MCSCCE
(Mains)
Previous Year Paper
Chemistry Paper-I 2016

Chemistry
Paper-I

Time Allowed: Three Hours **Maximum Marks: 300**

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) Ferrodoxins

   (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 Schotty 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 ΔH° and ΔE° 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_2 (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^-. 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 1.30×10^{-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) $Co(CO)_4$ and $Mn(CO)_5$ dimerize but $V(CO)_6$ does not. Explain. 10