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# E–515

## M. Sc. (Second Semester) (ATKT)

## EXAMINATION, May-June, 2021

CHEMISTRY

Paper No. CH–7

**(Transition Metal Complexes)**

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

**Note :** Attempt all Sections as directed.

**Section—A** 1 each

**(Objective/Multiple Choice Questions)**

**Note :** Attempt all questions.

Choose the correct answer :

1. A reaction undergoes with formation of seven coordination transition state. The mechanism of reaction is :

   (a) $S_N^1$

   (b) $S_N^2$

   (c) Both (a) and (b)

   (d) None of the above





2. The correct order of hydrolysis of cobalt amine complex is :

   (a) $[Co(NH_3)_5Cl] > [Co(en)_2Cl_2]^+ > [Co(en)(NH_3)_2Cl]^{2+} > [Co(trien)Cl_2]^+$

   (b) $[Co(NH_3)_5Cl] < [Co(en)_2Cl_2]^+ < [Co(en)(NH_3)_2Cl]^{2+} < [Co(trien)Cl_2]^+$

   (c) $[Co(NH_3)_5Cl] > [Co(en)_2Cl_2]^+ > [Co(en)(NH_3)_2Cl]^{2+} = [Co(trien)Cl_2]^+$

   (d) $[Co(NH_3)_5Cl] > [Co(en)_2Cl_2]^+ > [Co(en)(NH_3)_2Cl]^{2+} < [Co(trien)Cl_2]^+$

3. Following reaction undergoes with :

   $[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(NH_3)_5H_2O]^{2+} + [Cr(H_2O)_5Cl]^{2+}$

   (a) Outer sphere mechanism

   (b) $S_N^2$ Mechanism

   (c) Inner-sphere mechanism

   (d) All of the above

4. Following reaction undergoes with

   $[(NH_3)_5Co(CO_3)]^+ + H_2O \rightarrow [(NH_3)_5Co(H_2O)]^{3+}$

   (a) Dissociation mechanism

   (b) Association mechanism

   (c) Electron transfer mechanism

   (d) Without bond breaking

5. The rate-law for square planar complex given below condition :
   (a) Two-path mechanism
   (b) Only $S_N^1$
   (c) Only $S_N^2$
   (d) None of the above

6. For chromium ion ($Cr^{3+}$), the transition $^4A_{2g} \rightarrow {}^4T_{2g}$ is :
   (a) Spin forbidden
   (b) Laporte allowed
   (c) Equivalent to 10 Dq
   (d) All of the above

7. The molar extinction coefficient (intensity) of transition is $(CoCl_4)^{2-}$ is higher than transition in $[Co(H_2O)_6]^{2+}$, become :
   (a) Transition is laporte allowed
   (b) Transition is spin allowed
   (c) Both (a) and (b)
   (d) None of the above

8. The $Cr^{3+}$ ion, the following transition may be assigned :
   $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) $\quad v_3 \quad 34,400$
   $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) $\quad v_2 \quad 22,700$
   $^4A_{2g} \rightarrow {}^4T_{2g} \quad v_1 \quad 14,900$
   Which transition will be responsible for the color in the visible region ?
   (a) $^4A_{2g} \rightarrow {}^4T_{2g}$
   (b) $^4A_{2g} \rightarrow {}^4T_{1g}$ (F)
   (c) $^4A_{2g} \rightarrow {}^4T_{1g}$ (P)
   (d) Both (a) and (b)

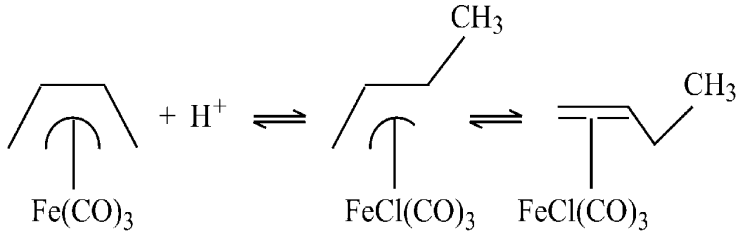




9. Number of microstates for the $P^3$ configuration will be :
   (a) 15
   (b) 20
   (c) 45
   (d) 10

10. Ground state term for $d^4$ and $d^6$ will be :
    (a) $^5D$ for both
    (b) $^5D$ for $d^4$ and $^6S$ for $d^6$
    (c) $^6S$ for $d^6$ and $^5D$ for $d^4$
    (d) $^3F$ for $d^4$ and $^4F$ for $d^6$

