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F - 515

M.Sc. (Second Semester)
EXAMINATION, May - June, 2022
CHEMISTRY
Paper No. CH - 7
(Transition Metal Complexes)

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

Note: Attempt all the sections as directed.

(Section - A)
(Objective/Multiple Choice Questions)

(1 mark each)

1. Which statement/s are incorrect for the rates of associative reaction mechanism:
   - (i) Increase with the concentration of nucleophile
   - (ii) Increase with the nucleophilicity of nucleophiles.
   - (iii) Increase with the sterics of the overall coordination environment:
   - (iv) Show a positive $\Delta S^{\pm}$
   - (A) Both (i) and (ii)
   - (B) Both (ii) and (iii)
   - (C) Both (iii) and (iv)
   - (D) Only (iv)

2. Ligand field activation energies (LFAE) for a square pyramidal transition state for Cr^{3+}, Co^{3+} and Pt^{2+} ions in low spin complexes are $+2Dq, +4Dq\ and +2Dq$, respectively. Which among the following statement is correct?
   - (A) Cr^{3+} Complexes are inert
   - (B) Co^{3+} Complexes are labile
   - (C) Pt^{3+} Complexes are labile
   - (D) Cr^{3+} Complexes are labile, but Co^{3+} and Pt^{2+} complexes are inert.

3. Correct match of the effect of the *trans* ligand (L) on the rate of substitution of *trans* $[Pt(PEt_3)_2LCI]$ in the following will be -

	L	k_1,s^{-1}
(a)	PEt_3	(i) 1.7×10^{-2}
(b)	H^-	(ii) 1.7×10^{-4}
(c)	CH_3^-	(iii) 1.8×10^{-2}
(d)	$C_6H_{5^-}$	(iv) 2.8×10^{-5}
(e)	$p-CH_3OC_6H_4$	(v) 3.3×10^{-5}

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

4. Base hydrolysis of $[CoCl(NH_3)_5]^{2+}$ is an overall second order reaction, whereas that of $[Co(CN)_6]^{3-}$ is of first order. The rate depend in both cases solely on the concentrations of the cobalt complex.

   This may be due to

   (a) Presence of ionizable proton in $[CoCl(NH_3)_5]^{2+}$ but not in $[Co(CN)_6]^{3-}$

   (b) S_N1_{CB} mechanism in the case of $[CoCI(NH_3)_5]^{2+}$ only

   (c) S_N1_{CB} mechanism in the case of $[Co(CN)_6]^{3+}$ only

   (d) S_N1_{CB} mechanism in both the complexes

   Correct explanation (s) is/are

   (A) (a) and (b)

   (B) (a) and (c)

   (C) (b) Only

   (D) (a) and (d)

5. Consider two redox pairs:

   (1) Cr(II)/Ru(III) (2) Cr(II)/Co(III)

   The rate of acceleration in going from a outer- sphere to inner- sphere mechanism is lower for (1) relative to (2). its correct explanation is:

   (A) HOMO/LUMO are $\sigma*$ and $\sigma*$ respectively

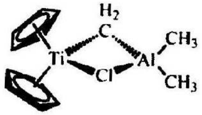
   (B) HOMO/LUMO are $\sigma*$ and $\pi*$ respectively

   (C) HOMO/LUMO are $\pi*$ and $\sigma*$ respectively

   (D) HOMO/LUMO are $\pi*$ and $\pi*$ respectively

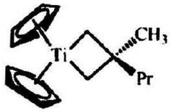
6. Correct match of the following is:

(a)



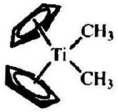
(i) Petasis reagent

(b)



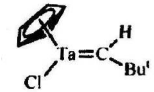
(ii) Schrock Carbene

(c)



(iii) Grubb's reagent

(d)



(iv) Tebbe's reagent

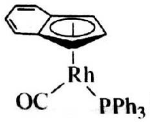
   (A) (a)-(i), (b)-(ii), (c)-(iii), (d)-(iv)

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

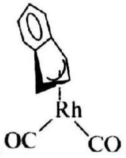
   (C) (a)-(iv), (b)-(iii), (c)-(i), (d)-(ii)

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

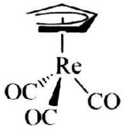
7. Which among the following do not obey the 18 electron rule?



