

Birla Institute of Technology and Science, Pilani (Rajasthan)

COMPREHENSIVE EXAMINATION, SEMESTER II (2015-16)

A

CHEM F241: Inorganic Chemistry II

Time: 60 min (maximum)

CLOSE BOOK

Paper: I

Marks: 30

Date: 6th May, 2016

Instructions: All the questions are multiple-choice type. Choose the right answer and write the corresponding letter in the square box as given under each question. Answer all the questions. Each question carries one mark. **For every two wrong answers 0.5 marks will be deducted.**

1. Which one shows the correct symmetry of six and four ligand group orbitals (LGO) in octahedral and tetrahedral complexes, respectively
(A) a_{1u} , e_u , t_{1g} and a_1 , t_2 (B) a_{1g} , e_g , t_{1u} and a_{1g} , t_{2u}
(C) a_{1g} , e_g , t_{1u} and a_{1u} , t_{2g} (D) a_{1g} , e_g , t_{1u} and a_1 , t_2

2. The ligand group orbitals capable of π interactions in an octahedral complex fall into the following symmetry categories:

- (A) t_{1g} and t_{2g} (B) t_{1u} and t_{2u}
(C) t_{1g} , t_{2g} and t_{1u} (D) t_{1g} , t_{2g} , t_{1u} and t_{2u}

3. Choose the correct option.

- (A) Both CN^- ion and $(CH_3)_3P$ ligands form $d\pi-d\pi$ and $d\pi-\pi^*$ types of π bonds with transition metal
(B) CN^- ion form $d\pi-d\pi$ and $d\pi-\pi^*$ type of π bonds while $(CH_3)_3P$ forms $d\pi-d\pi$ π bond with transition metal
(C) $(CH_3)_3P$ forms $d\pi-d\pi$ and $d\pi-\pi^*$ type of π bonds while CN^- forms $d\pi-\pi^*$ π bond with transition metal
(D) $(CH_3)_3P$ forms $d\pi-d\pi$ type of π bonds while CN^- forms $d\pi-\pi^*$ type π bond with transition metal

4. According to ligand field theory for $Cr(CO)_6$ complex, Δ_o is represented by the energy gap

~~between the orbitals of~~

- (A) t_{2g} and e_g (B) t^{*}_{2g} and e_g^* (C) t^{*}_{2g} and e_g (D) t_{2g} and e_g^*

5. Choose the correct option.

- (A) In complex, the electron-electron repulsion will decrease as compared to the free metal ions and hence the nephelauxetic value will decrease.
(B) In complex the electron-electron repulsion will decrease as compared to the free metal ions and hence the nephelauxetic value will increase.
(C) In complex the electron-electron repulsion will increase as compared to the free metal ions and hence the nephelauxetic value will increase.
(D) In complex the electron-electron repulsion will increase as compared to the free metal ions and hence the nephelauxetic value will decrease.

