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PG (NEW) CBCS M.Sc. Semester-III Examination, 2019 CHEMISTRY PAPER: CEM-302 (INORGANIC SPECIAL)

Full Marks: 40

GROUP-A

Answer any four questions from the following:

4×2=8

Time: 2 Hours

- 1. What do you mean by insertion reaction and oxidative coupling?
- 2. Why do the configuration dⁿ and d¹⁰⁻ⁿ give identical ligands field term in any given field symmetry?
- 3. What is the hole formalism?
- 4. Write some advantages of rhodium catalyst over cobalt catalyst for hydroformylation reaction.
- 5. What do you mean by 'Exclusion rule'?
- 6. What is "Sandwich compound"? Give an example.
- 7. Show that the f-orbital whose angular wave functions is constant times $Sin^2\theta Cos\theta Sin2\Phi$ is f_{xyz} orbital.
- 8. The addition of PPh₃ to RhCl (PPh₃)₃ reduces the hydrogenation TOF(Turn over frequency).-Justify.

GROUP-B

Answer any four questions from the following:

4×4=8

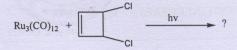
9. (a) How will you synthesize

via dehalogenation of cyclopropene starting from Ni(CO)4.

(P.T.O.)



(b) Complete the following reaction:



2+2

- 10. Briefly discuss the catalytic cycle for 'Monsento acetic acid' process using $[Rh(CO)_2I_2]^-$ catalyst. Mention oxidation states of 'Rh' in each step. 4
- 11. Write down the catalytic cycle for the hydroformylation reaction using HCo(CO)₄ as catalyst.
- 12. Establish the $\chi(\alpha) = \frac{Sin(l + \frac{1}{2})\alpha}{Sin(\frac{\alpha}{2})}$ relation:

Where the terms have usual significance.

4

2+2

- 13. (a) Show that the d-orbital whose angular wave function is constant times $(\sin^2\theta Cos2\theta)$ is $d_x^2-y^2$ orbital.
 - (b) State the spectral selection rules of the electronic dipole transition of the vibrationl modes of IR and Raman active molecules. 2+2
- 14. Find out the ground and excited state terms for d² free ion. Use Hund's rule to identify the ground state.
- 15. Predict the product of the following reaction:

(ii)
$$Fe(CO)_5 + Ph - C = C - Ph - ?$$

(P.T.O.)

DNAPOR

(3)

16. Find out IR and Raman active vibrational modes of NH₃ molecule. 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		x^2+y^2,z^2		
A_2	1	1	-1		R_z			
E	2	-1	0	(x,y)	(R_x, R_y)	$(x^2-y^2,xy)(yz,xz)$		

GROUP-C

Answer any two questions from the following:

8×2=16

- 17. Write down the complete reaction for the production of CH₃CHO from C₂H₄ by Wacker's process. Write down the rate equation for the process. Draw the catalytic cycle for the process.

 2+2+4
- 18. What is Ziegler-Natta catalyst? Mechanistically explain the stereo regularity of polymerization of olefin with this catalyst. 2+6
- 19. 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 C2'	σ_h	253	3 σ _v		
A ₁ '	1	1	1	1	1	1		$x^2 + y^2, z^2$
A2'	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		
A2"	1	1	-1	-1	-1	1	Z	
E"	2	-1	0	-2	1	0	(R _x , R _y)	(xz, yz)

20. Draw the correlation diagram of d² configuration in octahedral complexes. Character table for O_h point group is given below.

Oh	Е	8C3	6C2	6C4	3C ₂	i	654	856	3 _o h	6od		
Atg	1	1	1	1	1	1	1	1	1	1		x2+y2+z2
A2g	1	1	-1	-1	1	1	-1	1	1	-1		
A2g Eg T1g T2g	2	-1	0	0	2	2	0	1	2	0		222-22-12,22-12
Tig	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	1 XX IYA IZ	xz,yz,xy
Atu	1	1	1	1	1	-1	-1	-1	-1	-1		~-,,-,~,
A2u Eu	1	1	-1	-1	1	-1	1	-1	-1	1		
Eu	2	-1	0	0	2	-2	0	1	-2	0		
Tiu	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	7115	