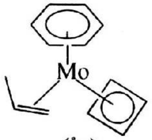
(i)



(ii)



(iii)



(iv)

   (A) Only (i)

   (B) (i) and (iii)

   (C) (i) and (iv)

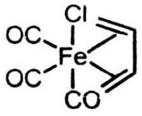
   (D) Only (ii)

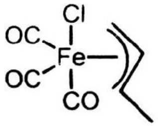
8. Correct match of the following is:

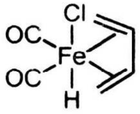
	Complex	Nature of hydrogen
(a)	$[Mo(CO)_3(PR_3)_2(H_2)]$	(i) dihydrogen
(b)	$[Mo(PR_3)_5(H)_2]$,	(ii) dihydride
(c)	$[Mn(CO)_4\{C(O)CH_3\}]$	(iii) Agostic

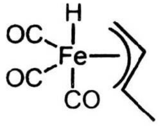
(A) (a)-(i), (b)-(ii), (c)-(iii)
(B) (a)-(ii), (b)-(i), (c)-(iii)
(C) (a)-(iii), (b)-(ii), (c)-(i)
(D) (a)-(i), (b)-(iii), (c)-(ii)

9. Treatment of $Fe(CO)_5$ with 1,3 butadiene (A) gives B that shows two signals in its ^1H NMR spectrum. B on treatment with HCl yield C which shows four signals in its ^1H NMR spectrum. The compound C is:

(A)


(B)


(C)


(D)


10. Identify the order according to increasing stability of the following organometallic compounds.

$TiMe_4, Ti(CH_2Ph)_4, Ti(i-\mathrm{Pr})_4$ and $TiEt_4$

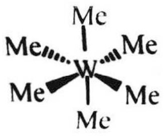
(A) $Ti(CH_2Ph)_4) < Ti(i-\mathrm{Pr})_4 < TiEt_4 < TiMe_4$

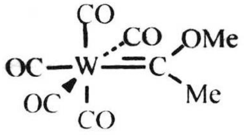
(B) $TiEt_4 < TiMe_4 < Ti(i-\mathrm{Pr})_4 < Ti(CH_2Ph)_4$

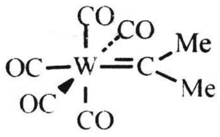
(C) $Ti(i-\mathrm{Pr})_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$

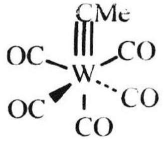
(D) $TiMe_4 < TiEt_4 < Ti(i-\mathrm{Pr})_4 < Ti(CH_2Ph)_4$

11. $W(CO)_6$ reacts with MeLi to give an intermediate which upon treatment with CH_2N_2 gives a compound. The compound is:

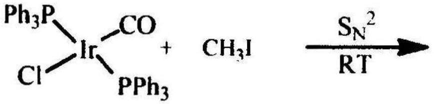
(A)


(B)


(C)


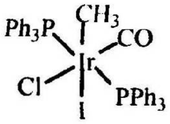
(D)


12. Consider the following reaction:

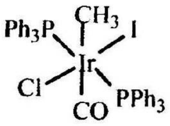


Product of this reactions is :

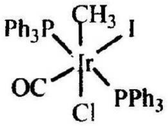
(A)



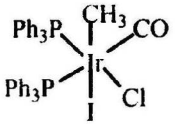
(B)



(C)



(D)



13. The three electronic transitions at 14,900, 22,700, and 34400 cm^{-1} are observed in the absorption spectrum of $[CrF_6]^{3-}$. The o value (in cm^{-1}) and the corresponding transitions is:

(A) 7800 and ${}^4A_{2g} \to {}^4T_{2g}$

(B) 14900 and ${}^4A_{2g} \to {}^4T_{2g}$

(C) 14900 and ${}^4T_{2g} \to {}^4T_{1g}(F)$

(D) 7800 and ${}^4T_{2g} \to {}^4T_{1g}(F)$

14. The ground state of d^6 in weak field and strong ligand fields are:

(A) ${}^5T_{2g}$ *and* ${}^1A_{1g}$

(B) ${}^5E_g$ *and* ${}^1A_{1g}$

(C) ${}^5T_{1g}$ *and* ${}^5Eg$

(D) ${}^5T_{2g}$ *and* ${}^5E_g$

15. The spin only magnetic moment and the spectroscopic ground state term symbol of manganese center in $[MnF_6]^{3-}$ ion respectively. are

(A) 4.9 BM and ^{5}D

(B) 4.9 BM and ^{4}F

(C) 3.9 BM and ^{3}D

(D) 4.9 BM and ^{3}F

16. The electronic absorption spectrum of an aqueous solution of $[Ni(en)_3]^{2+}$ exhibits three broad absorptions. Which bands is/are in the visible region?

(A) ${}^3A_{2g} \to {}^3T_{2g}$

(B) ${}^3A_{2g} \to {}^3T_{1g}(F)$

(C) ${}^3A_{2g} \to {}^3T_{1g}(P)$

(D) ${}^3T_{1g} \to {}^3T_{2g}$

17. In the presence of an external magnetic field (normal Zeeman effect), the transition ${}^1D_2 \rightarrow {}^1P_1$ splits into:

(A) 6 lines

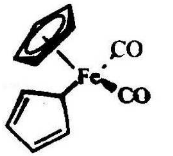
(B) 8 lines

(C) 7 lines

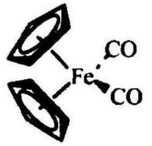
(D) 9 lines

18. The ^{1}H NMR spectrum of $(C_5H_5)_2Fe(CO)_2$ show two peaks of equal area at room temperature but has four resonances of relative intensity 5:2:2:1 at low temperatures. The structure of the molecule is:

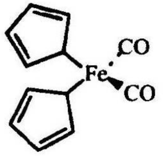
(A)



(B)



(C)



(D) None of these

19. Which statement (s) is/are incorrect:

(i) Fischer carbene complexes are more properly called electrophilic metal - carbene complexes.

(ii) Schrock carbenes are called nucleophilic metal-carbene complexes.

(iii) At least one electronegative heteroatom, e.g, O or N should present in substituent on the carbene carbon of Schrock carbenes.

(iv) Oxidation state of mental in Fischer carbenes are low

(A) (i) and (ii)

(B) (iii) and (iv)

(C) Only (iii)

(D) Only (iv)

20. Which among the following is not called piono stool complex.

(A) $(C_4H_4)Fe(CO)_3$

(B) $CpFe(CO)_2l$

(C) $CpCo(CO)_2$

(D) $(Arene)_2Cr$

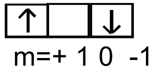
Section - B

(Very Short Answer Type Question)

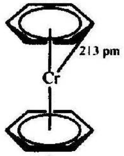
(2 marks each)

Note: Attempt all questions.

1. Draw the energy profile diagram of associative and dissociative mechanism of an organic compound.
2. What will be the state generated from t_{2g}^2 configuration under strong ligand field?
3. For the p^2 configuration given below, what will be the allowed values of the term symbols?



4. What do you mean by hepticity?
5. Based on the following structure and data, which compound will show high reactivity towards electrophilic substitution reaction into the η^6-arene ring?



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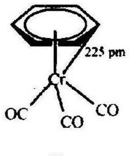


II

6. State the Marcus-Hush equation/principle.
7. Complete the following reaction:
   (i) $Fe(\eta^5 - C_5H_5) + CH_3COCI / AlCl_3 \rightarrow$
   (ii) $(OC)_5Cr = C(OMe)R + HNR'R'' \rightarrow$
8. Find out the CFSE value of $Cr(H2O)_6^{2+}$ in both low spin high spin complexes.