6. Choose the correct option.
- (A) NiFe_2O_4 and Mn_3O_4 both are normal spinels
 (B) NiFe_2O_4 and Mn_3O_4 both are inverse spinels
 (C) NiFe_2O_4 is a normal spinel whereas Mn_3O_4 is inverse spinel
 (D) NiFe_2O_4 is an inverse spinel whereas Mn_3O_4 is normal spinel
-
7. Capped trigonal prism geometry is an example of
 (A) 5-coordination (B) 7-coordination (C) 8-coordination; (D) 9-coordination compound
-
8. Indicate the most stable pair of compounds:
- (A) $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$ and $[\text{Co}(\text{CN})_5\text{SCN}]^{3-}$
 (B) $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$ and $[\text{Co}(\text{CN})_5\text{SCN}]^{3-}$
 (C) $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$ and $[\text{Co}(\text{CN})_5\text{NCS}]^{3-}$
 (D) $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$ and $[\text{Co}(\text{CN})_5\text{NCS}]^{3-}$
-
9. Choose the correct option.
- (A) Both *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]$ and *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]$ are optically active
 (B) *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]$ is optically active but the *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]$ isomer is optically inactive
 (C) *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]$ is optically inactive but *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]$ is optically active
 (D) Both *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]$ and *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]$ are optically inactive
 (en = ethane-1,2-diamine)
-
10. For the case of 3d transition metal ions
- (A) with electronic configuration of d^2 and d^3 , the magnetic moment can be calculated from $\mu = [4S(S + 1)]^{1/2}$ as there has no orbital contribution of d^2 and d^3 configuration
 (B) with electronic configuration of d^2 , the magnetic moment has to be calculated from $\mu = [4S(S + 1) + L(L + 1)]^{1/2}$ because of consideration of orbital contribution for the d^2
 (C) with electronic configuration of d^2 and d^3 , the magnetic moment has to be calculated from $\mu = [4S(S + 1) + L(L + 1)]^{1/2}$ because of consideration of orbital contribution for the d^2 and d^3 both
 (D) with electronic configuration of d^3 , the magnetic moment has to be calculated from $\mu = [4S(S + 1) + L(L + 1)]^{1/2}$ because of consideration of orbital contribution for the d^3 ion
 (S = resultant spin quantum number; L = resultant orbital quantum number)
-
11. ${}^1\text{G}$ is a free ion term for d^2 electronic configuration in an octahedral field. Which terms are the correct form of representation in weak field.
- (A) ${}^3\text{T}_{1g}$, ${}^3\text{T}_{2g}$, ${}^1\text{E}_g$ and ${}^1\text{A}_{1g}$
 (B) ${}^1\text{T}_{1g}$, ${}^1\text{T}_{2g}$, ${}^3\text{E}_g$ and ${}^3\text{A}_{1g}$
 (C) ${}^1\text{T}_{1g}$, ${}^1\text{T}_{2g}$, ${}^1\text{E}_g$ and ${}^1\text{A}_{1g}$
 (D) (B) ${}^1\text{T}_{1g}$, ${}^1\text{T}_{2g}$, ${}^3\text{E}_g$ and ${}^3\text{A}_{1g}$
-
12. The excited state term of d^9 electronic configuration in tetrahedral field is
- (A) ${}^2\text{E}$ (B) ${}^2\text{E}_g$ (C) ${}^2\text{T}_2$ (D) ${}^2\text{T}_{2g}$
-
13. Which transition is spin allowed for d^3 electronic configuration in octahedral field
- (A) ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (F) (B) ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (G) (C) ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ (F) (D) ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ (G)
-

14. For the case of tetrahedral complex using Ligand Field Theory
- (A) t_2 LGOs can interact with t_2 orbitals (consisting of d orbitals) and results two sets of sigma MOs
- (B) t_2 LGOs can interact with t_2 orbitals (consisting of d and p orbitals) and results three sets of sigma MOs
- (C) t_2 LGOs can interact with t_1 orbitals (consisting of d orbitals) and results two sets of sigma MOs
- (D) t_2 LGOs can interact with t_1 orbitals (consisting of d and p orbitals) and results three sets of sigma MOs.

15. The electronic transition for the complex, $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$,

- (A) Both Laporte and Spin selection rule are forbidden
- (B) Laporte selection rule is allowed while Spin selection rule is forbidden
- (C) Laporte selection rule is forbidden while Spin selection rule is allowed
- (D) Both Laporte and Spin selection rule are allowed

16. Which of the following statement is not correct –

- (A) Metal clusters are only formed when carbonyl groups are attached with metal
- (B) Many metal clusters are known which contain double and triple metal-metal bonds
- (C) Metal clusters have metal-metal bond
- (D) Halide type metal clusters are also known

17. The number of bridging CO group and M-M bond in $\text{Mn}_2(\text{CO})_{10}$, respectively is -

- (A) 1 and 1 (B) Zero and 1 (C) Zero and Zero (D) 3 and 1

18. Using the 18 electron rule, the value of n in $\text{Co}_n(\text{CO})_{12}$ is –

- (A) 3 (B) 5 (C) 6 (D) 4

19. Trialkyl aluminium + TiCl_4 is used for –

- (A) Synthesis of gasoline (B) Polymerisation of alkene
(C) Cracking of hydrocarbons (D) Hydrogenation of olefins

20. In linear and a bent nitrosyl ligand, NO acts as a/an –

- (A) One and three electron donor (B) Two electron donor
(C) Three and one electron donor (D) One electron donor

21. CH_2^+ is a main group fragments is isolobal with which of the following transition metal fragments

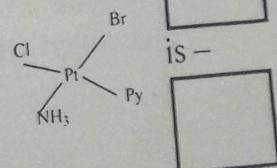
- (A) $\text{Cr}(\text{CO})_2\text{Cp}$ (B) $\text{Co}(\text{CO})\text{Cp}$ (C) $\text{Fe}(\text{CO})_2\text{Cp}$ (D) NiCp_2

