

SC

(A-57)

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SARDAR PATEL UNIVERSITY
M.Sc. (SEMESTER-II) EXAMINATION

2015

Tuesday, 21st April

02.30 p.m. to 05.30 p.m.

CHEMISTRY: PS02CCHE01
(INORGANIC CHEMISTRY-II)

Note:-figures to the right indicate full marks.

Total marks: 70

Q.1. Answer the following:

[8]

- Which of the following orbital is most stabilized in square pyramidal complexes of oxovanadium(IV)?
 - dz^2
 - d_{xy}
 - dx^2-y^2
 - dxz
- According to molecular orbital diagram, the number of non-bonding electrons in $[\text{Co}(\text{NH}_3)_6]^{3+}$ complex is:
 - Two
 - Zero
 - Six
 - Three
- The ground state of $[\text{V}(\text{CN})_6]^{4-}$ complex is:
 - ${}^4A_{2g}$
 - ${}^4F_{3/2}$
 - 3F_2
 - ${}^3T_{1g}$
- Which of the following system have similar Orgel diagram?
 - $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Cr}(\text{CN})_6]^{4-}$
 - $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Cu}(\text{CN})_6]^{4-}$
 - $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Ni}(\text{CN})_6]^{4-}$
 - $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{V}(\text{CN})_6]^{3-}$
- Due to spin orbit coupling, effective magnetic moment value of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ complex is :
 - Greater than spin only value.
 - Less than spin only value.
 - Similar to spin only value.
 - None of the above.
- The correct order of effective magnetic moment value of the following coordination compounds is :
 - $[\text{Co}(\text{NH}_3)_6]^{2+}$
 - $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{V}(\text{NH}_3)_6]^{3+}$
 - $i < ii < iii < iv$
 - $iv < iii < ii < i$
 - $ii < iv < i < iii$
 - $iii < iv < i < ii$

2....

7. Which of the following compounds is diamagnetic?

- a. $[\text{Ce}(\text{CN})_6]^{3-}$
- b. $[\text{Am}(\text{DMG})_3]$
- c. $[\text{Gd}(\text{H}_2\text{O})_6]^{3+}$
- d. $[\text{Pr}(\text{CN})_6]^{3-}$

8. The complex ion with a CFSE equal to $-12 Dq + 3P$ is:

- (a) $[\text{Fe}(\text{CN})_6]^{4-}$
- (b) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
- (c) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
- (d) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

Q.2. Attempt any **SEVEN** of the following:

[14]

1. Calculate the number of microstate for the following terms and arrange in the increasing order of energy.
a. 4F , b. 4G , c. 1I , d. 1H
2. The term symbols for d^3 and d^7 -configurations are 4F . Explain.
3. Ground state remains same with the change in the strength of the ligand field for Ni(II) complex. Explain.
4. Prove that $15B = v_3 + v_2 - 3v_1$ for $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ complex.
5. Differentiate Neel temperature and Curie temperature.
6. Differentiate ξ and λ . Give the value of λ for high-spin d^1 to d^{10} configurations.
7. Explain the effect of pressure on spin pairing.
8. Explain the effect of substitution in ligands on cross over region.
9. Write a short note on potential energy curves.

Q.3.A. Answer the following:

[6]

1. Explain the splitting of d-orbitals in $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ complex.
2. Explain the structure of $[\text{Mn}(\text{CN})_6]^{3-}$ and $[\text{Mn}(\text{Br})_6]^{3-}$ complexes.

B. Answer the following:

1. Differentiate spectrochemical series and nephelauxetic series.
2. On the basis of molecular orbital theory, show that $[\text{CoF}_6]^{3-}$ is outer sphere complex.

[6]

OR

B. Answer the following:

1. Derive the terms arising out of p^2 -system and indicate the order of increasing energy of these terms.
2. Define Baricentre and explain the Hund's rule for deriving term symbols for several electron system.

Q.4.A. Predict the types of transitions in the following complexes giving proper explanations. [6]

1. $[\text{Cu}(\text{NH}_3)_6]^{2+}$,
2. $[\text{Co}(\text{NH}_3)_6]^{3+}$,
3. $[\text{Co}(\text{NH}_3)_6]^{2+}$,
4. $[\text{Ni}(\text{Ox})_3]^{4-}$,
5. $[\text{Ti}(\text{SCN})_6]^{4-}$,
6. $[\text{MnF}_6]^{4-}$.

B. Draw and explain the correlation diagram for $[\text{V}(\text{en})_3]^{3+}$ complex. [6]

OR

B. Derive the configuration interaction term (χ) for $[\text{Ti}(\text{CN})_6]^{4-}$ and $[\text{V}(\text{Ox})_3]^{4-}$ coordination compounds. Calculate the crystal field splitting energy, nephelauxetic ratio, covalent character, ionic character, Racah parameter and configuration interaction term for the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex. Given: $\nu_1 = 8,100 \text{ cm}^{-1}$, $\nu_2 = 16,000 \text{ cm}^{-1}$, $\nu_3 = 20,000 \text{ cm}^{-1}$ and B_0 for $\text{Co}(\text{II}) = 971 \text{ cm}^{-1}$.

Q.5.A. Derive the equation $\mu_{\text{eff}} = 2.83 (\chi_M \times T)^{1/2}$ B.M. for calculating experimental magnetic moment of the $[\text{Zn}(\text{en})_3]^{2+}$ chelate.

B. What are the sources of paramagnetism? Derive the orbital magnetic moment equation. Find out the diamagnetic correction for 1,10-phenanthroline and ethylenediaminetetraacetic acid. Given: $\chi_A \rightarrow \text{C} = -6.0 \times 10^{-6}$ cgs units, $H = -2.93 \times 10^{-6}$ cgs units, $O = -4.61 \times 10^{-6}$ cgs units, $O_2 = -7.95 \times 10^{-6}$ cgs units, $N_{(\text{open chain})} = -5.57 \times 10^{-6}$ cgs units and $N_{(\text{ring})} = -4.61 \times 10^{-6}$ cgs units. $\lambda \rightarrow \text{C} = -0.24 \times 10^{-6}$ cgs units and $\text{C}=\text{N} = +8.15 \times 10^{-6}$ cgs units. [6]

OR

B. Discuss the antiferromagnetic exchange pathways.

Q.6.A. Explain the spin-orbit coupling on A, E and T terms. Calculate the effect of spin-orbit coupling on effective magnetic moments value of $[\text{Cr}(\text{NCS})_6]^{4-}$ complex. [Given: $\lambda = 315 \text{ cm}^{-1}$ and $Dq = 900 \text{ cm}^{-1}$]. [6]

B. Answer the following: [6]

1. Explain the spin pairing in octahedral complexes.
2. What are the conditions for orbital contribution? Predict the orbital contributions in $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Ni}(\text{H}_2\text{O})_6] \cdot \text{Cl}_2$ complexes giving proper justification.

OR

B. Answer the following:

1. Derive the term symbols and calculate the effective magnetic moments value for $\text{Cm}(\text{III})$ ($z = 96$), $\text{Pu}(\text{III})$ ($z = 94$) and $\text{Cf}(\text{III})$ ($z = 98$).
 2. Explain the role of lanthanide complexes in ^1H NMR spectroscopy.
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