

2015

CHEMISTRY

( Major )

Paper : 5.4

( Inorganic Chemistry )

Full Marks : 60

Time : 3 hours

*The figures in the margin indicate full marks for the questions*

1. Choose the correct answer from the following : 1×5=5

(a) The point group symmetry of  $\text{PCl}_3$  is

(i)  $D_{3h}$

(ii)  $C_{3v}$

(iii)  $D_3$

(iv)  $C_{3h}$

(b) Number of  $C_4$  rotation axes present in the  $O_h$  point group is

(i) 2

(ii) 3

(iii) 6

(iv) None of the above

(c) In biological systems, the metal ion involved in dioxygen transport besides Fe is

(i) Co

(ii) Zn

(iii) Mg

(iv) Cu

(d) Which of the following organometallic compounds is the strongest base?

(i)  $(\text{CH}_3)_2\text{CuLi}$

(ii)  $\text{CH}_3\text{Li}$

(iii)  $\text{CH}_3\text{ZnBr}$

(iv)  $\text{CH}_3\text{MgBr}$

(e) Which of the following is the correct order of ligand strength?

(i)  $\text{H}_2\text{O} < \text{ox} < \text{NH}_3 < \text{NCS}^-$

(ii)  $\text{NCS}^- < \text{H}_2\text{O} < \text{ox} < \text{NH}_3$

(iii)  $\text{ox}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{NH}_3$

(iv)  $\text{NCS}^- < \text{NH}_3 < \text{H}_2\text{O} < \text{ox}^{2-}$

2. Answer the following very short-type questions : 2×5=10

(a) A given molecule is assigned with the point group  $D_{3h}$ . What information will it provide in terms of symmetry? 2

- (b) Explain why square-planar  $d^8$  complexes of  $Rh^+$ ,  $Ir^+$ ,  $Ni^{2+}$ ,  $Pd^{2+}$ ,  $Pt^{2+}$  and  $Au^{3+}$  are stable with  $16e^-$  configurations. 2
- (c) From the qualitative molecular orbital diagram, calculate the bond order of  $[Mo_2(HPO_4)_4]^{2-}$  and  $[Re_2Cl_4(PMe_2Ph)_4]^+$  ions. 2
- (d) Explain how the geometry of a complex affects the magnitude of crystal field splitting. 2
- (e) What are metalloenzymes? Name two such enzymes in which the active site is a  $Zn^{2+}$  ion. 1+1=2

3. Answer the following short-type questions (any three) : 5×3=15

- (a) What is crystal field stabilization energy (CFSE)?  $H_2O$  forms stable complexes with  $Co(II)$ , whereas  $NH_3$  does with  $Co(III)$  in octahedral ligand environment. Explain the fact with the help of CFSE. 1+4=5
- (b) What is meant by hapticity of ligands? Giving suitable example, show that the hapticity of a ligand varies from one organometallic species to another. 2+3=5

- (c) Write two methods of preparation of ferrocene. Describe various reactions of ferrocene which establish the aromatic character of its cyclopentadienyl rings.

2+3=5

- (d) What is the origin of paramagnetism in inorganic compounds? How is magnetic moment ( $\mu$ ) related to the number of unpaired electrons, if the magnetism is due solely to the electron spins?  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is more paramagnetic than  $[\text{Fe}(\text{CN})_6]^{3-}$ . Why?

1+2+2=5

- (e) Write a note on synthetic dioxygen carriers.

5

4. Answer the following essay-type questions (any three) :

10×3=30

- (a) What are symmetry elements and how do they form a point group? Why is a point group called so? Illustrate all possible symmetry elements of  $\text{Ni}(\text{CO})_4$  molecule with the help of a diagram.

4+1+5=10

- (b) Discuss the experimental evidences to establish that metal-ligand bonding in coordination complexes is not purely electrostatic in nature as is assumed in crystal field theory.

10

- (c) Draw the molecular orbital energy-level diagram for the  $\pi$  system of octahedral complexes with (i)  $\pi$  donor and (ii)  $\pi$  acceptor ligands. How will you correlate the spectrochemical series with the  $\pi$ -bonding ability of ligands?  $3+3+4=10$
- (d) What is Wilkinson's catalyst? Discuss the mechanism of alkene hydrogenation catalyzed by Wilkinson's catalyst. Name the fundamental chemical processes occurring in each of the steps of the catalytic process.  $1+5+4=10$
- (e) Explain the terms 'cooperative effect' and 'Bohr effect'. What explanation is offered for the cooperativity effect in hemoglobin?  $5+5=10$

\*\*\*