

Total Pages – 6

M.Sc. RNLKWC-/CEM-203/22

2022

CHEMISTRY

M.Sc. Second Semester End Examination - 2022

PAPER - CEM-203

(Inorganic Chemistry - II)

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

Group - A

1. Answer any four questions. 2½×4=10
- (a) How metal-dioxygen complexes are prepared?
- (b) Why heavier transition metals form more dinitrogen complexes than lighter elements?
- (c) Determine the number of IR active ν_{CO} stretching mode of the following compounds.
- (i) $\text{cis-Mo(CO)}_4(\text{PMe}_3)_2$ (ii) $\text{Ni(CO)}_3(\text{PPh}_3)$

(Turn Over)

(2)

- (d) Briefly explain the term 'Agostic interaction'.
- (e) $W(CO)_6$ reacts with MeLi to give an intermediate which upon treatment with CH_2N_2 gives compound X. Find X.
- (f) The molecule $(CO)_5M=C(OMe)Ph$ obeys 18 electron rule. What are the two metals from 3d and 5d which satisfy the condition?

Group - B

Answer any four questions.

5×4=20

2. (a) Give possible explanation of increased reactivity of dioxygen upon coordination with metal. Give examples of some reactions of metal-dioxygen complexes.
- (b) Draw the structure of Creutz-Taube complex and explain with reasoning of its high intense color. 2+3
3. (a) Write short notes on 'Vaska's complex'.
- (b) Give a scheme in which metal-dinitrogen complexes produce pyrrole and N-aminopyrrole. 3+2
4. Extend the concept of SALC to construct the MOS of cyclic H_3^+ using the character table of C_3 point group.

(3)

C_3	E	C_3^1	C_3^2	$\varepsilon = e^{2\pi i/3}$
A_1'	1	1	1	
E'	1 1	ε ε'	ε' ε	

5

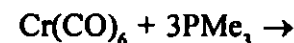
5. Decompose the following direct product in O point group.

(1) $T_1 \times T_2$ (2) ExT_2

O	E	$8C_3$	$3C_2(=C_2')$	$6C_4$	$6C_2$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

5

6. a) Discuss the bonding of metal-alkene complexes with orbital diagram.
- (b) Comment on the major and minor product of the given reaction with explanation.



3+2

(4)

7. (a) Match the $[\text{Rh}(\text{CO})(\text{Phosphine})_2\text{Cl}]$ complexes with their corresponding CO stretching frequencies ($\nu_{\text{CO}} \text{ cm}^{-1}$). Give explanation for selection.

Phosphine	$[\nu_{\text{CO}} \text{ cm}^{-1}]$
(i) $\text{P}(\text{C}_6\text{H}_5)_3$	1923
(ii) $\text{P}(\text{p-C}_6\text{H}_4\text{F})_3$	1965
(iii) $\text{P}(\text{p-C}_6\text{H}_4\text{Me})_3$	1984
(iv) $\text{P}(\text{t-C}_4\text{H}_9)_3$	2004

- (b) Explain why $\text{Fe}(\text{CO})_5$ shows only one peak at room temperature while 2 peaks at low temperature in ^{13}C nmr spectroscopy. 3+2

Group - C

Answer any one question. 10×1=10

8. (a) Determine the symmetry types of the genuine vibrations in furan ($\text{C}_4\text{H}_4\text{O}$, Point group : C_{2v}) by Cartesian coordinate method. How many of them are Raman active? The character table for C_{2v} point group is given below. 6

(5)

C_{2v}	E	$\text{C}_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

- (b) Comment on the feasibility of following transitions in C_{3v} point group. [2+2=4]

$\text{A}_1 \rightarrow \text{A}_2$ and $\text{E} \rightarrow \text{E}$

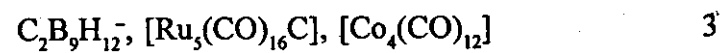
The Character Table for C_{3v} is shown below :

C_{3v}	E	2C_3	$3\sigma_v$	
A_1	1	1	1	Z
A_2	1	1	-1	R_z
E	2	-1	0	(x,y)
				(R_x, R_y)

9. (a) Calculate the styx numbers of B_6H_{10} and B_5H_{11} . Determine and draw the most probable structures of these compounds. Classify these compounds as closo, nido, arachano and hypho type. (2+2+1)

(6)

(b) Classify the following compounds by structural type



(c) Complete the following reaction – 2

