(b) Discuss, with illustration, the structural changes that occur in the active site of deoxyHb upon dioxygen binding. In this context, explain the 'co-operativity' effect. 4+2=6

(c) Draw and briefly discuss the active site structure of oxyhemocyanin including its magnetic behaviour. 3

10. (a) Explain, with illustration of active site structures, oxygen transportation by the non-heme iron protein, hemerythrin. Mention its two major point of differences with that of dioxygen transport heme-protein, hemoglobin. 5+2=7

(b) Furnish an account of active site structure of $[Mn_4]$-cluster protein in Photosystem-II and explain the cyclic e-transfer process along with the oxidation levels. 3+4=7

★★★

PG EVEN SEMESTER EXAMINATION, 2023

CHEMISTRY

2nd Semester

Course No. : CHM - 551

(Inorganic Chemistry II)

Full Marks : 70

Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

(Answer five questions, selecting one from each unit)

UNIT - I

1. (a) Find out the relation between orbital magnetic moment (μ_l) and orbital angular momentum quantum number (l). 3

(b) Derive all the Russell-Saunders terms for a p^2 system and indicate the order of these terms. 3+1= 4

(c) Define ferromagnetism. Plot the magnetic susceptibility (χ) versus temperature (T) for a ferromagnetic substance and briefly discuss. Compound NiF_2 shows weak ferromagnetism in the absence of an external magnetic field. Give reason. 1+2+1=4

(d) How does the temperature independent paramagnetism arise? Give example. 3

2. (a) Give an idea of the Russell-Saunders coupling and, in this connection, explain Hund's first and second rules. 2+2=4

(c) The magnetic moment of the high spin octahedral cobalt(II) complexes is higher than the spin-only magnetic moment. Explain. 3

(d) 'The ferrimagnetism is observed in magnetite' - explain. 3

(e) Briefly discuss the antiferromagnetic exchange pathway in the compound (i) $Cu_2(CH_3COO)_4.2H_2O$ and (ii) $K_4[Ru_2OCl_{10}]$ 2+2=4

UNIT - II

3. (a) Draw the Orgel diagram of $[CoCl_4]^{2-}$ and show the possible transitions. 3

(b) The d-d transitions are Laporte forbidden yet transition metal complexes are colored. Explain. 4

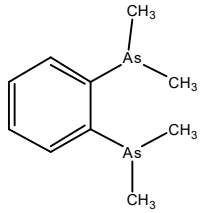
(c) Discuss Nephelauxetic effect. The electronic spectrum of $[Ni(NH_3)_6]Cl_2$ shows bands at 10750, 17500 and 28200 cm^{-1}. Calculate the value of Racah (B) and Nephelauxetic (β) parameter (where $B^0 = 1030\ cm^{-1}$). 3+4=7

4. (a) The color of the aqueous permanganate solution is more intense than aqueous manganous ion. Explain. 3

(b) Electronic spectra of $[Co(H_2O)_6]^{2+}$ shows a weak but well resolved absorption band at about 800 cm^{-1} and a multiple

SCN^- forms $[Co(diarsine)_2(NCS)(NO)]^+$ in which N-O distance is 185 pm and CoNO angle is 135°". Explain. 3

Diarsine =



(e) "NO^+ is a bad donor but good acceptor while CN^- is a good donor but bad acceptor." Explain. 2½

8. (a) Propose a set of reactions for the formation of $[W(C(OCH_3)Ph)(CO)_5]$ starting with hexacarbonyltungsten and other reagents of your choice. 3

(b) Draw the structure of the following:
(i) $Ir_4(CO)_{12}$ (ii) $[Co_3(CH)(CO)_9]$ 3

(c) Complete the following reactions:
(i) $3Co_2(CO)_8 + 2\ Co\ (C_7H_{15}CO_2)_2 + 2H_2 \longrightarrow$
(ii) $3Co_2(CO)_8 + 12Py \longrightarrow$
(iii) $Co_2(CO)_8 + 2NO \longrightarrow$ 1½x3=4½

(d) What is Wade's rule? Apply Wade's rule to determine the structure of $Os_5C(CO)_{15}$. 3½

UNIT - V

9. (a) Discuss the role and active site structure of $[Fe_3S_4]$ type ferredoxin. State the possible oxidation levels. What happens when the protein is treated with HCl ? 3+1+1=5

absorption band corresponding to three overlapping peaks at around 20,000 cm^{-1}. Explain the observation. 4

(c) Construct the σ-molecular orbital diagram for a complex of octahedral symmetry. Explain the effect of π-bonding on the Δ value of an octahedral complex. 4+3=7

UNIT - III

5. (a) Write the electron configurations of Cerium in Ce (atom), Ce^{3+} ion and $(NH_4)_2[Ce(NO_3)_6]$. Furnish the synthesis, geometry and structure of $Ce(NO_3)_4(Cy_3PO)_2$ and $[Ce(NO_3)_3(Et_3PO)_3]+$ from cerium(IV) ammonium nitrate (CAN). 1+4=5

(b) Describe the lanthanide separation using (i) Valence change and (ii) ion exchange method. 3

(c) Illustrate the process of luminescence (with diagram) in lanthanide complexes and comment on the fluorescence properties of lanthanide elements. 3+1=4

(d) Complete the following reactions, give structures and oxidation states of actinides. 2×1 = 2

(i) $U(Cp^*)_2(CH_3)Cl + Li[PhN\text{-}N{=}N\text{-}N(H)Ph] \longrightarrow$

(ii) $ThCl_4 + TlCp \longrightarrow$

6. (a) Illustrate the classical (dihydride) and non-classical (dihydrogen) bonding in $M(H_2)$ fragment. Describe the structure and bonding of $MH_4(PR_3)_3$ (M=Fe, Ru, Os). 2+2=4

(b) Explain why $Ti(H_2O)_6]^{3+}$ is violet in solution but become colourless on heating. 2

(c) Furnish the synthesis and structures of VF_5 and CrF_4 in gas and solid states. 3

(d) Compare and give reason for the acid-base, redox and magnetic properties MnO, MnO_2 and Mn_3O_7. 2

(e) Calculate the magnetic moment for a complex of Ce^{3+} and compare with complex of Ti^{3+}. 3

UNIT - IV

7. (a) Assuming the 18-electron rule to be valid, find the number of Os-Os bonds in $Os_4(CO)_{14}$. 2

(b) Provide plausible reasons for the differences in ν_{CO} (IR spectra) of the following compounds :

$Mo(CO)_3(PF_3)_3$ --- 2040, 1991 cm^{-1}

and $Mo(CO)_3(PMe_3)_3$--- 1945, 1851 cm^{-1} 2

(c) Starting from $Mn_2(CO)_{10}$ how are the following compounds prepared?

(i) $NaMn(CO)_5$

(ii) $MeMn(CO)_5$

(iii) $[(CO)_5Mn\text{-}Re(CO)_5]$ 4½

(d) "The N-O distance in $[Co(diarsine)_2NO]^{2+}$ is 168 pm and the CoNO angle is 180°. Reaction of the complex with