

(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 :

(i) $[\text{Co}(\text{NH}_3)_6]^{2+}$ (ii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (iii) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (iv) $[\text{V}(\text{NH}_3)_6]^{3+}$

 - $i < ii < iii < iv$
 - $iv < iii < ii < i$
 - $ii < iv < i < iii$
 - $iii < iv < i < ii$

2....

7. Which of the following compounds is diamagnetic?
- $[\text{Ce}(\text{CN})_6]^{3-}$
 - $[\text{Am}(\text{DMG})_3]$
 - $[\text{Gd}(\text{H}_2\text{O})_6]^{3+}$
 - $[\text{Pr}(\text{CN})_6]^{3-}$
8. The complex ion with a CFSE equal to $-12 Dq + 3P$ is:
- $[\text{Fe}(\text{CN})_6]^{4-}$
 - $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

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

[14]

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

Q.3.A. Answer the following:

[6]

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

B. Answer the following:

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

[6]

OR

B. Answer the following:

- Derive the terms arising out of p^2 -system and indicate the order of increasing energy of these terms.
- 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, $\text{H} = -2.93 \times 10^{-6}$ cgs units, $\text{O} = -4.61 \times 10^{-6}$ cgs units, $\text{O}_2 = -7.95 \times 10^{-6}$ 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.