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**PG CBCS**  
**M.Sc. Semester-III Examination, 2020**  
**CHEMISTRY**  
 PAPER: CEM 302  
 (INORGANIC SPECIAL)

Full Marks: 40

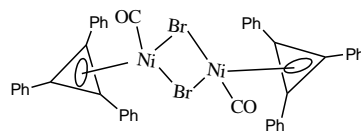
Time: 2 Hours

Answer any four questions from the following:

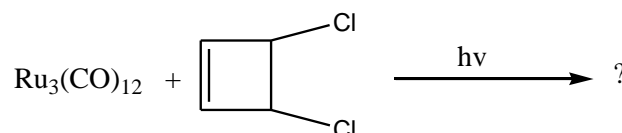
4x10 =40

1. (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) What is the hole formalism?
- (d) Write some advantages of rhodium catalyst over cobalt catalyst for hydroformylation reaction. 2.5 × 4
2. (a) What do you mean by 'Exclusion rule'?
- (b) What is "Sandwich compound"? Give an example.
- (c) What is the role of hydroiodic acid in Monsanto process of acetic acid synthesis?
- (d) Show that the f-orbital whose angular wave functions is constant times  $\sin^2\theta\cos\theta\sin 2\phi$  is  $f_{xyz}$  orbital. 2.5 × 4

3. (a) How will you synthesize

via dehalogenation of cyclopropene starting from  $\text{Ni}(\text{CO})_4$ .

(b) Complete the following reaction:

(c) The addition of  $\text{PPh}_3$  to  $\text{RhCl}(\text{PPh}_3)_3$  reduces the hydrogenation TOF (Turn over frequency).-Justify. 4+3+3

P.T.O.

(2)

4. (a) Briefly discuss the catalytic cycle for 'Monsanto acetic acid' process using  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  catalyst. Mention oxidation states of 'Ru' in each step.

(b) Write down the catalytic cycle for the hydroformylation reaction using  $\text{HCo}(\text{CO})_4$  as catalyst.

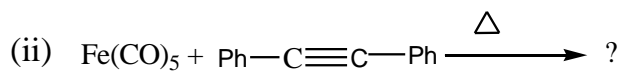
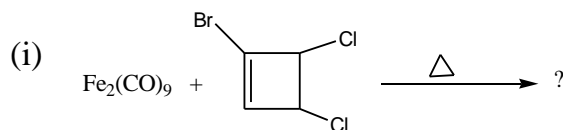
(c) Establish the relation:  $\chi(\alpha) = \frac{\text{Sin}(l + \frac{1}{2})\alpha}{\text{Sin}(\frac{\alpha}{2})}$   
Where the terms have usual significance. 4+3+3

5. (a) Show that the d-orbital whose angular wave function is constant times  $(\text{Sin}^2\theta\text{Cos}2\theta)$  is  $d_{x^2-y^2}$  orbital. 2

(b) State the spectral selection rules of the electronic dipole transition of the vibrational modes of IR and Raman active molecules. 2

(c) Find out the ground and excited state terms for  $d^2$  free ion. Use Hund's rule to identify the ground state. 4

(d) Predict the product of the following reaction: 1+1



6. Find out IR and Raman active vibrational modes of  $\text{NH}_3$  molecule. Character table for  $C_{3v}$  point group is given below. 10

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

7. Write down the complete reaction for the production of  $\text{CH}_3\text{CHO}$  from  $\text{C}_2\text{H}_4$  by Wacker's process. Write down the rate equation for the process. Draw the catalytic cycle for the process. 3+3+4

8. What is Ziegler-Natta catalyst? Mechanistically explain the stereo regularity of polymerization of olefin with this catalyst. 3+7

P.T.O.

(3)

9. What is projection operator? Find the SALCs of cyclopropenyl cation using projection operator technique and draw the energy level diagram. 1+6+1

Character table for  $D_{3h}$  point group is given below.

$D_{3h}$	E	2 $C_3$	3 $C_2'$	$\sigma_h$	2 $S_3$	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)

10. Draw the correlation diagram of  $d^2$  configuration in octahedral complexes. Character table for  $O_h$  point group is given below. 10

$O_h$	E	8 $C_3$	6 $C_2$	6 $C_4$	3 $C_2'$	i	6 $S_4$	8 $S_6$	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	$R_x, R_y, R_z$
$T_{2g}$	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	

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