PG CBCS
M.SC. Semester-III Examination, 2021
CHEMISTRY
PAPER: CEM 302

(INORGANIC SPECIAL)

Full Marks: 40   **Time: 2 Hours**

Answer any <u>FOUR</u> questions from the following: 4x10=40

1. (a) Find out the state of hybridization of the central atom in BF_3 and then find the expression of the hybrid orbitals in term of atomic orbitals (LCAO's).

    Character table for D_{3h} point group is given below.   8+2

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

    (b) Why polarization effect is not observed for cubic or higher symmetry group?

2. (a) Prove that the representation of direct product Γ_{AB} will contain the totally symmetric representation if the irreducible Γ_A = the irreducible Γ_B.

    (b) Explain why CoF_6^{3-} exhibit single peak but $[Co(en)_3]^{3+}$ exhibit double peak in their electronic spectra?

    (c) What is the "Hole Formalism"?   5+3+2

3. With help of group theoretical principle, find the splitting of d orbitals of the central atom in octahedral environment. Following is the character table for 'O'group.   10

O	E	$8C_3$	$3C_2(=C_4^2)$	$6C_4$	$6C_2$	linears, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2), (x^2-y^2)$
T_1	3	0	-1	1	-1	$(R_x,R_y,R_z), (x, y, z)$	
T_2	3	0	-1	-1	1		(xy, xz, yz)

4. For trans-dichlorobis(ethylenediamine)cobalt(III) complex the ground state is $^1A_{1g}$ and excited singlet states are $^1A_{2g}$, ^1E_g and $^1B_{2g}$. Show that

(P.T.O.)

(i) $^1A_{1g} \rightarrow {}^1A_{1g}$ transition is vibronically allowed with (x,y) polarized light but forbidden with z-polarized light.

(ii) $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1B_{2g}$ transitions are vibronically allowed with (x,y) and z-polarized light.

Character table for D_{4h} point group is given below:-   10

D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linears, rotations	quadratic
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	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

5. (a) Draw the MO diagram of NH_3 molecule using projection operator method.

Character table for C_{3v} point group is given below:

C_{3v}	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

(b) How does group theory help in determining the zero and non-zero values of spectroscopic transition moment integral?

(c) State the selection rules for IR active and Raman active molecules.   5+3+2

6. (a) Predict the total number of Fe-Fe bonds and show the most stable structure of $[\eta^5$-$CpFe(CO)_2]_2$.

(b) Between the following octahedral complexes (*fac* isomer), in which case do you observe lowest stretching frequency of CO? Give reasons.

(i) $[(PPh_3)_3Mo(CO)_3]$ (ii) $[Py_3Mo(CO)_3]$ (py = pyridine)

$$[Fe(CO)4]^{2-} \xrightarrow{RBr} ? \xrightarrow{CO} ? \xrightarrow{H^+} \text{organic product ?}$$
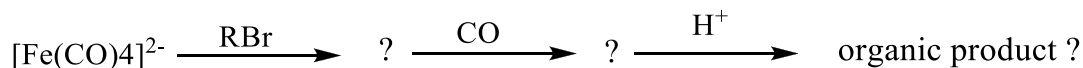
(c) Write down the expected intermediates and products asked in the following schemes.

(d) $[\eta^5\text{-}CpFe(CO)]_4$ shows a single stretching frequency at 1640 cm^{-1}. ^1H NMR spectrum shows a single line. Predict the structure based on the given data.

(e) What is *agostic* Hydrogen? Show the corresponding interacting orbitals with proper labelling.   1.5+2+1.5+3+2

7. What is Ziegler-Natta catalyst? Mechanistically explain the stereo regularity of polymerization of olefin with this catalyst.   2+6

8. (a) What is "Sandwich compound"? Give an example.

(b) What is the role of hydroiodic acid in Monsento process of acetic acid synthesis? Briefly discuss the catalytic cycle for 'Monsento acetic acid' process using $[Rh\,(CO)_2I_2]^-$ catalyst. Mention oxidation states of 'Rh' in each step.

(c) What is meant by insertion reaction and oxidative coupling?   2+(2+4)+2

9. Write down the complete reaction for the production of CH_3CHO from C_2H_4 by Wacker's process. Write down the rate equation for the process. Draw the catalytic cycle for the process.   2+2+4

10. (a) Write down the catalytic cycle for the hydroformylation reaction using $HCo(CO)_4$ as catalyst.

(b) Establish the relation:
$$\chi(\alpha) = \frac{Sin(l + \frac{1}{2})\alpha}{Sin(\frac{\alpha}{2})}$$

Where the terms have their usual significance.

(c) Show that the d-orbital whose angular wave function is constant times $(Sin^2\theta Cos2\theta)$ is $d_{x^2-y^2}$ orbital.   4+4+2

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