

**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  $\text{Na}^+$  ions interlocked with a similar lattice of  $\text{Cl}^-$  ions and has a density of  $2.17 \text{ g/cm}^3$ .
- (i) Draw the unit cell structure of NaCl.
  - (ii) Calculate the number of  $\text{Na}^+$  and  $\text{Cl}^-$  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  $5.9^\circ$ . 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 :  $h = 2.179 \times 10^{-18} \text{ J}$ . 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  $25^\circ\text{C}$ . 10

- Q2.** (a) If uncertainty in position is written as  $\Delta x$  and in momentum as  $\Delta p$ , then Heisenberg Uncertainty principle is  $\Delta p \Delta x \geq h/4\pi$ . If the position of an electron is known to within  $10^{-12} \text{ m}$ , 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  $100^\circ\text{C}$  and 1 atm.



The heat of vapourisation of water is  $9720 \text{ cal/mol}$ . Calculate  $W$ ,  $\Delta E$ ,  $\Delta H$  and  $\Delta S$ . 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 BaCl<sub>2</sub>. 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 CO<sub>2</sub> in a volume of 1 litre at 0°C. 10

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

(d) For the photochemical reaction



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

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

**Q4.** (a) Considering molecular-orbital energy level diagram, justify the O – O bond distances in O<sub>2</sub>, O<sub>2</sub><sup>-</sup> and O<sub>2</sub><sup>2-</sup> as 1.21, 1.28 and 1.49 Å, respectively. 10

(b) Draw and discuss the pressure-temperature diagram for H<sub>2</sub>O. Apply the phase rule to the diagram. 10

(c) Calculate the equilibrium constant for the following reaction at 25°C :  
$$\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$$
 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  $\alpha$ .

Given : At  $250^\circ\text{C}$  and 1 atm,  $K_p$  for the above reaction is 1.78.

Calculate  $\alpha$ .

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  $\sigma$ -type and  $\pi$ -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  $\Delta_0$  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