

PG (CBCS)
M.Sc. Semester-III Examination, 2022
CHEMISTRY
PAPER: CEM-302

ADVANCED INORGANIC CHEMISTRY-I (INORGANIC SPL.)

Full Marks: 40

Time: 2 Hours

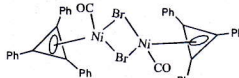
GROUP - A

1. Answer any four questions from the following questions: 2×4 = 8

- a) What do you mean by insertion reaction and oxidative coupling?
- b) Why do the configuration d^n and d^{10-n} give identical ligands field term in any given field symmetry?
- c) Calculate the number of microstates for np^2nd^2 electronic configuration.
- d) Mention the advantages of rhodium catalyst over cobalt catalyst for hydroformylation reactions.
- e) What do you mean by 'Exclusion rule'?
- f) What are the advantages and disadvantages of the homogeneous and heterogeneous Catalysis?
- g) The addition of PPh_3 to $RhCl(PPh_3)_3$ reduces the TOF of hydrogenation reaction.-Justify.
- h) Show that the d-orbital whose angular wave function is constant times $(\sin^2\theta \cos 2\theta)$ is $d_{x^2-y^2}$ orbital.

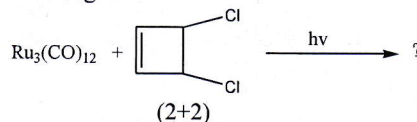
GROUP - B

2. Answer any four questions from the following questions: 4×4 = 16

- a) (i) How will you  synthesize

via dehalogenation of cyclopropene starting from $Ni(CO)_4$.

- (ii) Complete the following reaction:



- b) Briefly discuss the catalytic cycle for 'Monsanto acetic acid' process using $[Rh(CO)_2I_2]^-$ catalyst. Mention oxidation states of 'Ru' in each step. (4)
- c) (i) Between the following octahedral complexes (*fac* isomer), in which case lowest stretching frequency of CO is observed? Give reasons.

(A) $[(PPh_3)_3Mo(CO)_3]$ (B) $[Py_3Mo(CO)_3]$ (py = pyridine)

(P.T.O.)



- (ii) $[V^5-CpFe(CO)_2]_2$ shows a single stretching frequency at 1640 cm^{-1} . 1H NMR spectrum shows a single line. Predict the structure of the complex. (2+2)
- d) Establish the relation: (2)

$$\chi(\alpha) = \frac{5\pi(\alpha + \frac{1}{2})\sigma}{5\pi(\frac{\alpha}{2})}$$

Where the terms have their usual significance. (4)

- e) Construct qualitative π -molecular orbital energy level diagram of trans-butadiene molecule and show that only two $\pi \rightarrow \pi^*$ bands are possible in the electronic spectra of the molecule. Character table for C_{2h} point group is given below.

C_{2h}	E	$C_2(z)$	i	σ_h	linear functions, rotations	quadratic functions	cubic functions
A_g	+1	+1	+1	+1	R_z	x^2, y^2, z^2, xy	-
B_g	+1	-1	+1	-1	R_x, R_y	xz, yz	-
A_u	+1	+1	-1	-1	z	-	$xz^2, yz^2, x^2y, xy^2, x^3, y^3$
B_u	+1	-1	-1	+1	x, y	-	$xz^2, yz^2, x^2y, xy^2, x^3, y^3$

- f) Find out the possible energy state for d^2 electronic systems and hence find out the ground state term symbol. (4)
- g) Predict the product of the following reaction: (2+2)
- (i)
- (ii) $Fe(CO)_5 + Ph-C \equiv C-Ph \xrightarrow{\Delta} ?$
- h) What is the rule of correspondence? Draw a correlation diagram for a d^2 ion in an octahedral crystal field. (4)

GROUP - C

3. Answer any two questions from the following questions: 8x2 = 16

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

(2)

(P.T.O.)

- c) 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	$2C_3$	$3\sigma_v$	Basis components
A_1	1	1	1	z
A_2	1	1	-1	(x, y)
E	2	-1	0	$(R_x, R_y), (x^2-y^2, xy), (yz, xz)$

- d) 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.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_6$	$3\sigma_v$	
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	$(R_x, R_y), (xy, yz)$
$\Gamma_g(R)$	3	0	1	3	0	1	

(3)