[103] SEAT No._____ No. Printed pages:3

SARDAR PATEL UNIVERSITY
M.Sc. (SEMESTER-I) EXAMINATION
2019
Monday, 18th November
10.00 a.m. to 01.00 p.m.
CHEMISTRY: PS01CCHE21
(Electron Spectroscopy and Magneto Chemistry)

Note:-figures to the right indicate full marks. **Total marks: 70**

Q.1. Answer the following: [8]

1. The ground state value of J for ^3F term derive from Co(III) is:
   a. One
   b. Two
   c. Zero
   d. Four
2. The term symbol for the microstate (3^+, -1^+) is:
   a. ^3G
   b. ^1G
   c. ^1D
   d. ^3D
3. The ground state for the $[Cr(CN)_6]^{3-}$ is:
   a. $^4T_{2g}$
   b. $^4A_{2g}$
   c. $^4T_{1g}$
   d. ^4E_g
4. The possible transition in $[Co(CN)_6]^{3-}$ is:
   a. $^1E_g \rightarrow {}^1T_{2g}$
   b. $^1A_{1g} \rightarrow {}^1T_{1g}$
   c. $^4T_{2g} \rightarrow {}^4E_g$
   d. $^4A_{2g} \rightarrow {}^4T_{1g}$
5. The number of Cu—O bonds in $[Cu(CH_3COO)_2 \cdot H_2O]_2$ is:
   a. 10
   b. 08
   c. 02
   d. 04
6. Which of the following complex ion has a magnetic moment value same as $K_3[Fe(CN)_6]$?
   a. $[Cu(NH_3)_4]^{2+}$
   b. $[Ni(DMG)_2]$
   c. $[Fe(H_2O)_6]^{3+}$
   d. $[Fe(H_2O)_6]^{2+}$
7. Which of the following metal ion exhibits highest magnetic moments value?
   a. Tm(III) z = 69
   b. Am(III) z = 95
   c. Cf(III) z =98
   d. Pm(III) z = 61

8. Which of the following lanthanides produce largest down-field shift?
   a. Gd(III)
   b. Dy(III)
   c. Tm(III)
   d. Pr(III)

Q.2. Attempt any **SEVEN** of the following: **[14]**

1. Which of the orbital is most destabilized in square pyramidal, square planar, trigonal prismatic and pentagonal bipyramidal geometries?
2. Differentiate regular octahedral, slightly distorted octahedral and highly distorted octahedral structures.
3. Derive the ground term and ground state for $[Cr(CN)_6]^{2-}$ and $[Ni(SCN)_4]^{2-}$.
4. Give the crystal field term for ^2S, ^3P, ^4D, ^5F, ^6G, ^2H and ^3I terms.
5. Differentiate hidden and overt.
6. Differentiate diamagnetism and anti-ferromagnetism.
7. Explain the effect of pressure on magnetic moments.
8. Explain the spin pairing in $[Ni(Cl)_4]^{2-}$ complex.
9. Explain the spin pairing in $[Pt(Cl)_4]^{2-}$ complex.

Q.3.A. Differentiate tetragonal elongation and tetragonal compression. Show that structure of $[Co(NH_3)_6]^{3+}$ is d^2sp^3 hybrid and $[Co(F)_6]^{3-}$ is sp^3d^2 hybrid on the basis of MOT. **[6]**

B. Answer the following: **[6]**

1. Calculate the number of microstate for the following configurations and arrange them in decreasing order of energy.
   $(t_{2g})^3(e_g)^1$, $(e_g)^4(t_{2g})^3$, $(e_g)^2(t_{2g})^3$ and $(t_{2g})^5(e_g)^1$.
2. Explain the Hund's rule for deriving term symbols. What do you mean by hole-equivalent?

OR

B. Define spectrochemical series and Nephelauxetic series.
(i) Arrange the following complexes in increasing order of crystal field splitting energy giving suitable reason.
1. $[Ir(NH_3)_6]^{3+}$, 2. $[Co(NH_3)_6]^{2+}$, 3. $[Co(H_2O)_6]^{2+}$,
4. $[Mn(Br)_6]^{4-}$, 5. $[Ni(SCN)_6]^{4-}$, 6. $[Mn(Br)_4]^{2-}$.

