2019

PG Even Semester (CBCS) Exam., May—2019

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)* Construct the relation between magnetic permeability (*P*) and magnetic susceptibility ( ) from Gauss' law. Draw the plots of versus *T* and 1/ versus *T* for paramagnetic substances. 2+1=3

(b) Give a qualitative interpretation of the spin-orbit coupling constant. How does it help in predicting the Russell-Saunders terms? 3+2=5

(c) Find out the ground state RS term symbol for p^2 configuration. How many microstates are present in the ground state term of p^2 configuration and what are they? 1+1+2=4

(d) Explain ferrimagnetism by taking a suitable example. 2

2. *(a)* Briefly discuss the temperature dependency of second-order magnetic susceptibility. 3

(b) Discuss antiferromagnetic exchange pathways by taking suitable examples. 5

(c) What is canting? How does canting give rise to weak ferromagnetism? Give examples. 3

(d) In high-spin octahedral as well as in tetrahedral complexes, Co(II) contains three unpaired electrons. But the magnetic moments of its octahedral complexes are much higher (4·8 to 5·2 BM) in comparison to the tetrahedral ones (4·2 to 4·8 BM). Comment. 3

UNIT—II

3. *(a)* Construct the Orgel diagram for d^8 ion in weak octahedral crystal field and show the possible transitions. 3

(b) *d-d* transitions are Laporte forbidden but transition metal complexes are often coloured. Explain. 3

(c) $[Mn(H_2O)_6]^{2}$ is weakly coloured in contrast to $[Re(H_2O)_6]^{2}$. Explain. 2

(d) Give a comparative account on the spectral patterns of $[Co(H_2O)_6]^{2}$ and $[CoCl_4]^{2}$. 4

(e) The value of the Racah parameter for a complex is less than that for a free ion. How do you explain this? What does this difference indicate? 2

4. *(a)* $NiCl_4^{2}$ gives more intense transitions than $NiCl_6^{4}$. Give reasons. 2

(b) Though three bands are expected $[Co(NCS)_4]^{2}$ shows only two bands in UV-vis spectrum. Explain. 3

(c) The electronic spectrum of $[Ni(NH_3)_6]Cl_2$ shows bands at 10750 cm ^{1}, 17500 cm ^{1} and 28200 cm ^{1}. Calculate the values of B, D_q and , where B_0 for Ni^{2} is 1030 cm ^{1}. 3

(d) Discuss the effect of -bonding on value for $[CoF_6]^{3}$ and the hypothetical $[Co(PR_3)_6]^{3}$ complexes. 3

(e) Explain MMCT and LLCT transitions by taking suitable examples. 3

UNIT—III

5. *(a)* "Reduction potentials of V^{3} /V^{2} and Mn^{3} /Mn^{2} in aqueous solution at 25 °C show deviation from steady increase for the first row transition metal series." Justify the statement. 3

(b) Describe the stability of high and low oxidation states of first-row transition metals. 2+1=3

(c) "CrO_4^{2} is intensely coloured but WO_4^{2} is colourless." Give reason. 2

(d) "Actinide elements exhibit greater multiplicity of oxidation states compared to lanthanides." Comment. 2

(e) Why does lanthanide show different formulae for estimating effective magnetic moment ($_{eff}$) value for transition metals? Calculate the $_{eff}$ value for Ce^{3} ? 1½+2½=4

6. *(a)* Write the chemistry of Cr(VI), giving example of fluoride, oxide, oxochloride and peroxo complexes. ½+½+½+½=2

(b) How is high coordination of transition metal obtained? 2

(c) Explain separation of the lanthanide elements using 'complex formation' and 'valence change' methods. 1½+1½=3

(d) Explain the temperature dependent magnetic properties of Sm^{3} and Eu^{3} . 2

(e) How do lanthanides differ from actinides? Discuss the chemistry of uranium(VI). 2+3=5

UNIT—IV

7. *(a)* Propose a mechanism for stoichiometric decarbonylation of $C_6H_5CH_2C(O)Cl$ by $Rh(PPh_3)_3Cl$ giving benzyl chloride. 5

(b) Draw the structures of the following : 1½×2=3

(i) $Os_4(CO)_{16}$

(ii) $[\ ^{5}\text{-}C_5H_5FeCO]_4$

(c) Predict the products in the following reactions : ½×4=6

(i) $MnCl_2 \quad 4Ph_2CONa \quad 10CO \xrightarrow[200\,^{\circ}C]{THF} ?$

(ii) $2[Co(H_2O)_4][OAc_2]_2$
$8Ac_2O \quad 8CO \xrightarrow{170\,^{\circ}C} ?$

(iii) $Zn[Co(CO)_4]_2 \quad [Rh(CO)_2Cl]_2 \quad ?$

(iv) $2Fe(CO)_5 \quad 6NH_3 \quad H_2O \quad ?$

8. *(a)* Propose a synthesis for $(OC)_5MnRe(CO)_5$ starting with $Mn_2(CO)_{10}$ as the source of Mn and other reagents of your choice. 4

(b) Apply electron counting schemes to obtain the structure of $[Fe_4C(CO)_{12}]^{2}$ and $Os_7(CO)_{21}$. 3

(c) Complete the following reactions : 1×3=3

(i) $Fe(CO)_5 \quad Ru_3(CO)_{12} \xrightarrow[\text{Sealed tube}]{110\,^\circ C} ?$

(ii) $12\,[Et_3NH][HFe_3(CO)_{11}] \quad 18\,HCl \quad ?$

(iii) $[Mn(CO)_3(NO)(PPh_3)] \quad PPh_3 \quad ?$

(d) Write a plausible chemical reaction for the reactant $Co_2(CO)_8$ and $AlBr_3$. Furnish structure of the product and give reason for the course of the reaction. 4

UNIT—V

9. *(a)* Give an account of structural distortion features associated with $T \rightleftharpoons R$ state transformation during dioxygen binding by hemoglobin. 5

(b) Discuss the active site structure of Rieske protein. Comment on its magnetic behaviour in reduced and oxidized state. 4

(c) Furnish an account of $[Mn_4]$-cluster in PS-II. Explain how the changes in electronic state occur during e-transfer process. 5

10. *(a)* Give the composition of mineral core of ferritin. Explain its active site structure and its role in biological system. 5

(b) Discuss 'trigger effect' in the context of dioxygen binding by hemoglobin. 4

(c) What is HiPIP? Discuss the oxidation levels associated with its e-transfer role. 5

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