# I.P.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.

$$\begin{split} h &= 6 \cdot 626 \times 10^{-34} \ Js & k_B = 1 \cdot 38 \times 10^{-23} \ JK^{-1} \\ R &= 8 \cdot 314 \ JK^{-1} \ mol^{-1} & \pi = 3 \cdot 14 \\ c &= 3 \times 10^8 \ ms^{-1} & F = 96500 \ C \\ N_A &= 6 \cdot 023 \times 10^{23} & 1 \ atm = 101325 \ Pa \end{split}$$

#### SECTION A

- Q1. (a) NaCl (molecular weight: 58·5) consists of a face-centred cubic lattice of Na<sup>+</sup> ions interlocked with a similar lattice of Cl<sup>-</sup> ions and has a density of 2·17 g/cm<sup>3</sup>.
  - (i) Draw the unit cell structure of NaCl.
  - (ii) Calculate the number of Na<sup>+</sup> and Cl<sup>-</sup> 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

$$A \rightarrow B + C$$

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.

- (c) What would be the value of the principal quantum number, if an electron in a hydrogen atom was in the orbital of energy  $-0.242 \times 10^{-18}$  J?

  Given:  $k = 2.179 \times 10^{-18}$  J.
- (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  $\Delta x$  and in momentum as  $\Delta p$ , then Heisenberg Uncertainty principle is  $\Delta p$   $\Delta x \ge h/4\pi$ . If the position of an electron is known to within  $10^{-12}$  m, what is the uncertainty in its momentum? Given  $h = 6.626 \times 10^{-34}$  Js and  $\pi = 3.14$ .
  - (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,  $\Delta E$ ,  $\Delta H$  and  $\Delta S$ .

5

		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 ${\rm CO_2}$ in a volume of 1 litre at 0°C.	10
		Given : $R = 0.082$ litre atm $a = 3.60 \text{ atm litre}^2/\text{mol}^2$ $b = 4.27 \times 10^{-2} \text{ litre/mol}$	
	(d)	For the photochemical reaction $A  o B$ ,	
		it is found that $1\cdot00\times10^{-5}$ mole of $B$ is formed, as a result of the absorption of $6\cdot00\times10^{7}$ ergs at 3600 Å. Calculate the quantum yield. Given : Avogadro number $6\cdot02\times10^{23}$ Planck's constant $6\cdot626\times10^{-34}$ J-sec Velocity of light $3\times10^{10}$ cm/sec	10
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 $\mathrm{H}_2\mathrm{O}$ . 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 $ Given at 25°C: $ E^0(Zn^{2+}/Zn) = -0.76 \text{ V and } $ $ E^0(Cu^{2+}/Cu) = 0.34 \text{ V} $	10
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How is molecular partition function defined? What is the physical

(c)

### (d) Consider the reaction:

$$\operatorname{PCl}_{5}\left(\mathbf{g}\right) \rightleftharpoons \operatorname{PCl}_{3}\left(\mathbf{g}\right) + \operatorname{Cl}_{2}\left(\mathbf{g}\right)$$

Derive the expression relating  $K_p$  and degree of dissociation  $\alpha$ .

Given : At 250°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) $[NiCl_4]^{2-}$ , 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 $\sigma$ -type and $\pi$ -type. In each case, show the counting of valence-electrons around the metal. $10+10=0$	=20
	(b)	Consider CO insertion reaction in [Rh(PPh <sub>3</sub> ) <sub>2</sub> (CO) <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> 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 $[Mn(H_2O)_6]^{3+}$ is 21,000 cm <sup>-1</sup> . For this metal ion, the value of pairing energy is 28,000 cm <sup>-1</sup> . Decide the spin-state of the complex. Briefly justify your answer.	5
	2		
Q7.	(a)	Draw the solid-state structure of $\mathrm{Co_2(CO)_8}$ 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.

5

10

<b>Q8.</b>	(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	10