2019

M.Sc.

2nd Semester Examination

CHEMISTRY

Paper - CEM 203

(Inorganic)

Full Marks : 40 Time : 2 Hours

The figures in the margin indicate full marks. Candidates are required to give their answers in their own words as far as practicable.

Group - A

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

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

(b) Determine the characters of irreducible representations of C_{3v} point group. Write the

appropriate Mulliken symbols for these irreducible representations.

(c) Classify the following compounds as closo, nido, arachno and hypo type

$B_{10}H_{12}$, B_6H_{14}, $[B_9H_{14}]^-$, $C_2B_{10}H_{12}$

(d) Complete the following reactions

(i) $B_4H_{10} + NaH \rightarrow$

(ii) $B_5H_{11} + 2CO \rightarrow$

(iii) $B_5H_9 + LiH \rightarrow$

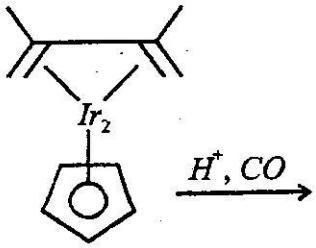
(iv) $B_4H_{10} + CN^- \rightarrow$

(e) Show that the representation of a direct product, Γ_{MN}, will contain the totally symmetric representation only if the irreducible Γ_M = irreducible Γ_N.

(f) The ground state of H_2O is A_1. To what excited states may it be excited by electric dipole tansitions, and what polarization of light is necessary to use ? Given below the character table for C_{2v} point group.

C_{2v}	E	$C_{2(z)}$	$\sigma_v(xz)$	$\sigma_{v'}(yz)$		
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, Ry	xz
B_2	1	−1	−1	1	y, R_x	yz

(g) Predict the product of the following reaction



(h) In *Ni* (CDT) complex, the CDT ligand is very labile. Explain.

(CDT = trans, trans, trans - 1, 5, 10-cyclo-dodecatriene)

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Group - B

Answer any *one* question.

2. (a) P_x and P_y orbitals provide basis for B_1 and B_2 representation, respectively, of C_{2v} point group. On the other hand P_x and P_y orbitals, as a pair provide basis for the E representation of C_{3v} point group. Explain. (Use the character tablel of C_{2v} point group given in Q. No. 1. The character table for C_{3v} point group is given below).

C_3v	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	–	Rz	
E	2	–1	0	$(x,y)(Rx,Ry)$	$(x^2-y^2, xy)(xz,yz)$

(b) Write short note on "spectral transition probabilities". 3

3. (a) Show that for $[Mo_2Cl_8]^{4-}$ species, the $\delta \rightarrow \delta^*$ transition is electric-dipole allowed with z-polarization and forbidden for radiation with its electric vector in the xy plane. Given below the character table for D_{4h} point group. 6

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x,R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

(b) Establish the relation

$$a_i = \frac{1}{h}\sum_R x(R)x_i(R)$$

Where the terms have usual significance. 2

[Turn Over]

Group - C

Answer any *two* question. 4×2=8

4. Reaction of cobaltocene with potassium and ethylene at −20°C produced 'A' which is an 18e' complex having labile ligand. 'A' further reacted with ethylene in presence of lithium produced 'B' which is an analogue of metal carboxylate anion.

   Identify '*A*' and '*B*'. 4

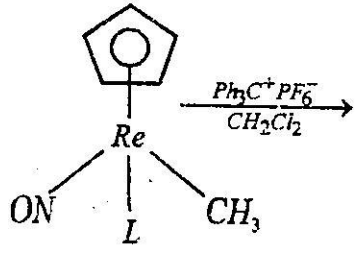
5. Discuss the bonding in Fishcher's carbene complex and also show the possible orbital interactions. 4

6. Discuss the origin of the electronic properties of Fischer's carbene by *MO*-approach. 4

7. Complete the follwing reactions : 4

   (i) $\left[C_pNi(CO)\right]_2 + R-C\equiv C-R \longrightarrow$

   (ii)



Group - D

Answer any *one* question. 8×1=8

8. 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, arachno and hypo type. 2+4+2

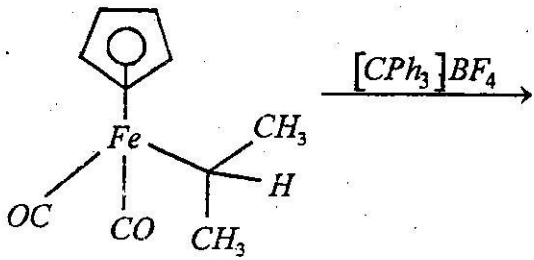
9. (i) For boron hydrides *P* and *Q*, the *styx* numbers are 2202 and 3203, respectively. Establish and draw the most probable structures of these boron hydrides. 6

(ii) Describe the synthetic procedure for the synthesis of different types of nidocarboranes. 2

Group - E

Answer any *two* question. 4×2=8

10. (i) Complete the following reaction.



Which type of reaction is this ? 2

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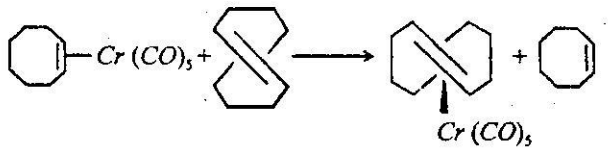
(ii) 

Explain the driving force of the abovementioned displacement reaction. 2

11. (i) Give two examples of each for 1st, 2nd and 3rd generation BNCT agents. 2

(ii) Complete the following reactions : 2

(a) $2B_4H_{10} + 2Na(Hg)Et_2O \rightarrow$

(b) $B_5H_9 + C_2H_4 + AlCl_3 \rightarrow$

(c) $B_5H_{11} + 2Na(Hg) + Et_2O \rightarrow$

(d) $B_4H_{10} + NaBH_4 \rightarrow$

12. Ground state of CH_2Cl_2 is B_1 in the group C_{2v}. To what excited stats may it be excited by electric-dipole transitions, and what polarization of light is necessary to use ? (Use the character table of C_{2v} point group given in Q. No. 1) 4

13. Use group theoretical principle to determine the symmetry of vibrational mode of trans N_2F_2

molecule using cartesian co-ordinate method. Identify the symmetry of *IR* and Raman active mode in this molecule. Given below the character table for C_{2h} point group. 4

C_{2h}	E	C_2	i	σ_n		
Ag	1	1	1	1	R_z	x^2, y^2, z^2, xy
Bg	1	−1	1	−1	R_x, R_y	xz, yz
Au	1	1	−1	−1	z	
Bu	1	−1	−1	1	x, y	