F - 305

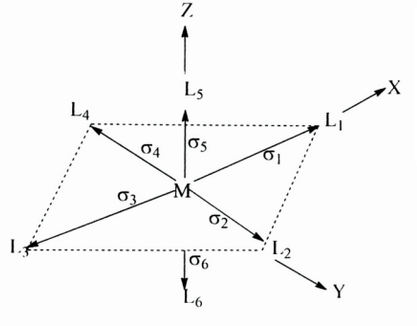
M. Sc. (First Semester)
Examination, Dec.-Jan., 2021-22
CHEMISTRY
Paper First
(Group Theory and Chemistry of Metal Complex)

Time : Three Hours] ***[Maximum Marks : 80***

Section-A **1 each**
(Objective/Multiple Choice Questions)

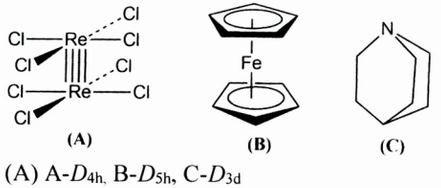
1. For a molecules with symmetry elements: E, $2C_3$, $3C_2$, σ_h, $2S_3$, $3\sigma_v$, the point group, number of classes and order of group are, respectively:
(A) D_{3h}, 12, 6
(B) C_{3h}, 6, 12
(C) C_{3v}, 6, 12
(D) D_{3h}, 6, 12

2. The coordinate system for octahedral complex ML_6 showing the M—L sigma (σ) bonding is presented below. The characters of the vectors under C_4 and S_4 classes will respectively be



(A) 0, 0
(B) 0, 4
(C) 2, 0
(D) 4, 0

3. Following molecule will belongs to the point group



(A) A-D_{4h}, B-D_{5h}, C-D_{3d}
(B) A-D_{4h}, B-D_{5d}, C-D_{3h}
(C) A-C_{4h}, B-D_{5d}, C-C_{3v}
(D) A-D_{4h}, B-D_{5d}, C-C_{3v}

4. The character table of C_{3v} point group is given below, along with an additional reducible representation, Γ.

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ	6	0	2

This reducible representation Γ will be reduced as:

(A) $A_1 + A_2 + 2E$
(B) $2A_1 + 2E$
(C) $2A_2 + 2E$
(D) $2A_1 + 2A_2 + 2E$

5. The partial character table of D_3 point group is given below with a missing row of irreducible representation.

D_3	E	$2C_3$	$3C_2$
A_1	1	1	1
??			
E	2	-1	0

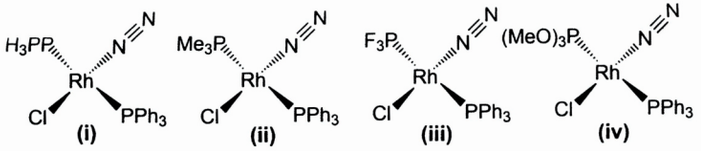
(A) A_2 1 1 -1
(B) A_2 1 -1 1
(C) B_1 1 -1 1
(D) B_2 1 -1 -1

6. The mission row will be:
The HOMO of CO is
(A) π-bonding
(B) σ-bonding
(C) π-antibonding
(D) σ-antibonding

7. Incorrect isolobal pair is
(A) CH_4 and $[Mn(CO)_6]^+$
(B) CH_3 and $[Mn(CO)_5]$
(C) CH_2 and $[Fe(CO)_5]^+$
(D) CH and $[Ni(CO)_3]^+$

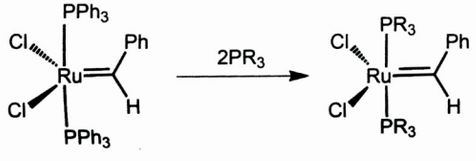
8. The arrangement of ligands on the basis of capability of delocalization of metal electrons in the ligand is known as:
(A) Spectrochemical series
(B) Trans effect series

9. The correct order of increasing N—N bond length in the following dinitrogen complex will be:



(A) (i) < (ii) < (iii) < (iv)
(B) (iii) < (iv) < (i) < (ii)
(C) (ii) < (i) < (iii) < (iv)
(D) (iii) < (iv) < (ii) < (i)

10. Which among the given phosphine will not be likely to give a positive reaction in the given scheme?



(A) When R = 4-FC_6H_4
(B) When R = Bu^t
(C) When R = Et
(D) When R = 4-$MeOC_6H_4$

11. The equilibrium for the reaction of Cd^{2+} with CH_3NH_2 and ethyelene diamine (en) are given below with the values of respective formation constants

(i) $[Cd(H_2O)_4]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+} + 4H_2O$; $K = 3.10 \times 10^6$
1 + 4 = 5 particles 1 + 4 = 5 particles

