

# Chemistry

## Paper-I

**Time Allowed: Three Hours**

**Maximum Marks: 300**

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*Note: Candidate should answer questions No. 1 and 5 which are compulsory and any **three** of the remaining questions, selecting at least **one** from each section.*

### SECTION - A

1. Answer any **three** of the following: 20×3=60
- (a) Give reasons why complexes of second and third row transition metals typically show a larger ligand field splitting than complexes of first row transition metals.
  - (b) Calculate the activation energy of a first order reaction the half life of which is 3000 minutes at 313 K and 600 minutes at 333 K.
  - (c) Write B.E.T. adsorption isotherm equation. How is the volume  $V_m$  (the volume adsorbed when the solid surface is completely covered by monolayers of the adsorbed gas) determined?
  - (d) Describe the X-ray diffraction technique for the determination of crystal structure.
2. (a) Explain the following: 6×5=30
- (i) Ferredoxins
  - (ii) Fixation of Nitrogen in Biological system
  - (iii) Chelate effect
  - (iv) Ion selective electrodes
  - (v) Lanthanide contraction

- (b) How did de-Broglie explain the wave nature of electron? 10
- (c) Give the important postulates of valence bond theory. Explain the formation of water molecule on the basis of VBT. 20
3. (a) What is the difference between a fuel cell and a battery? Describe the mechanism of electricity generation in: 20
- (i) Proton exchange membrane fuel cell (PEMFC) using proton conducting polymer membrane as the electrolyte
  - (ii) Solid oxide fuel cell (SOFC) using yttria-stabilized zirconia (YSZ) as the electrolyte.
- (b) Derive Clausius-Clapeyron equation for a system consisting of liquid in equilibrium with vapour. Give its applications. 20
- (c) State and explain the law of photochemical equivalence in the case of  $H_2 + Cl_2$  and  $H_2 + Br_2$  in gaseous phase. 20
4. (a) (i) Draw the shapes of s, p and d orbitals. Show their directional characteristics. 10
- (ii) With the help of an appropriate diagram, discuss the structure of electrode/ electrolyte interface. 10
- (b) What are crystal imperfections? Compare Schottky defects and Frenkel defects. 20
- (c) The standard enthalpy of combustion of crystalline benzoic acid to  $CO_2$  and  $H_2O$  is -3228.9 kJ per mole at 25 °C. The standard enthalpy of formation of  $CO_2$  (g) and  $H_2O$  (l) are -393.51 kJ and -285.84 kJ per mole respectively. Calculate  $\Delta H^\circ$  and  $\Delta E^\circ$  for the formation of crystalline benzoic acid from its elements at 25 °C. 20

## SECTION – B

5. Answer any three of the following 20×3=60
- (a) Explain fluorescence and phosphorescence using the Jablonski diagram.
  - (b) What do you understand by the isomerism of co-ordination compounds? Explain linkage isomerism with example.
  - (c) Discuss the structures of NaCl and TiO<sub>2</sub> (rutile)
  - (d) Discuss in details the kinetics of photochemical reactions of hydrogen with halogens.
6. (a) (i) Describe use of Born- Haber cycle to determine the lattice energy of ionic solids. 10
- (ii) What are the limitations of Arrhenius Theory of Dissociation? 10
- (b) How does the principle of 'maximum overlap' explain the stability of a chemical bond? Enumerate the essential conditions. 20
- (c) Draw molecular orbital diagram for the following molecules and compare bond order, bond length and magnetic properties: CN and CN<sup>-</sup>. Explain why the bonding in metal cyanides is between metal and carbon. 20
7. (a) Derive Bragg's equation and its use in crystal structure determination. 20
- (b) Describe Nernst Heat Theorem. How does Nernst Heat Theorem lead to the enunciation of the Third Law of Thermodynamics? Explain how the absolute entropy of a substance is determined with the help of Third Law of Thermodynamics. 20
- (c) Discuss the structural features of haemoglobin and myoglobin in detail and discuss their role in biological system. 20

8. (a) (i) A sample of gaseous HI was irradiated by light of wavelength 253.7 nm when 307J of energy was found to decompose  $1.30 \times 10^{-3}$ , calculate quantum yield for the dissociation of HI. 10
- (ii) Why value of  $C_p$  is greater than  $C_v$ ? Derive the relation between  $C_p$  and  $C_v$  for n moles of an ideal gas. 10
- (b) Discuss in brief the Debye Huckel Theory of strong electrolyte and its quantitative treatment. 20
- (c) (i) Derive the Gibbs-Helmoltz equation and explain the terms in it. 10
- (ii)  $\text{Co}(\text{CO})_4$  and  $\text{Mn}(\text{CO})_5$  dimerize but  $\text{V}(\text{CO})_6$  does not. Explain. 10