22. In Wilkinson catalyst, the oxidation state and coordination number of metal, respectively is –

- (A) 3 and 6 (B) 2 and 4 (C) 3 and 4 (D) 1 and 4

23. The correct order of addition of NH_3 , py, and Br^- to $\text{PtCl}_4^{2-}/\text{PtCl}_3(\text{NH}_3)$ to obtain

- (A) Py, Br^- , and NH_3 (B) Br^- , py, and NH_3
(C) NH_3 , py, and Br^- (D) NH_3 , Br^- , and py



is –

24. Designate the following complexes X, Y, and Z as inert or labile, $X = [Al(C_2O_4)_3]^{3-}$, $Y = [V(H_2O)_6]^{2+}$, and $Z = [Cr(C_2O_4)_3]^{3-}$ -

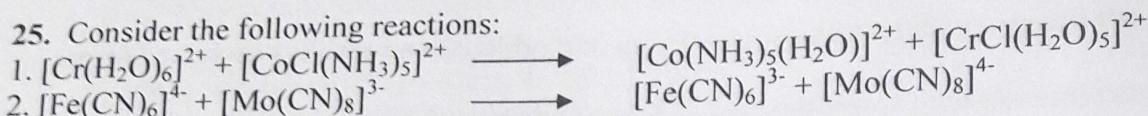
- (A) X and Y are inert; Z is labile
(C) X is inert; Y and Z are labile

- (B) X and Z are labile; Y is inert
(D) X is labile; Y and Z are inert

CH
TiIn
qu
qu1
b

C

25. Consider the following reactions:



Which one of the following statement is correct?

- (A) Both involve inner sphere mechanism with Cl^- and CN^- as bridging ligand
(B) Reaction 1 follows inner sphere with Cl^- as bridging ligand and reaction 2 follows outer sphere mechanism.
(C) Reaction 1 follows outer sphere and reaction 2 follows inner sphere mechanism with CN^- as bridging ligand.
(D) Both involve an outer sphere mechanism.

26. Reactions of $Fe(CO)_5$ with OH^- leads to complex A, which on oxidation with MnO_2 gives B.

Compounds A and B respectively are -

- (A) $[HFe(CO)_4]^-$ and $Fe_3(CO)_{12}$
(C) $[Fe(CO)_4]^{2-}$ and $Mn_2(CO)_{10}$
- (B) $[Fe(CO)_5(OH)]^-$ and $Fe_2(CO)_9$
(D) $[HFe(CO)_4]$ and Fe_2O_3

27. The incorrect statement regarding the Fischer-type metal carbene complexes is that -

- (A) Carbene acts as a σ -donor and π -acceptor
(B) all atoms directly connected to carbene C atom are coplanar
(C) The bond between the metal and the carbene C atom has partial double bond character
(D) The carbene C atom is nucleophilic

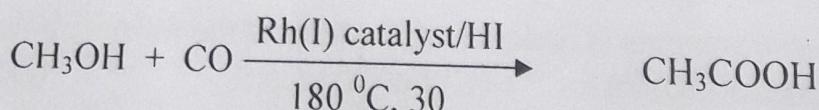
28. In metal-olefin interaction, the extent of increase in metal \rightarrow olefin π -back donation would -

- (A) lead to decrease in $C=C$ bond length
(B) Change the formal oxidation state of the metal
(C) Change the hybridization of the olefin carbon from sp^2 to sp^3
(D) increase with the presence of electron donating substituents on the olefin

29. The ligand/ligands that is/are fluxional in the complex $[Fe(\eta^5-C_5H_5)(\eta^1-C_5H_5)(CO)_2]$ is/are -

- (A) $\eta^5-C_5H_5$ (B) $\eta^1-C_5H_5$ (C) $\eta^1-C_5H_5$ and CO (D) $\eta^5-C_5H_5$ and CO

30. In monsanto acetic acid process shown below, the role of HI is -



- (A) To convert CH_3OH to a stronger nucleophile CH_3O^-
(B) To reduce the Rh(I) catalyst to Rh(0)
(C) To reduce a Rh(III) active species to a Rh(I) species in the catalytic cycle
(D) To convert CH_3OH to CH_3I

Birla Institute of Technology and Science, Pilani (Rajasthan)
COMPREHENSIVE EXAMINATION, SEMESTER II (2015-16)

CHEM F241: Inorganic Chemistry II

Time: 120 min

**OPEN BOOK
Paper: II**

**Marks: 60
Date: 6th May, 2016**

Instructions: There has a total seven questions in all under Group A & Group B. Attempt all the questions. Group A & Group B answers will be written in separate answerscript. Start answering each question on a fresh page and answer all parts in a question together.

