PG/IIS/CEM/203/25

M.Sc. 2nd Semester Examination, 2025

CHEMISTRY

(*Inorganic*)

PAPER – CEM-203

Full Marks : 50

Time : 2 hours

Answer **all** questions

The figures in the right hand margin indicate marks

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

GROUP – A

Answer any **four** questions : 2×4

1. What happens when :

   (*i*) $Mo(CO)_6$ is refluxed with norborane diene in octane ?

(*ii*) $Cr(CO)_6$ is reacted with $Li[N(i\text{-}pr)_2]$ in presence of Et_3O^+ ?

2. Complete the following reactions :

(*i*) $Re(CO)_5Cl + C_2H_4 \xrightarrow{AlCl_3}$

(*ii*) $ZrCl_4 + C_3H_5MgCl \xrightarrow[-78^\circ C]{Et_2O}$

3. The energy integral $\int \psi_i H \psi_j \, d\tau$ may be non-zero only if ψ_i and ψ_j belong to the same irreducible representation of the molecular point group. Explain.

4. Is p_x to p_y an allowed transition in a tetrahedral environment ? Explain.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
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)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

5. What is boron neutron capture therapy ? Give at least two examples of 1st and 2nd generation BNCT agents.

6. Write down all the product obtained from the polymerization chain reaction of BH_3 in a sealed glass tube.

GROUP – B

Answer any **four** questions : 4 × 4

7. (*i*) 'Highly explosive halogen substituted acetylenes can be stabilized by complex formation'–justify the statement with a suitable example.

(*ii*) Complete the following reaction :

$$[CpNi(CO)]_2 + RC \equiv CR \longrightarrow \quad 2\frac{1}{2}+1\frac{1}{2}$$

8. (*i*) How $(OC)_5 W \equiv C - R$ is synthesized from its corresponding carbene complex ?

(*ii*) Discuss the orbital interactions present in Scrock's carbyne complex. $1\frac{1}{2}+2\frac{1}{2}$

9. Determine the characters of irreducible representations for C_{4v} point group. Write the appropriate Mulliken symbols for these irreducible representations. 3 + 1

10. Based on group theoretical principle discuss on "spectral transition probabilities" of an electric dipole transition. 4

11. Complete the following reactions : $\frac{1}{2} \times 8$

(*i*) $B_4H_{10} + N(CH_3)_3 \rightarrow$

(*ii*) $B_4H_{10} + C_2H_2 \xrightarrow{100°C}$

(*iii*) $B_5H_9 + ROH \longrightarrow$

(*iv*) $B_5H_9 + C_2H_2 \xrightarrow{500°C}$

(*v*) $B_{10}H_{14} + CH_3Cl \xrightarrow{AlCl_3}$

(*vi*) $[B_{10}H_{10}]^{2-} + (CH_3)_2SO \longrightarrow$

(*vii*) $B_2H_6 + 2NaH \longrightarrow$

(*viii*) $[B_{10}H_{10}]^{2-} + SCN^- \longrightarrow$

12. Classify the following compounds with respect to closo, nido, arachno and hypo 4

$Cp_3Co_3B_4H_4$, $Cp_2Fe_2Me_4C_4B_8H_8$,

$(CH_3)_3C_2B_5H_{11}$, $Et_4C_4B_8H_8$.

GROUP – C

Answer any **two** questions : 8×2

13. (*i*) 'Highly strained cycloolefins are stronger

donors than non-cyclic olefins'-Justify the statement with an example.

(*ii*) Complete the following reaction and mention the oxidation state of the central metal ion.

$$Fe(C_5H_5)_2 \xrightarrow[\substack{-50^oC \\ TMEDA}]{Li,\ C_2H_4}$$

(*iii*) What happens when Mo(g) and 1,3-butadiene(g) is reacted at very low temperature.

(*iv*) Draw the orbital diagram to show the bonding model in Schrock carbene complex. 2 + 2 + 2 + 2

14. (*i*) Verify that p_x and p_y orbitals provide basis for B_1 and B_2 representation, respectively, of C_{2v} point group, whereas p_x and p_y orbitals as a pair provide basis for E represention of C_{3v} point Group.

(*ii*) Using group theoritical principle to justify that n→π* electronic transition is forbidden, whereas π → π* electronic transition is allowed in formaldehyde molecule.

(1 + 3) + 4

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
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

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

15. (*i*) Calculate the styx number of $[B_6H_{12}]^{2-}$, $[B_8H_{14}]$ and established the most probable structure.

(*ii*) With the help of styx number 3411 and 2221 derive the formula of the boron hydride and draw the probable structures of these. 4 + 4

16. (*i*) Show that the representation of a direct product Γ_{XY}, will contain the totally symmetric representation only if the irreducible Γ_X = the irreducible Γ_Y.

(*ii*) Classify the following compounds with respect to closo, nido, arachno and hypo
$Cp_3Co_3B_4H_4$, Cp_2Fe_2 $Me_4C_4B_8H_8$,
$(CH_3)_3C_2B_5H_{11}$, $Et_4C_4B_8H_8$
4 + 4

[Internal Assessment — 10 Marks]