

CHEMISTRY**Paper – I****Time Allowed : Three Hours****Maximum Marks : 200****Question Paper Specific Instructions**

Please read each of the following instructions carefully before attempting questions :

There are **EIGHT** questions in all, out of which **FIVE** are to be attempted.

Questions no. **1** and **5** are **compulsory**. Out of the remaining **SIX** questions, **THREE** are to be attempted selecting at least **ONE** question from each of the two Sections A and B.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly. Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it.

Answers must be written in **ENGLISH** only.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary and indicate the same clearly.

Neat sketches may be drawn, wherever required.

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$c = 3 \times 10^8 \text{ ms}^{-1}$$

$$N_A = 6.023 \times 10^{23}$$

$$k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

$$\pi = 3.14$$

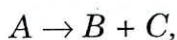
$$F = 96500 \text{ C}$$

$$1 \text{ atm} = 101325 \text{ Pa}$$

SECTION A

- Q1.** (a) NaCl (molecular weight : 58.5) consists of a face-centred cubic lattice of Na^+ ions interlocked with a similar lattice of Cl^- ions and has a density of 2.17 g/cm^3 .
- (i) Draw the unit cell structure of NaCl.
 - (ii) Calculate the number of Na^+ and Cl^- ions that are present in a unit cell.
 - (iii) Calculate the volume of the unit cell.
 - (iv) The first-order reflection from the d_{100} planes of NaCl occurs at 5.9° . Calculate the wavelength of X-ray. 5+5+5+5=20

- (b) For the reaction



the following data were obtained :

t in sec	0	900	1800
conc. of A	50.8	19.7	7.62

Prove that the reaction is of the first order. 5

- (c) What would be the value of the principal quantum number, if an electron in a hydrogen atom was in the orbital of energy $-0.242 \times 10^{-18} \text{ J}$?
Given : $k = 2.179 \times 10^{-18} \text{ J}$. 5
- (d) Calculate the work done when 1 mole of He expands isothermally and reversibly from a volume of 1 litre to a volume of 10 litres at 25°C . 10

- Q2.** (a) If uncertainty in position is written as Δx and in momentum as Δp , then Heisenberg Uncertainty principle is $\Delta p \Delta x \geq h/4\pi$. If the position of an electron is known to within 10^{-12} m , what is the uncertainty in its momentum ? Given $h = 6.626 \times 10^{-34} \text{ Js}$ and $\pi = 3.14$. 5

- (b) One mole of water is vapourised reversibly at 100°C and 1 atm.



The heat of vapourisation of water is 9720 cal/mol . Calculate W , ΔE , ΔH and ΔS . 20

- (c) How is molecular partition function defined ? What is the physical significance of this property ? Discuss the effect of temperature on the molecular partition function. 10
- (d) Write brief notes on n-type and p-type semiconductors. 5

- Q3.** (a) Calculate the mean activity coefficient at 25°C of (i) 0.01 molal solution of LiCl, and (ii) 0.001 molal solution of BaCl₂. Given : $A = 0.509$ for water at 25°C. 10
- (b) Consider the Arrhenius equation. Derive the expression relating rate-constant, energy of activation and frequency factor, in the form of a straight line equation. 10
- (c) According to Van der Waals' equation, calculate the pressure required to confine one mole of CO₂ in a volume of 1 litre at 0°C. 10

Given : $R = 0.082$ litre atm
 $a = 3.60$ atm litre²/mol²
 $b = 4.27 \times 10^{-2}$ litre/mol

- (d) For the photochemical reaction



it is found that 1.00×10^{-5} mole of B is formed, as a result of the absorption of 6.00×10^7 ergs at 3600 Å. Calculate the quantum yield. 10

Given : Avogadro number 6.02×10^{23}
 Planck's constant 6.626×10^{-34} J-sec
 Velocity of light 3×10^{10} cm/sec

- Q4.** (a) Considering molecular-orbital energy level diagram, justify the O – O bond distances in O₂, O₂⁻ and O₂²⁻ as 1.21, 1.28 and 1.49 Å, respectively. 10
- (b) Draw and discuss the pressure-temperature diagram for H₂O. Apply the phase rule to the diagram. 10
- (c) Calculate the equilibrium constant for the following reaction at 25°C : 10



Given at 25°C :

$$E^0(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V and}$$

$$E^0(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$$

(d) Consider the reaction :



Derive the expression relating K_p and degree of dissociation α .

Given : At 250°C and 1 atm, K_p for the above reaction is 1.78.

Calculate α .

8+2=10

SECTION B

- Q5.** (a) Draw the structures and d-orbital splitting diagrams of (i) $[\text{NiCl}_4]^{2-}$, and (ii) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$. Calculate their crystal-field stabilization energy (CFSE) and spin-only magnetic moment values. 10+10=20
- (b) Draw the structures of the proteins (i) de-oxy myoglobin, and (ii) oxidised form of cytochrome-c. Comment on the properties of de-oxy myoglobin. 5+5+10=20
- Q6.** (a) Explain the structure and bonding in $[\text{Cr}(\text{CO})_6]$ and $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$, showing metal-ligand orbital interactions, both σ -type and π -type. In each case, show the counting of valence-electrons around the metal. 10+10=20
- (b) Consider CO insertion reaction in $[\text{Rh}(\text{PPh}_3)_2(\text{CO})_2(\text{CH}_2\text{CH}_2\text{R})]$. Draw the structure of the reactant and the product. Also identify the oxidation state of Rh in the reactant and in the product, showing valence-electron count around Rh in each case. 15
- (c) The Δ_0 value for $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ is $21,000 \text{ cm}^{-1}$. For this metal ion, the value of pairing energy is $28,000 \text{ cm}^{-1}$. Decide the spin-state of the complex. Briefly justify your answer. 5
- Q7.** (a) Draw the solid-state structure of $\text{Co}_2(\text{CO})_8$ and show valence-electron count around Co atom. 10
- (b) Explain the term 'over potential'. Discuss the application of over potential in (i) electro-deposition of metals from solutions, and (ii) corrosion of metals. 15
- (c) Consider the complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. Draw the structures of possible geometrical isomers. 5
- (d) Draw the structure of ferrocene. Showing the number of electrons contributed, count the number of valence-electrons around the Fe atom. 10

- Q8. (a) Comment on the consequences of 'Lanthanide Contraction'. 10
- (b) Derive the B.E.T. equation for adsorption on a solid surface. How can the surface area be determined with the help of B.E.T. equation? 10
- (c) Discuss the merits and demerits of liquid hydrogen fluoride as a non-aqueous solvent. Give the chemical reactions which take place in this solvent. 10
- (d) What do you understand by quantum yield? Discuss high and low values of quantum yield by taking suitable examples. 10