(ii) Arrange the following complexes in increasing order of 15B value:
(1). $[Cr(H_2O)_6]^{2+}$
(2). $[Cr(F)_6]^{4-}$
(3). $[Cr(Br)_6]^{4-}$
(4). $[Cr(NH_3)_6]^{2+}$

Q.4.A. Derive the configuration interaction term (x) for the $[Cr(H_2O)_6]^{3+}$ and $[Ni(Cl)_6]^{4-}$. Calculate crystal field splitting energy, nephelauxetic ratio, covalent character, ionic character and Racah parameter for the $[Mn(H_2O))_6]^{2+}$. **[6]**
Given: $\nu_1 = 18{,}600\ cm^{-1}$, $\nu_2 = 22900\ cm^{-1}$, $\nu_3 = 24900$ $\nu_4 = 25150$ and B_0 for Mn(II) $= 860\ cm^{-1}$.
From theoretical plot:
Ratio $\nu_3/\nu_2 \approx 1.1$ correspond E/B= 24 and E/B= 24 correspond to $^4T_{1g}$.

B. Draw and explain the Orgel and TS-diagram for $[Co(CN)_6]\cdot Cl_3$ complex. **[6]**

3...

OR

B. Differentiate forbidden and allowed transitions giving suitable examples. Calculate crystal field splitting energy, nephelauxetic ratio, covalent character, ionic character and Racah parameter for the $[V(H_2O))_6]^{3+}$ and predict the types of transition v_1 and v_2.

Given: $v_1 = 17{,}200\ cm^{-1}$, $v_2 = 25600\ cm^{-1}$ and B_0 for V(III) $= 860\ cm^{-1}$.

From theoretical plot:

E/B= 20 corresponds to Dq/B =2.5 for $^3T_{1g}(F)$ and E = 17,200 cm^{-1}

Dq/B =2.5 corresponds to E/B= 30 for $^3T_{1g}(P)$

Dq/B =2.5 corresponds to E/B= 45 for $^3A_{2g}$.

Q.5.A. Derive the equation for molar diamagnetic susceptibility and show that diamagnetism is negative and indirectly dependent on temperature. **[6]**

B. Answer the following: **[6]**

1. Calculate the effective magnetic moment value of $[Ni(en)_3]^{2+}$, $[Co(H_2O)_6]\cdot Cl_3$ and $[Ni(CO)_4]$.

2. Find out the diamagnetic susceptibility correction for salicylaldeneglycine and 2-methyl aniline.

Given: $\chi_A \rightarrow C = -6.0 \times 10^{-6}$ cgs units, $H = -2.93\times10^{-6}$ cgs units, $O = -4.61\times10^{-6}$ cgs units, $O_2 = -7.95\times10^{-6}$ cgs units, $N_{(Open\ chain)} = -5.57 \times 10^{-6}$ cgs units and $N_{(ring)} = -4.61 \times 10^{-6}$ cgs units.

$\lambda \rightarrow C = -0.24\times10^{-6}$ cgs units and $C{=}N = +8.15\times10^{-6}$ cgs units.

OR

B. Differentiate the ferromagnetism and ferrimagnetism. Discuss the spontaneous magnetism theory.

Q.6.A. Explain the spin-orbit coupling and calculate the value of λ for high-spin d^1 to d^{10}. What is the effect of spin-orbit coupling on effective magnetic moments value of $[Cr(H_2O)_6]^{3+}$? Given $\lambda = 315\ cm^{1-}$ and $Dq = 800\ cm^{1-}$. **[6]**

B. Answer the following: **[6]**

1. Explain the relative change in electron exchange energy.
2. Define the Lande's interval rule and calculate the energies of J-levels for f^2-system.

OR

B. Answer the following:

1. Which of the orbital contribution condition are satisfy in the following complexes? (i). $[Fe(SCN)_4]^{3-}$ (ii). $[Co(NH_3)_6]\cdot Cl_3$, (iii). $[Mn(CN)_6]^{4-}$.
2. Derive the term symbols and magnetic moments of the following systems. (i). Pu(III) z = 94 (ii). Dy(III) z = 66 (iii).Yb(III) z = 70.