

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) Zinc does not show variable oxidation state because of
- (b) Explain with reasons any three:
 - (i) Co^{3+} and Ni^{3+} are unstable while Fe^{3+} is stable
 - (ii) Transition metals in their higher oxidation state act as strong oxidizing agents while in their lower oxidation states act as reducing agent.
 - (iii) Ferric salts are more stable than the corresponding ferrous salts.
 - (iv) MnO_2 is basic whereas Mn_2O_7 is acidic
- (c) What is d-d transition? Mention the different factors responsible for exhibiting colour in complexes of transition elements.
- (d) What is the most stable oxidation state of lanthanides? In which case these elements show +2 and +4 oxidation states? Also explain why Lanthanides do not resemble transition elements in complex formation.

Q2.

- (a) Ionization isomer for $[\text{Co}(\text{NH}_3)_5\text{SO}_4] \text{Br}$ is
- (b) Write the formula of the following:
- (i) diaquodiiiododinitritopalladium (IV)
 - (ii) tris (ethylenediamine) cobalt (III) sulphate
 - (iii) μ -hydroxo- μ -imido bis[bisethylene] diamine cobalt (III) nitrate
 - (iv) pentacarbonyltriphenylphosphinechromium (0)
 - (v) chlorocyanonitrotriamecobalt (III)
 - (vi) octaamine- μ -amido- μ -nitrodicobalt (II) nitrate
- (c) Calculate crystal field splitting energy (CFSE) of tetrahedral and octahedral complexes with configuration d^5 and d^6 in weak and strong ligand field.
- (d) Explain why (any three):
- (i) $[\text{Cu}(\text{CN})_4]^{2-}$ is square planar while $[\text{CuCl}_4]^{2-}$ is tetrahedral.
 - (ii) Square planar structure is more stable than octahedral.
 - (iii) Tetrahedral complexes are generally high spin.
 - (iv) $[\text{CoF}_6]^{3-}$ is paramagnetic while $[\text{Co}(\text{NH}_3)_6]$ is diamagnetic.

Q3.

- (a) Linkage isomer of $[\text{Co}(\text{NH}_3)_5(\text{ONO})\text{Cl}_2]$ is
- (b) Describe in detail d-orbital splitting in square planar complexes. Explain why the crystal field splitting in tetrahedral complexes is just opposite to octahedral complexes.
- (c) What is Jahn Teller effect? Why distortion is found in octahedral complexes? Explain with examples
- (d) What is the effect of nature of ligand on Δ_o . Determine the number of unpaired electrons and CFSE for
- (i) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
 - (ii) $[\text{Cr}(\text{NH}_3)_6]^{3+}$

Section B

Physical Constants

Planck's constant $6.626 \times 10^{-34} \text{ Js}$

Velocity of light $3 \times 10^8 \text{ m/s}$

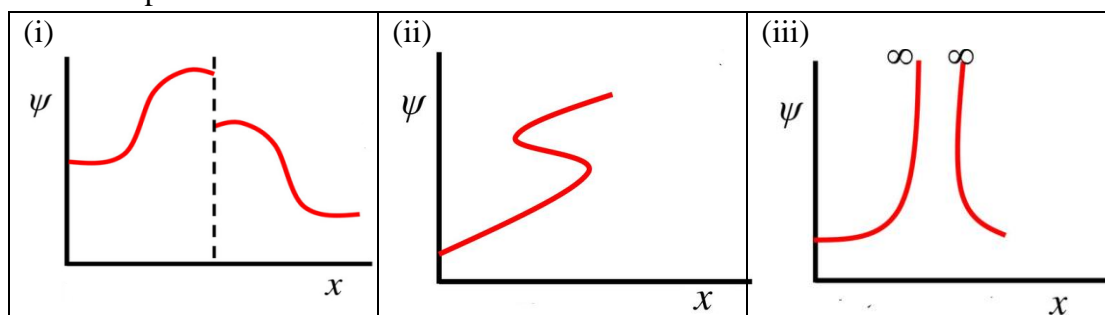
Atomic mass unit $1.661 \times 10^{-27} \text{ kg}$

Avogadro's number $6.023 \times 10^{23} \text{ mol}^{-1}$

Mass of electron $9.109 \times 10^{-31} \text{ kg}$

Q4

- (a) The square of the magnitude of the wave function is called _____.
- (b) The following figure shows three wave functions in the region $x > 0$. Indicate and explain for each wave function whether the wave function is an acceptable or unacceptable wave function.