Group A

1. The electronic absorption spectrum of $[VF_6]^{3-}$ was observed at 14,800 and 23,250 cm⁻¹ with a third band found in UV region.

(a) Use the Tanabe-Sugano diagram to identify the predicted spectral bands.

(b) Calculate the ligand field stabilization energy in cm⁻¹ only (no credit will be given in other form).

(c) Sketch the π MO diagram including the electrons in the resulting MOs for this compound.

$$2 + 5 + 2 = 9M$$

2. A 2×10^{-4} M solution of $Fe(S_2CNEt_2)_3$ in chloroform at 25°C has absorption bands at 350 nm ($A = 2.34$) and 1540 nm ($A = 0.0016$) apart from other two absorption bands.

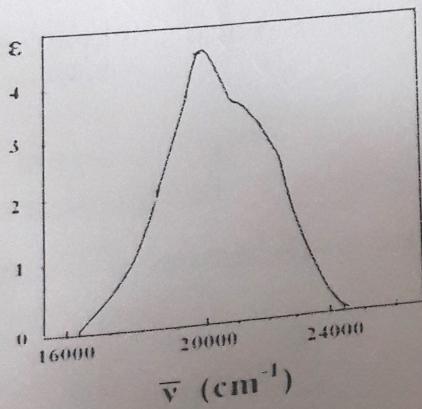
(a) Calculate the molar absorptivity for this compound at 350 and 1540 nm wavelengths.

(b) Assign the type of transitions at 350 and 1540 nm wavelengths based on the calculated values of molar absorptivity with reasons.

$$2 + 3 = 5M$$

3. (a) Determine M_L values and total degenerate states possible for 4F term.

(b) Which transition metal complexes is expected to show the following absorption spectrum (given below) recorded by electronic spectroscopy [only mention the 3d transition metal ions in +2 oxidation state with proper oxidation number ($\epsilon =$ molar absorptivity)].



(c) For the isoelectronic series $[\text{V}(\text{CO})_6]^-$, $[\text{Cr}(\text{CO})_6]$ and $[\text{Mn}(\text{CO})_6]^+$ would you expect the energy of metal to ligand charge transfer bands to increase or decrease with increasing charge on the complex? Why?

$$2 + 2 + 2 =$$

D
2
fr

6
re
C
C

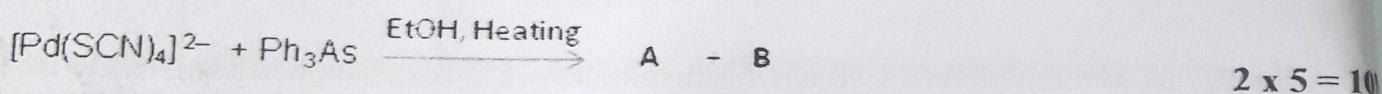
4. (a) Comment on the stability of the following complexes based on crystal field theory. (i) $[\text{Co}(\text{CO})_6]$ vs $[\text{Co}(\text{CO})_6]^-$; (ii) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ vs $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.

(b) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is a strong oxidizing agent that will oxidize water, but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is stable in aqueous solution. Explain this difference based on CFSE of CFT model.

(c) Solid CrF_3 contains a Cr(III) ion surrounded by six fluoride ions in an octahedral geometry, with distances of 190 pm. However, MnF_3 is in a distorted geometry, with Mn–F distance of 179, 191, 209 pm (two of each). Suggest an explanation.

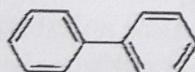
(d) The stepwise stability constants in aqueous solution at 25°C for the formation of the $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Cu}(\text{en})_3]^{2+}$ are observed to be 1×10^9 and 0.1, respectively. Explain it.