Section - C

(Short Answer Type Question)

(3 marks each)

Note: Attempt all questions.

1. Rate constant and activation parameters for selected self-exchange electron transfer reactions at 25 ^{0}C is tabulated below.

Coordination complex	$k, M^{-1}S^{-1}$	$\Delta H^{\pm}, kJ/mol$	$\Delta S^{\pm}, Jk.mol$
$[V(H_2O)_6]^{3+/2+}$	1.0×10^{-2}	53	-105
$[Fe(H_2O)_6]^{3+/2+}$	3.3	39	-105
$[Co(H_2O)_6]^{3+/2+}$	2.5	53	-59
$[Co(NH_3)_6]^{3+/2+}$	8×10^{-6}	---	---

Using the data in the above table, explain the differences between the rate constants for self-exchange reactions for the following pairs.

(a) $[V(H_2O)_6]^{3+/2+}$ versus $[Fe(H_2O)_6]^{3+/2+}$ and

(b) $[Co(H_2O)_6]^{3+/2+}$ versus $[Co(NH_3)_6]^{3+/2+}$

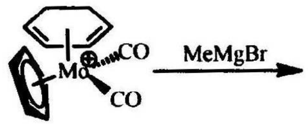
2. What are the classical and non-classical modes of coordination of hydrogen? Give evident for such metal coordination of hydrogen.

3. What is trans directing series? Why $\pi -$bonding ligands show large trans directing effect?

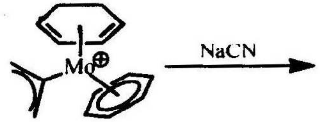
4. Give a quantitative energy level diagram of the d-orbital splitting followed by the crystal field theory of distorted octahedral system.

5. Complete the following reactions.

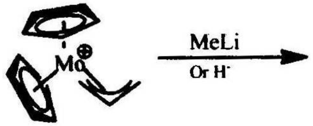
(a)



(b)



(c)



6. Using Orgel diagram, discuss the electronic transitions in $[Co(NH_3)_6]^{2+}$ and $CoCl_4^{2-}$ compounds. Further write down the transitions responsible for their colour change.

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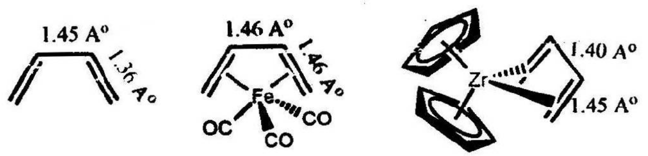
7. Consider the binding of 1,3 butadiene to Fe and Zr, and explain the bond length data.



8. Discuss the structure and bonding of Zeise's salt.

Section - D

(Long Answer Type Questions)

(5 marks each)

1. What are electron transfer reactions? Discuss the mechanism of outer- sphere mechanism of electron transfer reaction.

OR

Discuss the substitution reactions in the square planar complex under the following:

(i) Trans effect

(ii) Mechanism

2. What do you mean by charge transfer transitions? Discuss the types of charge transfer. Why MnO_4- ion is pink violet in colour. Which transition is responsible for the colour of this ion?

OR

What is Curie-Weiss law? Explain all the terms involved. Plot a diagram reciprocal of magnetic susceptibility vs three magnetic behaviours:

(i) Curie law

(ii) Ferromagnetic substance with Tc.

(iii) Antiferromagnetic substance with T_N

Calculate the paramagnetic moment of
$Yb_2(SO_4).8H_2O$

3. Discuss the structure and bonding of ferrocene.

OR

Discuss the mechanism of coordinated alkene, which is exposed to nucleophilic attack.

4. Free cyclobutadiene is antiaromatic whereas cyclobutadiene coordinated to metal atom is aromatic. Explain clearly with suitable examples using molecular orbital approach.

OR

How do the molecular fluxionally differ from tautomerism? How temperature dependent NMR spectral analysis may help to understand the fluxional behaviour of organometallic compounds? Discuss the fluxional behaviour of allyl, diene and cyclopentadienyl complexes.