2018

PG Even Semester (CBCS) Exam., May—2018

CHEMISTRY

(2nd Semester)

Course No. : CHMCC–201

(Inorganic Chemistry)

Full Marks : 70
Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, taking **one** from each Unit

UNIT—I

1. *(a)* Explain the terms ferromagnetism and anti-ferromagnetism. Distinguish between the properties of the compounds exhibiting such phenomena. 2+2=4

(b) The brown ring compound $[Fe(H_2O)_5(NO)]SO_4$ has a magnetic moment of 3·7 BM. Can you predict the valence of iron in this compound? 2

(c) What is a cross-over region? A metal complex is close to the cross-over region. Will its magnetic moment be anomalous? 1+2=3

(d) Describe the 90° super exchange pathway for ferromagnetic Cr^3 -Cr^3 coupling. 5

2. *(a)* Write down the first- and second-order Zeeman magnetic susceptibility equations. Explain the temperature dependence of second-order magnetic susceptibility. 2+2=4

(b) Find out the ground state *R-S* term symbol for $3d^3$ configuration. Show the splitting of $3d^3$ ion *R-S* terms in weak octahedral crystal field. 1+2=3

(c) Magnetic moment observed for tetrahedral CoX_4^2 complexes are

X	SCN	Cl	Br	I
(BM) =	4·4	4·6	4·7	4·8

Comment. 3

(d) High-spin octahedral complexes of Co(II) have magnetic moments much higher than the spin-only value for 3 electrons (4·8–5·2 BM vs. 3·88 BM) in contrast low-spin Oh complexes of Co(II) have magnetic moments which are only slightly higher than the spin-only value for 1 electron (1·8–1·9 BM vs. 1·73 BM). Comment. 4

UNIT—II

3. *(a)* Prove that the transition moment integral, | | has finite value for *d-d* transition. 4

(b) Briefly discuss the band intensities in *d-d* (Oh and Td complexes) and charge transfer transitions. 6

(c) What is Nephelauxetic effect? Briefly discuss. Write down the significance of Nephelauxetic parameter. 2+2=4

4. *(a)* Deduce the values of $_0$, B and for $[Co(en)_3]^3$ (en=ethylenediamine) from the following data : 6

$^1A_{1g}$ $^1T_{1g}$ 21550 cm ^{1}

$^1A_{1g}$ $^1T_{2g}$ 29600 cm ^{1}

$\frac{0}{B}$ 40, $\frac{E}{B}$ 38 and B_0 1065 cm ^{1}

(b) Construct a -bond molecular orbital diagram for an octahedral complex and explain. 6

(c) Give examples and explain the following : 2

(i) MMCT

(ii) LLCT

UNIT—III

5. *(a)* What is meant by 'non-innocent' ligand? Citing example, explain the variation of metal oxidation states (MOS) with non-innocent ligand. 1+1=2

(b) Describe the chemistry of titanium(IV) giving example of halides, oxohalides, aqua- and peroxo-complexes (show probable structures). 6

(c) Show the pictorial representation of *f* orbitals and their splitting in octahedral ligand field. 2+1=3

(d) Discuss in brief the separation of lanthanides using ion-exchange process. 3

6. *(a)* Account the relative stability and bonding of dihydrogen (H_2) molecule in $M(PH_3)_3H_4$, where M Fe, Rn, Os. 4

(b) $Fe(CO)_5$ is intensely coloured but its heavier analogues are colourless. Give explanation. 2

(c) Ce^3 (f^1) shows $_{exp}$ value 2·3–2·5 BM whereas Yb^3 (f^{13}) containing same number of unpaired electron shows $_{exp}$ value 4·4–4·9 BM. Explain. 4

(d) Describe the use of lanthanides in NMR shift reagent. 2

(e) Why does *f-f* transition exhibit very sharp bands? 2

UNIT—IV

7. *(a)* Rationalize the trends in the following sets of IR active CO stretching frequencies (in cm^{-1}) : 2

$W(CO)_5P(n\text{-}Bn)_3$: 2068, 1936, 1943
$W(CO)_5PPh_3$: 2075, 1944, 1942
$W(CO)_5P(o\text{-}Bn)_3$: 2079, 1947, 1957

(b) Draw at least two possible structures of $Os_3(CO)_9(PPh_3)_2$. The IR spectrum of this compound in CH_2Cl_2 has CO stretches at 1962 cm^{-1} and 1917 cm^{-1}. How does this knowledge help to ascertain the actual structure of the compound? 4

(c) Propose a set of reactions for the formation of $[W(C(OCH_3)Ph)(CO)_5]$ starting with hexacarboxyl tungsten(O) and other reagents of your choice. 5

(d) "CO ligand can be oxidized in presence of a strong base." Explain the statement with appropriate example. 3

8. *(a)* Complete the following reactions : 3

(i) $[Mn(CO)_5]^- + [ReBr(CO)_5] \longrightarrow ?$

(ii) $[Mo_2(CO)_{10}] +$  $\longrightarrow A \xrightarrow{Ph_3CBF_4} B$

(iii) $Co(acac)_3 + 3Ph_3N + N_2 \xrightarrow{Al(iso\text{-}C_4H_9)_3} ?$

(b) Propose a synthesis of $MnH(CO)_5$ starting with $Mn_2(CO)_{10}$ as the source of Mn and other reagents of your choice. 4

(c) What is Wade rule? Apply Wade rule to find the structure of $Os_5C(CO)_{15}$. 3

(d) Predict the product for the following reactions : 1+2+1=4

(i) $(PhMeP)_4Mo(N_2)_2 + 2HX \longrightarrow ?$

(ii) $Cp(CO)_2Mn(N_2) \xrightarrow{MeLi} A \xrightarrow{Me_3^+OBF_4^-} B$

(iii) $[(CN)_5Fe(NO)]^{2-} + RS^- \longrightarrow ?$

UNIT—V

9. *(a)* Briefly discuss the active site structure of $[Fe_4S_4]$ type ferredoxin. Show the different oxidation levels associated with the metalloprotein. Furnish the active site structure of $[Fe_3S_4]$ type ferredoxin present in aconitase. 2+2+2=6

(b) Give an account of O_2-binding by hemoglobin as a function of pH and explain Bohr effect. 4

(c) Is 'ferritin' merely an iron storage protein? Explain in relation to its role in biological system. What is the nature and composition of its mineral core? 4

10. *(a)* Furnish an account of the active site structure of O_2-transport protein, hemerythrin. Explain the mechanistic pathway for the dioxygen transport. 6

(b) Explain 'cooperativity effect' in O_2-binding by hemoglobin. 4

(c) Briefly discuss the role and active site structure of cytochrome C. 4

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