

MAY 2015

P/ID 40128/PCHH

Time : Three hours

Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

1. What is fluxional behaviour?
2. What is carbonylation reaction? Give example.
3. The 17 electron species $\text{Mn}(\text{CO})_5$ dimerises forming $\text{Mn}_2(\text{CO})_{10}$ but the 17 electron species $\text{V}(\text{CO})_6$ does not dimerise. Why?
4. Sketch various vibrational modes of CO_2 .
5. Explain why d-d transitions are considered to be symmetry forbidden transitions?
6. Explain why nuclei with $I = \frac{1}{2}$ do not have quadrupole moment.
7. What is meant by Doppler effect?
8. The ^{19}F NMR spectrum of IF_5 contains only a single resonance at room temperature. Explain.

9. Photoelectrons ejected from N_2 with He(I) radiation had kinetic energy of 5.63 eV. What are their ionisation energy? Wave length of He(I) radiation is 58.43 nm.
10. EPR spectra are generally recorded in the derivative mode. Why?

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

11. (a) Identify the products in the following reactions
- (i) $W(CO)_6 + LiPh \longrightarrow$
- (ii) $Ti(NR_2)_4 + 4CS_2 \longrightarrow$
- (iii) $RuCl_2(PPh_3)_2 + H_2 + Et_3N \longrightarrow$
- (iv) $Mn_2(CO)_{10} + H_2 \xrightarrow[200 \text{ atm}]{200^\circ C}$
- (v) $(\eta^5 - Cp)_2Fe + CH_3COCl \longrightarrow$
- (vi) $CrCl_3 + Al + 6CO \xrightarrow{h\nu}$
- (vii) $[Fe(CN)_5NO]^{2-} + OH^- \longrightarrow$
- (viii) $[CP_2ReH] + CH_3Li \longrightarrow$

(8 × 2½ = 20)

Or

2 P/ID 40128/PCHH

(b) (i) Write the mechanism of hydroformylation of propene catalysed by $\text{HRh}(\text{CO})(\text{PPh}_3)_2$. (10)

(ii) Explain the catalytic cycle involved in the production of acetic acid. (10)

12. (a) Write notes on : (4 × 5 = 20)

- (i) Magnetically non dilute system.
- (ii) Temperature independent paramagnetism.
- (iii) Charge transfer spectra.
- (iv) Rule of mutual exclusion.

Or

(b) (i) Describe the electronic spectra of $\text{trans-}[\text{Cr}(\text{en})_2\text{F}_2]^+$ and $[\text{Co}(\text{OX})_3]^{3-}$. (10)

(ii) Describe the effect of distortion and spin orbit coupling on the electronic spectra of complexes. (10)

13. (a) Discuss the Mössbauer spectra of

- (i) Sodium nitroprusside
- (ii) Spin paired Fe(II) and Fe(III) complexes.
- (iii) Hemoglobin and oxyhemoglobin
- (iv) SnF_4 . (4 × 5 = 20)

Or

3 P/ID 40128/PCHH

- (b) (i) Illustrate the use of NMR in providing information about fluxional behaviour of organometallic compounds. (10)
- (ii) Explain the effect of magnetic field on the NQR spectra with suitable examples. (10)
14. (a) (i) Discuss the theory and applications of Auger electron spectroscopy and compare with XPS. (10)
- (ii) Describe Kramers degeneracy rule and explain its important applications in structural elucidation. (10)

Or

- (b) (i) A one electron paramagnetic complex can have two charge distributions $\text{Cu}^{\text{II}} - \text{L}$ or $\text{Cu}^{\text{I}} - \text{L}^{(-)}$ [L = organic ligand]. How can they be distinguished by ESR spectroscopy?
- (ii) Sketch the ESR spectrum of $\text{VO}(\text{SO}_4)_2$ in ethanol at room temperature. The nuclear spin for $^{51}\text{V} = \frac{7}{2}$ and explain.
- (iii) Sketch the ESR spectrum of NH_2 radical and explain.
- (iv) Sketch the ESR spectrum of bis (salicylaldehyde) copper (II) complex and explain. (4 × 5 = 20)