- (c) Define eigen value. Which of the following functions are eigen functions of d^2/dx^2 :

- (i) $\sin 3x$
 (ii) $5x^2$

Give the eigen value wherever appropriate.

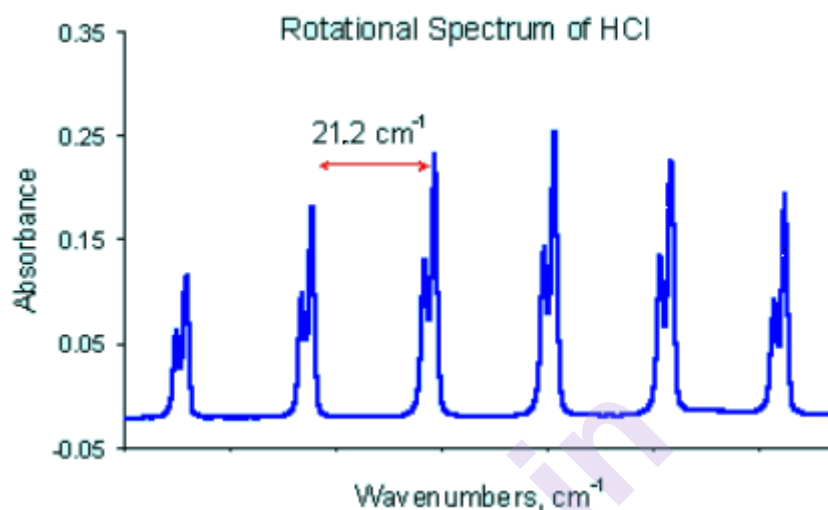
- (d) Solve Schrödinger wave equation for a particle of mass 'm' moving in 1-D box of length 'l'. Calculate the ground state energy (in kJ mol^{-1}) for an electron that is confined to a one –dimensional infinite potential well with a width of 0.2 nm.

Q5

- (a) The emission of light as a result of chemical action is called _____.
- (b) An aqueous solution of KMnO_4 gives maximum absorbance at 310 nm. Find the value of radiation in
 (i) J molecule^{-1} ,
 (ii) kJ mol^{-1} ,
 (iii) cm^{-1}
- (c) Distinguish between the primary and secondary process in a photochemical reaction. How does the distinction permit the explanation of quantum yield of 2 in the dissociation of HI?
- (d) The drug Tolbutamine (molar mass = 270) has a molar absorptivity of 703 at 262 nm. One tablet is dissolved in water and diluted to a volume of 2L. If the resulting solution (taken in a cell of 1 cm) exhibits an absorbance equal to 0.687 at 262 nm, how many grams Tolbutamine are contained in the tablet?

Q6

- (a) Selection rule for microwave spectroscopy is _____.
- (b) From the following rotational spectrum of $^1\text{H}^{35}\text{Cl}$, find the bond length of the H-Cl.



How would substitution of ^{35}Cl by ^{37}Cl alter the microwave spectrum of $^1\text{H}^{35}\text{Cl}$?

- (c) State the conditions for a molecule to be rotationally and vibrationally active. Which of the following molecules will give rise to observable rotational and vibrational spectra HCl, N₂, CO, H₂O?
- (d) The force constant of HF molecule is 970 Nm^{-1} . Calculate the fundamental vibrational frequency as well as the zero-point energy.