

OCTOBER 2012

P/ID 40128/PCHH

Time : Three hours

Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

All questions carry equal marks.

1. Complete: $\text{Co}_2(\text{CO})_8 + \text{NO} \rightarrow ?$ (at 40°C)
2. Give the EAN for $[\text{Fe}(\text{CO})_2(\text{NO})_2]$
3. What is turnover number in catalysis?
4. What is a catalyst poison? Given an example.
5. Draw the symmetric and anti symmetric stretching modes of $(\text{CN})_2$.
6. Proton chemical shifts of CH_3I , SiH_3I , GeH_3I are 2.0, 3.4 and 3.5 ppm respectively, show an increasing trend. – Why?
7. What is the effect of Doppler broadening on Mossbauer spectra?
8. What is EFG?

9. What are Kramer's doublets?
10. Why does the PES spectrum of p orbital electron show two signals?

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

All questions carry equal marks.

11. (a) (i) Discuss the bonding in linear and bent metal nitrosyls with suitable orbital overlap diagrams. (10)
- (ii) What is fluxional behaviour? Explain with suitable example. (10)

Or

- (b) (i) Discuss the use of Wilkinson catalyst in the hydrogenation/process with a probable mechanistic pathway. (10)
- (ii) Write on polymerization catalysed by Zeigler-Natta catalyst. (10)
12. (a) (i) Identify the isomers of $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2]^+$ and explain as to how IR spectroscopy can be used to identify them. (5)
- (ii) Calculate the spin only magnetic moment of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. What is the standard used in the Gouy balance? (5)

- (iii) Discuss the use of Gouy balance in the determination of magnetic moment of a compound. (10)

Or

- (b) (i) Compare the electronic spectra of $[\text{Co}(\text{en})_3]^{2+}$ with the those of cis and trans- isomers of $[\text{Co}(\text{en})_2\text{F}_2]^+$ and comment on them. (10)
- (ii) For $[\text{Co}(\text{CO})\text{NO}(\text{PCL}_x\text{PPh}_{3-x})_2]$, the CO stretching frequency decreases as the number of x increases. – Explain. (10)
13. (a) (i) $\text{PF}_4\text{N}(\text{Me})_2$ shows a triplet of triplets in its ^{31}P spectrum at low temperature and at higher temperature it becomes a regular quintet. Explain. (10)
- (ii) Write on shift reagents and their use in NMR spectral measurements. (10)

Or

- (b) (i) Enumerate the conditions for recording the MB spectrum and discuss the need for a special unit on the x -axis of the spectral method. (10)
- (ii) How is NQR useful in the structural study of M-X bonds? Explain. (10)

14. (a) (i) Predict the esr spectrum of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ion and draw suitable energy level diagram for the transitions. (10)
- (ii) Predict the esr spectra of benzene radical anion and pyrazine anion with suitable explanation. (10)

Or

- (b) (i) State Koopman's theorem. Discuss the N1s XPS spectrum of $[\text{Co}(\text{en})_2(\text{NH}_3)_2](\text{NO}_3)_3$ and predict the ordering of N1s binding energies for the nitrogens. (10)
- (ii) With a suitable energy diagram explain the esr spectrum of bis(salicylaldiminato)copper (II). (10)
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