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63/2 (SEM-4) CHM 403

2023

**CHEMISTRY**

(Theory Paper)

Paper Code : CHM 403

**(Transition Metals and Inorganic Materials)**

Full Marks – 80

Pass Marks – 32

Time – Three hours

The figures in the margin indicate full marks  
for the questions.

1. Choose the correct answers : 1×4=4

(a)  $\text{Ni}^{2+}$  can have two unpaired electrons in

(i) Octahedral geometry only

(ii) Square planner geometry only

(iii) Tetrahedral geometry only

(iv) Both Tetrahedral geometry and  
Octahedral geometry

[Turn over

(b) For a  $d^2$  system where electron spins are parallel its spin multiplicity is

- (i) 1                      (ii) 2  
(iii) 4                    (iv) 3

(c) Doping of silicon (Si) with boron (B) leads to

- (i) n-type semiconductor  
(ii) p-type semiconductor  
(iii) metal  
(iv) insulator

(d) Magnetic moment of a metal complex is 5.9 B.M. Number of unpaired electrons in the complex is

- (i) 2                      (ii) 3  
(iii) 4                    (iv) 5

2. Answer any *five* of the following questions :

5×5=25

(a) Deduce the matrices for the symmetry operations in point group  $C_{3v}$  considering the transformations of the general point (x, y, z). State and explain what is meant by representation of group.

(b) What are direct product representations ? State and explain how direct products are useful in bonding theories and spectroscopy.

(c) Evaluate the following :

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

(d) Derive the matrix representation for reflection operation.

(e) Determine the trace value or character of each symmetry operations present in cis-butadiene molecule ?

(f) Identify the point group of  $BCl_3$  molecule? Find the symmetry elements present ?

(g) Construct the hybrid orbital for linear molecule ?

3. Answer any *four* of the following questions :

4×4=16

(a) What are the factors that affect the magnitudes of splitting ( $\Delta$ ) of d-orbitals ?

- (b) What are correlation diagrams ? Construct the correlation diagram for a  $d^2$  ion and indicate how the corresponding Tanabe-Sugano diagram may be obtained from it.
- (c) State what spin-orbit coupling is and explain its importance in the ligand field theoretical treatment of the electronic structure of metal complexes.
- (d) Comment on 'ligand field theory' as applied to coordination complexes and discuss how it is related to or different from crystal field theory.
- (e) Write down the spectroscopic (free ion) ground terms as well as the weak field (tetrahedral) ground terms for the bivalent first row transition metal ions.

4. Answer any *three* of the following questions :

5×3=15

- (a) Why the intensities of absorption band in octahedral complexes are weaker than in tetrahedral complexes ? Give reasons.

- (b) Describe the selection rules for electronic spectra.
- (c)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  shows absorption bands at  $17000\text{ cm}^{-1}$ ,  $24000\text{ cm}^{-1}$  and  $37000\text{ cm}^{-1}$ . Calculate the absorption frequency corresponding to  $10\text{ Dq}$ .
- (d) Point out the differences between Static and Dynamic Jahn-Teller effect ? Explain with suitable examples.

5. Answer any *two* of the following questions :

5×2=10

- (a) The ionic radius of  $\text{K}^+$  is 133 pm, whereas that of  $\text{Na}^+$  is 98 pm. Do you expect  $\text{K}^+$  to be a common substitution impurity in compounds containing  $\text{Na}^+$  ? Give reason.
- (b) Show that, under  $O_h$  symmetry, the LGO in diagram (a) belongs to a  $t_{2g}$  set.
- (c) Write short notes on :
  - (i) Molecular magnets
  - (ii) Piezo-electric materials.

6. Answer any *two* of the following questions :

5×2=10

- (a) What causes electrons, which repel each other because of their negative charge, to pair up and travel together in superconductors ? Discuss the superconductivity in high-T<sub>c</sub> cuprates from maximal to minimal dissipation.
- (b) What are solid electrolysis ? Give some example and explain how those materials are useful in battery applications.
- (c) What is the piezoelectric effect in ultrasound ? What happens when stress is applied to a piezoelectric material ?