(ii) $[Cd(H_2O)_4]^{2+} + 2\,(en) \rightleftharpoons [Cd(en)_2]^{2+} + 4H_2O$; $K = 3.20 \times 10^{10}$
1 + 2 = 3 particles 1 + 4 = 5 particles

The incorrect statement for these equilibrium are:

(A) ΔG^o, ΔH^o and ΔS^o values for equilibrium (i) will be negative
(B) ΔG^o value for equilibrium (ii) will be more negative
(C) ΔS^o value for equilibrium (ii) will be more positive
(D) ΔH^o value for both equilibrium (i) and (ii) are comparable

12. In styx code, '*t*' stand for
(A) Number of B—H—B bond
(B) Number of B—B—B bonds
(C) Number of B—B bonds
(D) Number of BH_2 units

13. According to Wades rule, the number of framework electron equals 2n+2 will have structure:
(A) *Closo*
(B) Nido
(C) Arachno
(D) Hypo

14. The order of increasing Bronsted acidity for boron hydride is:

(A) $B_5H_9 < B_6H_{10} < B_{10}H_{14}$
(B) $B_{10}H_{14} < B_5H_9 < B_6H_{10}$
(C) $B_6H_{10} < B_{10}H_{14} < B_5H_9$
(D) $B_{10}H_{14} < B_6H_{10} < B_5H_9$

15. The bond order of the $[Mo_2Cl_8]^{4-}$ and $[Os_2Cl_8]^{2-}$ are respectively:
(A) Both 4
(B) Both 3
(C) 3 and 4 respectively
(D) 4 and 3 respectively

16 The reaction of BCl_3 with NH_4Cl gives product **A** which upon reduction by $NaBH_4$ gives product **B**. Product **B** upon reacting with HCl affords compound **C**, which is
(A) $B_3N_3H_6$
(B) $[ClBNH]_3$
(C) $Cl_3B_3N_3H_9$
(D) $(ClH)_3B_3N_3(ClH)_3$

17. The correct arrangement of $[Ni(en)_3]^{2+}$, $[Ni(EDTA)]^{2-}$, and $[Ni(NH_3)_6]^{2+}$ in the order of increasing overall formation constant is:

(A) $[Ni(NH_3)_6]^{2+} < [Ni(en)_3]^{2+} < [Ni(EDTA)]^{2-}$
(B) $[Ni(en)_3]^{2+} < [Ni(EDTA)]^{2-} < [Ni(NH_3)_6]^{2+}$
(C) $[Ni(EDTA)]^{2-} < [Ni(NH_3)_6]^{2+} < [Ni(en)_3]^{2+}$
(D) $[Ni(NH_3)_6]^{2+} < [Ni(EDTA)]^{2-} < [Ni(en)_3]^{2+}$

18. Which Among the following polyanion, the face sharing of octahedral unit of oxyanion is occur?
(A) $[H_2W_{12}O_{40}]^{6-}$
(B) $[H_2W_{12}O_{42}]^{10-}$
(C) $[Mo_7O_{24}]^{6-}$
(D) $(NH_4)_2H_6CeMo_{12}O_{42}$

19. Correct match of different class of carbide is

	Class		Carbide
(i)	Methanides:	(a)	Na_2C_2, CaC_2
(ii)	Acetylides	(b)	B_4C, $B_{25}C$
(iii)	Allylides	(c)	Al_4C_3, Mg_2C
(iv)	Covalent carbides	(d)	Li_4C_3, Mg_2C_3

(A) (i)-(a), (ii)-(b), (iii)-(c), (iv)-(d)
(B) (i)-(c), (ii)-(a), (iii)-(d), (iv)-(b)
(C) (i)-(a), (ii)-(c), (iii)-(b), (iv)-(d)
(D) (i)-(c), (ii)-(d), (iii)-(a), (iv)-(b)

20. Using the crystal field stabilization energy (CFSE) to account the thermodynamic properties, correct match of the following is:

	Oxide		Lattice enthalpy (kJ mol^{-1})
(a)	CaO	(i)	3460
(b)	TiO	(ii)	3875
(c)	VO	(iii)	3913
(d)	MnO	(iv)	3810

(A) (a)-(ii), (b)-(i), (c)-(iv), (d)-(iii)
(B) (a)-(i), (b)-(ii), (c)-(iii), (d)-(iv)
(C) (a)-(iii), (b)-(iv), (c)-(ii), (d)-(i)
(D) (a)-(iv), (b)-(iii), (c)-(ii), (d)-(i)

Section-B 2 each
(Very short Answer Type Questions)

1. What are the symmetry criteria for a molecule to be chiral?
2. What will be the symmetry of p_x orbital of oxygen in water molecule?
3. Predict which of the complexes $[V(CO)_6]^-$, $Cr(CO)_6$, or $[Mn(CO)_6]^+$ has the shortest C—O bond, and why?
4. The $[RuCl(NO_2)(PPh_3)_2]^+$ complex exhibits two ν(NO) stretchs in its vibrational spectrum: one at 1845 cm^{-1} and the other at 1687 cm^{-1}. Sketch a reasonable geometry for the compound.
5. What are isopoly and heteropoly acids?
6. Given that $K_1 = 2.1 \times 10^3$ and $K_2 = 8.2 \times 10^3$, calculate the over-all stability constant β_2 for the formation of $[Ag(NH_3)_2]^+$. Why $K_2 > K_1$?
7. What are catenation and heterocatenation?
8. What are the carboranes?