(e) Write down the structure of the products A and B as expected in the following reaction:



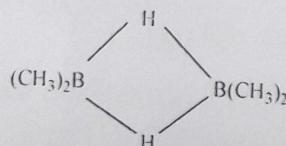
Group B

5. (a) Identify whether the following molecules have any permanent dipole moment (yes/no). Justify your answer in light of symmetry of the molecule.



(b) Methane (CH_4) is an example of tetrahedral (T_d) point group, which contains E , $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$ symmetry elements. Suppose that individually you are operating C_3 and C_2 symmetry elements on CH_4 molecule. Identify the number of unshifted atoms when you operate C_3 and C_2 symmetry elements.

(c) Identify optical activity for the following molecule. Justify your answer in terms of symmetry of the molecule.



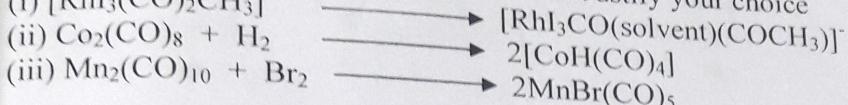
(d) In a C_{3v} point group the characters of a reducible representation are given below.

Operations	E	$2C_3$	$3\sigma_v$
T_{total}	12	0	2

Determine how many times "A₂" irreducible representation of C_{3v} point group is continued in T = 12_0 2 ? Find out the number of Raman active modes using the expression of T_{vib} and justify your answer from the character table of C_{3v}.

$$[1+1] + 2 + 2 + [2+2+1] = 11M$$

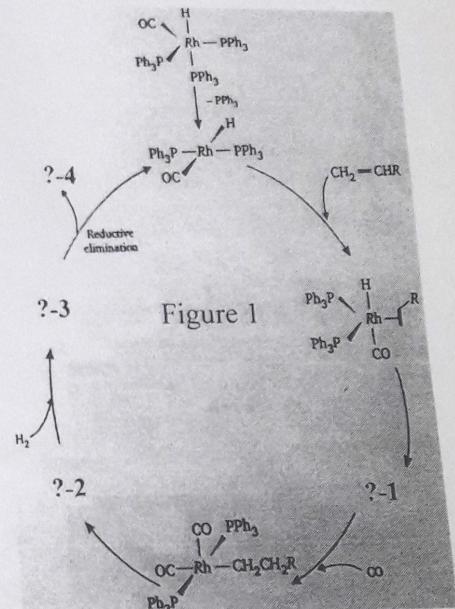
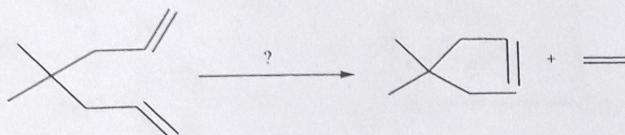
6. (a) From the following reactions identify the type of reaction involved viz., oxidative addition, reductive-elimination, insertion or addition. Justify your choice



- (b) In the following catalytic cycle (Figure 1) HRh(CO)(PPh₃)₃ is used as catalyst to convert alkene to aldehyde. (i) Identify the catalytic cycle (name of the reactions) and (ii) Identify the missing products ?-1 to ?-4 (product structures should be clear).

- (c) Comment on "phosphines with PEt₃ ligand allow isolation of Pt(PEt₃)₄ complex, whereas, ligands with PBu^t₃ allow isolation of Pt(PBu^t₃)₂ instead of Pt(PBu^t₃)₄".

- (d) Write the name of the catalyst (?) for the following ring closing metathesis reaction.



$$3 + [1+2] + 2 + 1 = 9M$$

7. (a) Which of the two chromium compounds [Cr(CO)₅(PEt₃)] and [Cr(CO)₅(PPh₃)] will have the lower CO stretching frequency and why? Which will have the shorter M-C bond?

- (b) Formulate the simplest neutral compound that matches to the 18-electron rule for each of the following metal and ligand combinations. Draw a plausible structure. (i) Fe, CO, COT (cyclooctatetraene); (ii) Ru, Ph₃P, NO (used both linear and bent)

- (c) Ligand exchange in [Fe(phen)₃]³⁺ and [Fe(bpy)₃]²⁺ complexes is much slower than the transfer of an electron from the bipyridine complex to the phenanthroline complex. Why does this rule out an inner sphere electron transfer mechanism?

- (d) In acid hydrolysis of an octahedral complex, why divalent monochloro complexes react about 100 times slower than the monovalent dichloro-complexes?

$$[2+1] + 3 + 2 + 2 = 10M$$

END