

DECEMBER 2015

P/ID 40128/PCHH

Time : Three hours

Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

1. Free benzene undergoes electro philic substitution where as coordinated benzene under goes nucleophilic substitution explain.
2. Explain insertion and elimination reactions.
3. Complexes such as $[Cr(CNR)_6]$ exists but not $[Cr(NCR)_6]$ why? Explain.
4. Write and explain Frank-Condon principle.
5. Potential energy curve is broader in the excited state that of in the ground state why? Explain.
6. List out the possible electronic transitions for a carbonyl group in terminal and bridging carbonyl compounds.
7. Find out the differences between singlet and triplet states.
8. Quadrupole splitting is observed in SnF_4 but not in $SnCl_4$. Explain the reason.
9. Write Kramers rule.
10. What is meant by isotropy and anisotropy in the crystals?

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

11. (a) (i) Discuss stereo chemistry and mechanism addition reaction of X-Y molecule in the complex.



- (ii) Complete the reactions with appropriate products :

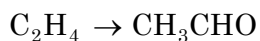


Or

- (b) Discuss with suitable examples the use of

(i) Wilkinson's Catalyst

(ii) Catalytic use of Pd in the reaction



(iii) $\text{CH}_3\text{OH} \xrightarrow{\text{Carbonylation}} \text{---}$

(iv) Explain carbonyl scrambling.

2 P/ID 40128/PCHH

12. (a) (i) The molar extinction coefficient in $(Ni(H_2O)_6)^{2+}$ complex is low explain.
- (ii) The molar absorptivity of singlet \rightarrow triplet transition is less-what is the reason?
- (iii) The anions ClO_4^- and SO_4^{2-} show very intense bands in uv region – explain.
- (iv) MnO_4^- and CrO_4^{2-} – show intense colours – explain.

Or

- (b) (i) Explain fundamental vibrations and selection rules applicable in assigning the vibrational characteristics to metal complexes. (8)
- (ii) Explain the significance of $3N - 6$ and $3N - 5$ rule. (6)
- (iii) Write selection rules which are necessary to observe Raman effect. (6)
13. (a) Discuss the NMR spectra of the following cases :
- (i) Solution of equimolar quantities of TiF_6^{2-} and TiF_4 in methanol.

- (ii) ^{31}P NMR spectrum of $\text{HPO}(\text{OH})_2$
- (iii) ^{31}P NMR spectrum of H_3PO_2 .

Or

- (b) (i) Explain efg with suitable diagrams.
 - (ii) Sketch NQR energy level diagrams with and without applied magnetic field for NH_3 ($I = 1$)
14. (a) (i) Calculate the g value if the methyl radical shows a EPR signal at 3290 G at 9230 MHz of the radiation.
- (ii) Write down some applications of ESR spectrum with example in structural elucidation of metal complexes.

Or

- (b) (i) Write the structure of DPPH
- (ii) What are Raman lines and how these are different from Releigh line?
- (iii) Write and explain Koopman theorem.
- (iv) Fine structure utility in PES spectrum.