2016

CHEMISTRY

(Major)

Paper : 5.4

(Inorganic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

Objective-type questions (choose the correct option) : 1×5=5

1. The point-group symmetry of $P(C_6H_5)_3$ is

(a) D_{3h}

(b) C_3

(c) D_3

(d) C_{3v}

2. TEL is an/a

(a) ionic organometallic compound

(b) sigma-bonded organometallic compound

(c) electron-deficient organometallic compound

(d) None of the above

3. Vitamin B_{12} contains

(a) Zn

(b) Fe

(c) Co

(d) Mo

4. Which of the following statements is true about the octahedral complexes of Ni^{2+}?

(a) Both strong- and weak-field complexes are diamagnetic

(b) The strong-field complex is diamagnetic and the weak-field complex is paramagnetic

(Continued)

(c) The strong-field complex is paramagnetic and the weak-field complex is diamagnetic

(d) Both strong- and weak-field complexes are paramagnetic

5. $[Fe_2(CO)_9]$ is diamagnetic, because of

(a) the presence of one CO as a bridging ligand

(b) the metal-metal (Fe—Fe) bond in the molecule

(c) the presence of a monodentate CO ligand

(d) the oxidation state of iron is zero

Very short answer-type questions : 2×5=10

6. What are the symmetry point groups for the eclipsed and staggered forms of ferrocene? State which one between the two will have the centre of inversion (*i*) as one of the symmetry elements.

(Turn Over)

7. Do the following organometallic species obey the 18-electron rule?

   (a) $[Fe(CO)_5]$

   (b) $[Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$

8. What is the Cr—Cr bond order in the compound $Cr_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2$?

9. Iron(II) salts undergo oxidation in air but the cobalt(II) salts do not. Explain.

10. Predict the magnetic properties of the species $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$.

Short answer-type questions (any *three*) : 5×3=15

11. What are spinels? Why do some AB_2O_4 compounds having transition elements as A and/or B prefer the inverse spinel structure and some others the normal spinel structure? Predict the structure of the following spinels : 1+2+2=5

    Co_3O_4 and Fe_3O_4

12. What are organometallic compounds? Comment on the stability of the M—C bond in organometallic compounds. Explain giving suitable examples. 2+3=5

13. Give the methods of preparation of Zeise's salt and discuss its structure. For a given metal-ethylene complex, the IR stretching frequency of the C=C bond is found to be $1516\ cm^{-1}$ whereas the corresponding frequency for free C_2H_4 is observed at $1625\ cm^{-1}$. Explain. 3+2=5

14. What is the nature of the dioxygen binding site in haemoglobin? How do you conclude that the protein part of haemoglobin is also involved in the reversible binding of O_2? 5

15. The spin-only magnetic moments (μ) for $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ ions have been found to be 2·87 BM and 0 BM respectively. Using the μ values, predict the geometry of the complex ions and also comment on the hybridization of Ni^{2+} ion in each case. 3+2=5

Essay-type questions (any *three*) : 10×3=30

16. What are symmetry elements and symmetry operations? Illustrate the improper rotation operation S_4 with the help of a diagram. Discuss how both tetrahedral and octahedral geometries may be stated to have cubic symmetry. Take help of diagrams as appropriate. 3+2+5=10

17. Discuss the importance and shortcomings of crystal-field theory. Does this theory address the formation of metal-ligand bonds? Use crystal-field theory to predict the electronic spectrum of $[Ti(H_2O)_6]^{3+}$ and the magnetic moment of the species $[Co(SCN)_4]^{2-}$. 6+2+2=10

18. *(a)* Give the method of preparation for the binuclear species $[Re_2Cl_8]^{2-}$ and discuss its bonding giving an appropriate diagram. 5

(b) Comment on the organometallic compounds of Sn and describe their utilities. 5

19. Distinguish between homogeneous and heterogeneous catalyses. Discuss the catalytic cycle of hydroformylation of alkenes by a cobalt carbonyl catalyst. An increase in CO partial pressure above a certain threshold decreases the rate of the cobalt-catalyzed hydroformylation of 1-pentene. Suggest an interpretation of this observation. 1+6+3=10

20. Write short notes on any *two* of the following topics : 5×2=10

(a) Ziegler-Natta catalysts

(b) Molecular-orbital theory in coordination chemistry

(c) Role of metal ions in biology

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