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SEAT No.

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SARDAR PATEL UNIVERSITY
M.Sc. (SEMESTER-I) EXAMINATION
2018

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10.00 a.m. to 01.00 p.m.

CHEMISTRY: PS01CCHE21
(Electron Spectroscopy and Magneto Chemistry)

Total marks: 70

Note:-figures to the right indicate full marks.

[8]

Q.1. Answer the following:

1. The number of way in which electron spin can be arranged for the spin multiplicity $2S + 1 = 1$ is :
- One
 - Three
 - Two
 - Zero

2. Which of the following system exhibits regular octahedral structure?
- low spin- d^9
 - high spin- d^5
 - low spin- d^4
 - high spin- d^6

3. The ground state for the $[\text{Fe}(\text{CN})_6]^{3-}$ is:
- ${}^2T_{2g}$
 - ${}^1A_{1g}$
 - ${}^3T_{1g}$
 - 2E_g

4. Arrange the following term in decreasing order of the energy:

- 2F
- 3G
- 4I
- 4H

- (iv) > (iii) > (i) > (ii)
- (iii) > (iv) > (ii) > (i)
- (i) > (ii) > (iv) > (iii)
- (ii) > (i) > (iii) > (iv)

5. Below Neel temperature substance behave like :
- Paramagnetic
 - Antiferromagnetic
 - Ferromagnetic
 - Ferrimagnetic

(1)

(P.T.O.)

6. The correct order of effective magnetic moment value of the following coordination compounds is :

(i) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (ii) $[\text{Ni}(\text{CN})_4]^{2-}$ (iii) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (iv) $\text{K}_3[\text{Fe}(\text{CN})_6]$

- a. $i < iii < iv < ii$ b. $iv < iii < ii < i$
c. $ii < iv < iii < i$ d. $iii < iv < i < ii$

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 $-20Dq + 2P$ is:

- a. $[\text{Fe}(\text{CN})_6]^{3-}$
b. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
c. $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
d. $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$

Q.2. Attempt any SEVEN of the following:

[14]

1. Calculate the number of microstate for $(t_{2g})^2(e_g)^2$ and $(t_{2g})^3(e_g)^1$ configurations.
2. The term symbols for d^4 and d^6 - configuration is 5D . Explain.
3. The Orgel diagram for d^4 and d^9 - configuration is identical. Explain.
4. Determine the M_L , M_S and term symbols of the $(2^+, 3^+)$ and $(0^+, 0^-)$ microstates.
5. Explain the σ -overlap and π - overlap.
6. Explain the delta bond.
7. Explain the effect of pressure on spin pairing.
8. Explain the effect of substitution in ligand on spin pairing.
9. Explain the potential energy curve for high-spin and low-spin complexes.

Q.3.A. Answer the following:

[6]

1. Differentiate the splitting of d-orbitals in $[\text{Ni}(\text{CN})_6]^{4-}$ and $[\text{Ni}(\text{Cl})_4]^{2-}$ complexes.
2. Explain the splitting of d-orbitals in $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ complex.

B. Answer the following:

[6]

1. Derive the terms for p^2 - configuration and show that 3P is ground state and 1S is higher energy state.
2. Explain the structure of $[\text{Cr}(\text{CN})_6]^{4-}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ complexes.

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OR

B. Answer the following:

1. Differentiate tetragonal elongation and tetragonal compression.
2. Differentiate spectrochemical series and nephelauxetic series.

Q.4.A. Draw and explain the Orgel and Tanabe Sugano diagram for $[\text{Mn}(\text{CN})_6]^{3-}$ complex. [6]

B. Predict the types of transitions for the following complexes: [6]

- (i) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, (ii) $[\text{Co}(\text{edta})]^{2-}$, (iii) $[\text{V}(\text{NH}_3)_6]^{4+}$
(iv) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, (v) $[\text{Fe}(\text{SCN})_6]^{4-}$, (vi) $[\text{Mn}(\text{CN})_6]^{4-}$.

OR

B. Derive the configuration interaction term (x) for $[\text{Co}(\text{en})_3]^{2+}$ and $(\text{Cr}(\text{Ox})_3)^{3-}$ coordination compounds. Calculate crystal field splitting energy, nephelauxetic ratio, covalent character, ionic character, Racah parameter and configuration interaction term for the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex. Given: $\nu_1 = 7,980 \text{ cm}^{-1}$, $\nu_2 = 11,980 \text{ cm}^{-1}$, $\nu_3 = 23,580 \text{ cm}^{-1}$ and B_0 for $\text{Ni}(\text{II}) = 1040 \text{ cm}^{-1}$.

Q.5.A. Define the magnetic susceptibility and derive the equation for diamagnetic susceptibility [6]

B. Differentiate ferromagnetism and ferrimagnetism. Derive the Curie Weiss equation. [6]

OR

B. Answer the following:

1. Find out the diamagnetic susceptibility correction for bis(salicylidene)ethylenediamine and salicylidene glycine.

Given: $\chi_A \rightarrow C = -6.0 \times 10^{-6}$ 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.

$\lambda \rightarrow C = -0.24 \times 10^{-6}$ cgs units and $C=N = +8.15 \times 10^{-6}$ cgs units.

2. Derive the effective magnetic moment equation for multiplet width is small as compared to thermal energy.

Q.6.A. 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 $[\text{Cr}(\text{H}_2\text{O})_6] \cdot \text{Cl}_3$ complexes giving proper justification.

B. Answer the following: [6]

1. Explain the application of coordination compounds of lanthanides in ^1H NMR spectroscopy.
2. Differentiate the electronic spectra of lanthanide complexes and actinide complexes.

OR

B. Derive the L, S, J, g, μ_J and term symbols for actinides.

