

(Time: 3 Hours)

Total marks: 100

N.B. (1) All Questions are compulsory.

(2) Figures to the right indicate full marks.

(3) Use of logarithmic table/non-programmable calculator is allowed.

Q.1. Answer **Any Four** of the following:-

- A. Give any five limitations of valence bond theory as applied to metal-ligand bonding. 5
- B. Explain the splitting of d orbitals of the central metal atom in square planar crystal fields. 5
- C. How does crystal field splitting affect hydration energy & enthalpy of formation in transition metal complexes? 5
- D. Write a note on Jahn-Teller distortions with reference to Zn^{2+} in situation in a complex with octahedral geometry. 5
- E. What is Crystal Field Stabilization Energy (CFSE)? Calculate CFSE for d^3 & d^4 configurations in weak field octahedral complexes. 5
- F. Explain how Electron Spin Resonance (ESR) spectra help as an evidence for covalence in metal complexes. 5

Q.2. Answer **Any Four** of the following:-

- A. Draw a neat labeled molecular orbital diagram for Hexafluoro ferrate (III) ion; $[FeF_6]^{3-}$. 5
- B. Discuss the terms thermodynamic stability & kinetic stability. 5
- C. What is the role of 'size & charge of the central metal ion' on the stability of the complexes. 5
- D. Write a note on the Dissociative mechanism for Ligand Substitution Reactions. 5
- E. Explain 'Anation Reactions' with respect to metal complexes. 5
- F. Discuss 'Intra ligand electronic transitions' in coordination compounds. 5

Q.3 Answer **any four** of the following:

- A. Discuss the following two methods of synthesis of organometallic compounds of main group elements. 5
 - (a) Metal-metal exchange reaction
 - (b) oxidative-addition reaction
- B. Explain the following chemical reactions of organometallic compounds of main group elements. 5
 - (a) reactions with protic reagents.
 - (b) reactions with oxygen and halogens.
- C. (a) Mention the requirements of metal to be a good catalyst. 3
 - (b) Write note on σ bonded covalent organometallic compounds. 2
- D. Describe the methods of preparation of ferrocene. 5
- E. Explain: sulphonation and alkylation reactions of ferrocene. 5
- F. Explain the mechanism involved in hydrogenation of alkene using Wilkinson's catalyst. 5

Q.4 Answer **any four** of the following:

- A. Define metallurgy. Write a brief note on the hydrometallurgy. 5
- B. Explain the following terms by giving examples. 5
 - (a) mineral (b) gangue
- C. (a) Give an account of the various reactions that takes place in the following process with respect to extraction of copper by pyrometallurgy (any one) 3
 - (i) roasting (ii) smelting
 (b) Discuss the Gravity separation method used for concentrating ores. 2
- D. Explain: (a) Neon is used in safety devices. 3
 - (b) Helium and neon do not form clathrate compounds. 2
- E. Give the preparation of the xenon hexafluoride and discuss their structure. 5
- F. Discuss the role of sodium and potassium ions in biological systems. 5

Q.5 A.State whether following statements are true or false:- (**Any Five**) 5

- (a) Crystal field theory takes into account overlapping of metal and ligand orbitals.
- (b) Weak field ligands form high spin complexes.
- (c) 10 Dq value in tetrahedral complexes is higher than in square planar complexes.
- (d) CO is a strong field ligand.
- (e) ESR spectrum of $[\text{IrCl}_6]^{2-}$ is a straight line.
- (f) In octahedral complexes metal d orbitals are split into two levels.
- (g) In tetrahedral complexes none of the ligands directly approach metal d orbitals.
- (h) $[\text{Fe}(\text{CN})_6]^{3-}$ is a high spin complex.

B. Fill in the blanks with appropriate words given in the bracket:- (**Any Five**) 5
 (SN^1CB , 50, more, diamagnetic, dissociation constant, 45, allowed, decreases, less, paramagnetic, association constant, SN^2 , forbidden, increases)

- (a) On the basis of magnetic behavior, $[\text{Fe}(\text{CN})_6]^{3-}$ is _____.
- (b) Reverse of stability constant is _____.
- (c) Complexes with chelate groups are _____ stable than those with unidentate ligands.
- (d) Base hydrolysis reaction with proton abstraction is supposed to take place by _____ mechanism.
- (e) Transitions which involve a change in the azimuthal quantum number are Laporte _____.
- (f) Number of microstates in d^2 configuration is _____.
- (g) Stability of complexes _____ with π bonding capacity of the ligands.

(C) Select and write the appropriate answers:

(Attempt **any five**)

- (a) In metathesis, organometallic compound when treated with a binary halide, exchange of a formal Carbanion R^- with a _____ takes place.
 (i) halide ion (ii) carbon (iii) metal
- (b) The metal hydrogen exchange reactions are called as _____ reactions.
 (i) metallation (ii) transmetallation (iii) methylene insertion
- (c) metal or nonmetal halides when treated with _____ under suitable conditions, methylene insertion takes place in M-Cl bond.
 (i) diazomethane (ii) alkyl group (iii) none of the above
- (d) During nitration ferrocene undergoes _____.
 (i) reduction (ii) substitution (iii) oxidation
- (e) Condensation of ferrocene rings with formaldehyde and amine is called _____ reaction.
 (i) hydrolysis (ii) alkylation (iii) Mannich
- (f) Ferrocene obeys _____ rule.
 (i) Pauli's (ii) Hund's (iii) 18 electron
- (g) When the reactants and catalyst are in the same phase, catalysis is referred as _____.
 (i) heterogeneous (ii) substitution (iii) homogeneous
- (h) A catalyst influences the rate of a Chemical reaction but it normally _____ the equilibrium of the reaction.
 (i) alters (ii) affects on (iii) does not alter

(D) State whether the following statements are **true** or **false**:

(Attempt **any five**)

- (a) Copper matte contains sulphides of copper and iron.
- (b) Highly pure Si can be obtained by Zone refining method.
- (c) The gas evolved during roasting of sulphides ore is H_2S .
- (d) $XeOF_4$ has a square pyramid structure.
- (e) Steric number of XeO_2F_2 is 4.
- (f) The transition element present in hemoglobin is iron.
- (g) To maintain high concentration of K^+ ion inside the cell and high concentration of Na^+ outside the cell in the blood plasma an ion pump is developed across the cell membrane.
