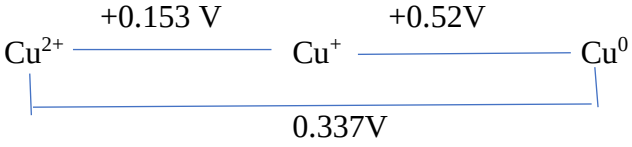
Q3.

(a) Tetragonal geometry is distorted octahedral geometry. Energy of …….. orbital decreases with increase in distortion.

(b) Describe the ion exchange method to separate lanthanides from the mixture of lanthanides.

(c) Explain Jahn Teller effect on the ground state of transition metal complexes with example Ti^{3+}. How is this effect related to the geometry of complexes? Explain the role of this effect in the complex of Cu^{2+} metal ion.

(d) A. With the help of reduction potential diagram



Find out, if
(i) Cu^+ will undergo disproportionation into Cu^{2+} and Cu^0
(ii) Cu^+ will readily change into Cu^0.

B. Distinguish between the following (any one):
(i) Inner orbital and outer orbital complexes
(ii) Linkage isomers and coordination isomers

Section B

Physical Constants

Planck's constant 6.626 x 10^{-34} *Js*

Velocity of light 3 x 10^{8} *m/s*

Atomic mass unit 1.661 x 10^{-27}*kg*

Avogadro's number 6.023 x 10^{23} mol^{-1}

Mass of electron 9.109 x 10^{-31} *kg*

Q4

(a) The mathematical relationship between absorbance and %transmittance is _____.

(b) In the photochemical reaction B →C, 1.00 x 10^{-5} mole of C is formed as a result of the absorption of 6.00 x 10^{7} ergs at 3600 Å. Calculate the quantum yield.

(c) Name and explain the theory which forms the basis for the electronic spectra of conjugated systems. What is the minimum excitation energy for linear molecule hexatriene, given that the average C-C bond distance is 140 pm?

(d) Explain why in the compound $C_6H_5 – (CH=CH)_n – C_6H_5$, the $\pi \leftarrow \pi^*$ transition shifts from UV to the visible region as *n* increases. Do you observe any change in the form of the absorbance bands while moving from non-polar to polar solvents? Explain.

Q5

(a) The ratio of the energy of the second energy level to the first energy level of a particle in one-dimensional box is equal to ___.

(b) What important aspect is signified by the property of commutation? Find the commutator $[\hat{x}, \hat{p}_x]$. Determine the result when $\hat{x}$ and $\hat{p}_x$ operate on $\psi_n(x) = N \sin\left(\frac{n\pi x}{L}\right)$ where *N* and *n* are constants.

(c) Which of the following mathematical functions are acceptable wavefunctions in the intervals given?

(i) $\psi = tanx$ $(0, 2\pi)$

(ii) $\psi = e^{-x}$ $(0,\infty)$

(iii) $\psi = \frac{\sin x}{x}$ $(0,\infty)$

(d) Solve Schrödinger wave equation for a particle of mass 'm' moving in 1-D box of length 'l'. Can "zero-point energy" of particle in 1-D box be zero? Explain.
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%.

Q6

(a) Number of vibrational degrees of freedom in CO_2 is _____.

(b) The rotational constant of $^{127}I\ ^{35}Cl$ is 0.1142 cm^{-1}. Calculate the ICl bond length. (m(^{35}Cl) = 34.9688 amu, m(^{127}I) = 126.905 amu.)

(c) A diatomic molecule AB undergoes vibrational motion according to the harmonic oscillator model. Write the mathematical expression for the Hamiltonian, Schrödinger's equation and the vibrational energy E_{vib} associated with this system. On what factors does the vibrational frequency of a molecule depend? What is order of decreasing vibrational frequency for C-Cl, C-Br, C-C,C-O,C-H? Justify your answer.

(d) The fundamental vibrational frequency of HF is 4141.3 cm^{-1}. Calculate the force constant of the H-F bond. Also, predict the fundamental vibrational frequency of DF.