11. In the following hypothetical reaction, hapticity of the $\pi$ -bonding ligands is/are :




    (a) $a-\eta^4, b-\eta^2, c-\eta^3$
    (b) $a-\eta^4, b-\eta^3, c-\eta^2$
    (c) $a-\eta^3, b-\eta^4, c-\eta^2$
    (d) $a-\eta^2, b-\eta^3, c-\eta^2$

12. Which statement is correct for metal alkene complexes ?

(a) The C-C bond length of alkene increases on complexation.

(b) The planar alkene molecule becomes non-planar on complexation.

(c) Pt-Cl bond length is trans to alkene is longer than other cis Pt-Cl bonds.

(d) None of the above

13. The correct order of M-$C_p$ (M-C) distance in metallocene is :

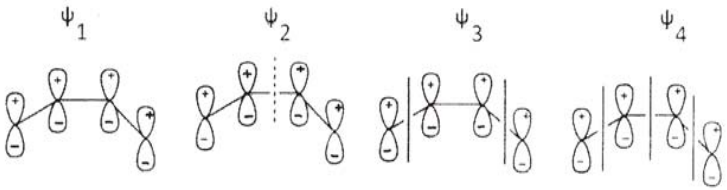
(a) $Fe(C_p)_2 > Co(C_p)_2 > Ni(C_p)_2$

(b) $Fe(C_p)_2 > Co(C_p)_2 > < Ni(C_p)_2$

(c) $Fe(C_p)_2 < Co(C_p)_2 > Ni(C_p)_2$

(d) $Ni(C_p)_2 > Co(C_p)_2 < Fe(C_p)_2$

14. The $\pi$-molecular orbitals of butadiene is given below :




The larger contribution of each molecular orbital will give rise to the different hapticity in M-L bonding the correct match is :

(a) $\psi_1 - \eta^4, \psi_2 - \eta^2, \psi_3 - \eta^1$ and $\eta^2$





(b) $\psi_1 - \eta^2, \psi_2 - \eta^1, \psi_3 - \eta^1$

(c) $\psi_1 - \eta^3, \psi_2 - \eta^2, \psi_3 - \eta^2$

(d) $\psi_1 - \eta^4, \psi_2 - \eta^3, \psi_3 - \eta^1$ and $\eta^2$

15. Which carbonyl do not obey the $18^{e-}$ rule ?

(a) $Mn_2(CO)_{10}$

(b) $V(CO)_6$

(c) $Fe(CO)_5$

(d) $Cr(CO)_6$

16. Grubb's catalyst is used for :

(a) Hydroformylation

(b) Alkene polymerization

(c) Hydrogenation

(d) Alkene metathesis

17. The observation that, $Fe(\eta^1 - C_5H_5)(CO)_2(\eta^5 - C_5H_5)$ gives two singlets at room temperature for the two cyclopentadienyl ligands. This behavior is because of :

(a) Tautomerism

(b) Ligand substitution

(c) Fluxionality

(d) Electron transfer reaction

18. The complex $(OC)_5Cr\{(OEt)Me\}$ is :

    (a) Schrock carbene

    (b) Grubb's catalyst

    (c) Fischer carbene

    (d) All of the above

19. The major decomposition pathways for alkyl is β-elimination, which converts a metal alkyl into a hydridometal alkene complex. These decomposition may occur when :

    (a) β-carbon of alkyl bears a hydrogen substituents.

    (b) The M-C-C-M unit is in coplanar conformation which brings the β-hydrogen close to the metal.

    (c) There is vacant site in the metal, cis to the alkyl.