Section-C 3 each
(Short Answer Type Question)

1. Discuss the self-conjugation, mutual conjugation and associative conjugation of elements of C_{3v} point group.

2. Character table of C_{4v} point group is given below with additional reducible representation. Reduce this reducible representation using standard reduction formula and find out the number of representations of each type.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_v'$		x^2+y^2, z^2
A_1	1	1	1	1	1	z	
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		
B_2	1	-1	1	-1	1		
E	2	0	-2	0	0	(x, y) (R_x, Ry)	(x^2-y^2, xy) (xz, yz)
Γ_{cart}	18	2	-2	4	2		

3. For series of ligand substitution reactions given by the chemical reaction below, value for the the rate constant are given in the table. Does this reaction occur by an associative or dissociative pathways? Explain your answer.

cis-$[Mo(CO)_4(PR_3)_2]$ + CO → *cis*-$[Mo(CO)_5(PR_3)]$ + PR_3

Table showing the rates of ligand substitution at 70° C in the reaction above as a function of PR_3.

PR_3	Cone Angle	k, s^{-1}
PMe_2Ph	122°	$< 1.0 \times 10^{-6}$
$PMePh_2$	136°	1.33×10^{-5}
PPh_3	145°	3.16×10^{-3}
$PPh(cyclohexyl)_2$	162°	6.40×10^{-2}

4. Sketch the molecular orbital diagrams for CO and CN^- to show why the cyanide ligand will often form M—C≡N—M' bridge, and why the carbonyl ligand bridging in this manner is rare.
5. What do you understand by chelate effect? How metal chelation may affect the stability of the complex?
6. What are the silicones? Write their applications.
7. What is Borazene. Is it shows similarities in structure and reactivity with benzene?
8. Discuss the structure and bonding in phosphazines.

Section-D
(Short Answer Type Question)

1. Character table for D_{3h} point group is given below with additional reducible representation ($\Gamma_{cart.}$):

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
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)
$\Gamma_{cart.}$	12	0	-2	4	-2	3		

Using character table, answer the following question:
(i) What is order of group?
(ii) What is number of classes in this group.
(iii) How many sub-groups you may find out in this group?
(iv) Which irreducible representation is totally symmetrical?
(v) Which irreducible representation(s) will be Infra-red (IR) active?
(vi) Find out the irreducible representations for translational and rotational motions.
(vii) Prove that

$$\sum_k g\,(R)\chi_i\,(A_1)\,\chi_j(A_2) = 0$$

(viii) Find out the symmetry of the orbitals which participates in hybridization in trigonal bipyramidal (TBP) compound.
(ix) What will be the order of rotational sub-group?
(x) Which irreducible representations will be Raman active?

OR

For a C_{2v} point group:
(i) Construct character table, and assigned Mulliken's symbols to the irreducible representations.
(ii) Obtain reducible and irreducible presentations for different motions in H_2O molecules.
(iii) Find out irreducible representation for fundamental modes of vibrations.
(iv) Show, which irreducible representations will be infra-red and Raman active?

2. What do you understand by π-acidity? What the different kinds of π-bonding may occur between metal and ligands? What is the consequence of π-bonding on the Δo values in octahedral complexes?

OR

For an octahedral complex, obtain metal orbital and ligand group orbitals (LGO) of suitable symmetry to participate in molecular orbital (MO) formation. Draw molecular orbital diagram showing MOs of metal and ligand character. Distribute the electrons in MOs for $[Co(NH_3)_6]^{3+}$ complex.

3. What are the stability constants? What are different methods for determination of stability constants? Discuss spectrophotometric method for determination of formation constant.

OR

What are the silicates? How silicates can be classified in different classes? Write some of the applications of the silicates.

4. What are the different kinds of binding occurs in higher boranes? Considering these bonding, discuss the structure of B_4H_9, B_5H_9 and B_5H_{11} boranes.

OR

Considering metal-metal bonding:
(i) Discuss the metal-metal bonding in $[Re_2Cl_8]^{2-}$.
(ii) Explain the variation in bond orders in the following compound/ions:

$[Mo(HPO_4)_4]^{2-}$	$[Mo_2(SO_4)_4]^{3-}$	$[Mo_2(SO_4)_4]^{4-}$
Mo—Mo = 223 pm	Mo—Mo = 217 pm	Mo—Mo = 211 pm
(Bond order = 3)	(Bond order = 3.5)	(Bond order = 4)