Exam. Code : 210401
Subject Code : 3806

M.Sc. (Chemistry) 1st Semester

LIGAND FIELD THEORY

Paper—Course–I

Time Allowed—3 Hours] [Maximum Marks—50

Note :— Attempt a total of **five** questions taking at least **one** from each section while **fifth** can be chosen from any Section. All questions carry equal marks.

SECTION—A

1. Prove using group theory that O_h point group splits a set of five d orbitals into two groups. 10

2. Construct the character table of C_{3v} from first principles. 10

SECTION—B

3. Draw a MOEL diagram for $[TiF_6]^{3-}$ complex showing both σ and π bonding. 10

4. Systematically derive all the spectroscopic terms of a d^2 configuration. 10

SECTION—C

5. Drive from first principle and draw correlation energy level diagram for a d^2 configuration in octahedral field using the O_h character table. 10

6. (a) Calculate the magnetic moment for Nd(III) ion. 8

   (b) Explain first and second order Zeeman effect. 2

SECTION—D

7. The six coordinated Ni(II) complex shows three spin allowed bands at 12800, 17350 and 31000 cm^{-1}. Assign the transitions and calculate 10Dq and B for the complex. 10

8. (a) The gas phase V^{3+} has ^3F as ground term. The ^1D and ^3P terms lie, respectively 10642 and 12920 cm^{-1} above it. The energies of the terms are given in terms of Racah parameters as $E(^3F) = A - 8B$, $E(^3P) = A + 7B$,

   $E(^1D) = A - 3B + 2C$.

   Calculate the values of B and C. 6

   (b) The ligand to Metal charge transfer transition in $PtBr_4^{2-}$ occurs at 36000 cm^{-1} while that for $PtCl_4^{2-}$ occurs at 44000 cm^{-1} why ? 2

   (c) Solutions of $[Cr(H_2O)_6]^{3+}$ are pale blue-green but the chromate CrO_4^{2-} is an intense yellow. Characterize the origins of the transitions and explain the intensities. 2

Character table for O_h point group

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1	
E_g	2	−1	0	0	2	2	0	−1	2	0	$2z^2-x^2-y^2$, x^2-y^2
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1	xz, yz, xy
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1	
E_u	2	−1	0	0	2	−2	0	1	−2	0	
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	x, y, z
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1	