    (d) All of the above

20. The nature of carbine carbon in Schrock carbene is :

    (a) Electrophilic

    (b) Nucleophilic

    (c) Both (a) and (b)

    (d) None of the above



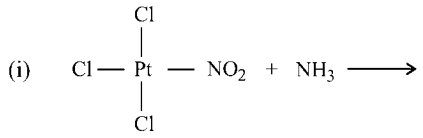


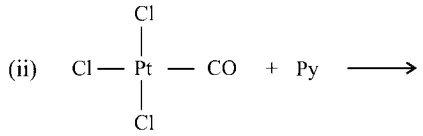
**Section—B** 2 each

**(Very Short Answer Type Questions)**

**Note :** Attempt all questions. Write answer in **2-3** lines.

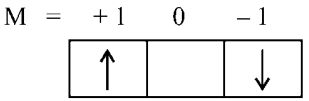
1. Complete the following reactions :





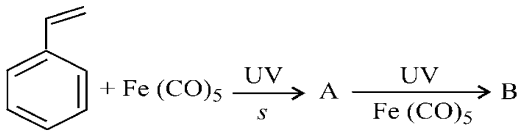
2. State the Marcus-Hush's equation/principle.

3. For the $p^2$ configuration given below, what will be the allowed value of term symbols ?



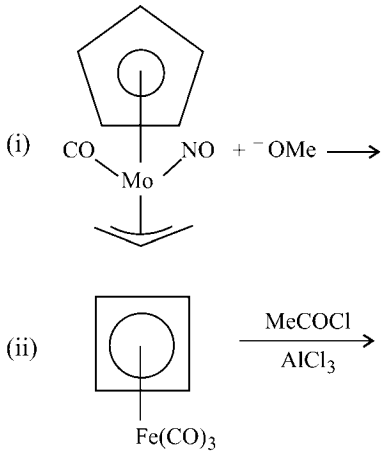
4. State the Curie's law of magnetic susceptibility.

5. Complete the following reactions :

(i) 

(ii) $Na[Mn(CO)_5] + CH_2 - CH - CH_2 - Br \rightarrow A \xrightarrow{h\nu \text{ or } 80^\circ C} B$

6. Complete the following reactions :




7. Why is Fischer carbene carbon electrophilic in nature ?
8. Complete the following reactions :

   (i) $Fe(\eta^5 - C_5H_5)_2 + Li + C_2H_5NH_2 \rightarrow$

   (ii) $(OC)_5Cr{=}C(OMe)R + HNR'R'' \rightarrow$

**Section—C** 3 each

**(Short Answer Type Questions)**

**Note :** Attempt all questions. Write answers in > **75** words.

1. How does $S_N1$ reaction undergo in octahedral complexes ?
2. Why bridging ligand is required for the inner-sphere electron transfer reactions ?
3. What is nephelauxetic effect ?
4. Draw Orgel diagram and assigned all the allowed transitions.





5. Why does ferrocene undergo electrophilic substitution reaction ?
6. Free cyclobutadiene is anti-aromatic. Complexed cyclobutadiene gives electrophilic substitution reaction. Why ?
7. Using MO approach explain the $\eta^1, \eta^2$ and $\eta^4$ mode of bonding in butadiene complexes.
8. Cyclopentadienyl complexes undergo electrophilic reaction. Explain.

**Section—D** 5 each

**(Long Answer Type Questions)**

**Note :** Attempt all questions. Write answers in **150** words.

1. Discuss the mechanism of outer-sphere electron transfer reaction.

   *Or*

   What do you mean by *trans*-effect ? Discuss the $\pi$-bonding theory of *trans*-effect. How substitution reaction undergoes with two-path mechanism ?

2. What do you mean by charge transfer transition ? Discuss the metal-to-ligand and ligand-to-metal and charge transfer transition.

   *Or*

   What are the selection rules for electronic transition ? How can they be breakdown ?

3. Discuss the structure and bonding of ferrocene.

*Or*

Discuss structure and bonding of dibenzene chromium.

4. What do you mean by molecular fluxionality ? How NMR spectroscopy can help to explain fluxional behavior ? Discuss the fluxional behavior of organometallic compounds.

*Or*

What are carbene complexes ? Discuss the differences between Fischer and Schrock carbene on the ground of structure, bonding and chemical reactivity.