I.F.S. EXAM-(M)2017

FSI-P-CHM

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.

$h = 6{\cdot}626 \times 10^{-34}$ Js | $k_B = 1{\cdot}38 \times 10^{-23}$ JK^{-1}

$R = 8{\cdot}314$ JK^{-1} mol^{-1} | $\pi = 3{\cdot}14$

$c = 3 \times 10^{8}$ ms^{-1} | $F = 96500$ C

$N_A = 6{\cdot}023 \times 10^{23}$ | 1 atm = 101325 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

$$A \rightarrow B + C,$$

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 $-0{\cdot}242 \times 10^{-18}$ J ? Given : $k = 2{\cdot}179 \times 10^{-18}$ 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 $h = 6{\cdot}626 \times 10^{-34}$ Js and $\pi = 3{\cdot}14$. *5*

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

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

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 $BaCl_2$. Given : $A = 0{\cdot}509$ 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_2 in a volume of 1 litre at 0°C. *10*

Given : $R = 0{\cdot}082$ litre atm

$a = 3{\cdot}60$ atm litre^2/mol^2

$b = 4{\cdot}27 \times 10^{-2}$ litre/mol

(d) For the photochemical reaction

$$A \rightarrow B,$$

it is found that $1{\cdot}00 \times 10^{-5}$ mole of B is formed, as a result of the absorption of $6{\cdot}00 \times 10^{7}$ ergs at 3600 Å. Calculate the quantum yield. *10*

Given : Avogadro number $6{\cdot}02 \times 10^{23}$

Planck's constant $6{\cdot}626 \times 10^{-34}$ 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 O_2, O_2^- and O_2^{2-} as 1·21, 1·28 and 1·49 Å, respectively. *10*

(b) Draw and discuss the pressure-temperature diagram for H_2O. Apply the phase rule to the diagram. *10*

(c) Calculate the equilibrium constant for the following reaction at 25°C :

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$ *10*

Given at 25°C :

$E^0(Zn^{2+}/Zn) = -\,0{\cdot}76$ V and

$E^0(Cu^{2+}/Cu) = 0{\cdot}34$ V

(d) Consider the reaction :

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

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) $[NiCl_4]^{2-}$, and (ii) $[Co(H_2O)_6]^{3+}$. 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 $[Cr(CO)_6]$ and $[PtCl_3(C_2H_4)]^-$, 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 $[Rh(PPh_3)_2(CO)_2(CH_2CH_2R)]$. 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 $[Mn(H_2O)_6]^{3+}$ is 21,000 cm^{-1}. For this metal ion, the value of pairing energy is 28,000 cm^{-1}. Decide the spin-state of the complex. Briefly justify your answer. *5*

Q7. (a) Draw the solid-state structure of $Co_2(CO)_8$ 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 $[Co(NH_3)_4Cl_2]^+$. 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*