# CHEMISTRY <br> 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.

$$
\begin{array}{ll}
\mathrm{h}=6.626 \times 10^{-34} \mathrm{Js} & \mathrm{k}_{\mathrm{B}}=1.38 \times 10^{-23} \mathrm{JK}^{-1} \\
\mathrm{R}=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1} & \pi=3 \cdot 14 \\
\mathrm{c}=3 \times 10^{8} \mathrm{~ms}^{-1} & \mathrm{~F}=96500 \mathrm{C} \\
\mathrm{~N}_{\mathrm{A}}=6.023 \times 10^{23} & 1 \mathrm{~atm}=101325 \mathrm{~Pa}
\end{array}
$$

## SECTION A

Q1. (a) NaCl (molecular weight : 58.5) consists of a face-centred cubic lattice of $\mathrm{Na}^{+}$ions interlocked with a similar lattice of $\mathrm{Cl}^{-}$ions and has a density of $2.17 \mathrm{~g} / \mathrm{cm}^{3}$.
(i) Draw the unit cell structure of NaCl .
(ii) Calculate the number of $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$ions that are present in a unit cell.
(iii) Calculate the volume of the unit cell.
(iv) The first-order reflection from the $\mathrm{d}_{100}$ planes of NaCl occurs at $5 \cdot 9^{\circ}$. Calculate the wavelength of X-ray.
(b) For the reaction

$$
A \rightarrow B+C
$$

the following data were obtained:

| $t$ in sec | 0 | 900 | 1800 |
| :--- | :--- | :--- | :--- |
| conc. of $A$ | $50 \cdot 8$ | $19 \cdot 7$ | $7 \cdot 62$ |

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 $-0.242 \times 10^{-18} \mathrm{~J}$ ?
Given : $k=2.179 \times 10^{-18} \mathrm{~J}$.
(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 $25^{\circ} \mathrm{C}$.

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 $10^{-12} \mathrm{~m}$, what is the uncertainty in its momentum ? Given $h=6 \cdot 626 \times 10^{-34} \mathrm{Js}$ and $\pi=3 \cdot 14$.
(b) One mole of water is vapourised reversibly at $100^{\circ} \mathrm{C}$ and 1 atm .

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

The heat of vapourisation of water is $9720 \mathrm{cal} / \mathrm{mol}$. Calculate $W, \Delta E, \Delta H$ and $\Delta S$.
(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.
(d) Write brief notes on n-type and p-type semiconductors.

Q3. (a) Calculate the mean activity coefficient at $25^{\circ} \mathrm{C}$ of (i) 0.01 molal solution of LiCl , and (ii) 0.001 molal solution of $\mathrm{BaCl}_{2}$. Given : $A=0.509$ for water at $25^{\circ} \mathrm{C}$.
(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.
(c) According to Van der Waals' equation, calculate the pressure required to confine one mole of $\mathrm{CO}_{2}$ in a volume of 1 litre at $0^{\circ} \mathrm{C}$.

$$
10
$$

Given: $\quad R=0.082$ litre atm
$a=3.60 \mathrm{~atm}$ litre $2 / \mathrm{mol}^{2}$
$b=4.27 \times 10^{-2}$ litre $/ \mathrm{mol}$
(d) For the photochemical reaction

$$
A \rightarrow B,
$$

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 $3600 \AA$. Calculate the quantum yield.
Given: Avogadro number $6.02 \times 10^{23}$
Planck's constant $6.626 \times 10^{-34} \mathrm{~J}$-sec
Velocity of light $3 \times 10^{10} \mathrm{~cm} / \mathrm{sec}$
Q4. (a) Considering molecular-orbital energy level diagram, justify the $\mathrm{O}-\mathrm{O}$ bond distances in $\mathrm{O}_{2}, \mathrm{O}_{2}^{-}$and $\mathrm{O}_{2}^{2-}$ as $1 \cdot 21,1.28$ and $1.49 \AA$, respectively. 10
(b) Draw and discuss the pressure-temperature diagram for $\mathrm{H}_{2} \mathrm{O}$. Apply the phase rule to the diagram.
(c) Calculate the equilibrium constant for the following reaction at $25^{\circ} \mathrm{C}$ :

$$
\begin{equation*}
\mathrm{Zn}+\mathrm{Cu}^{2+} \longrightarrow \mathrm{Zn}^{2+}+\mathrm{Cu} \tag{10}
\end{equation*}
$$

Given at $25^{\circ} \mathrm{C}$ :

$$
\begin{aligned}
& E^{0}\left(\mathrm{Zn}^{2+} / \mathrm{Zn}\right)=-0.76 \mathrm{~V} \text { and } \\
& E^{0}\left(\mathrm{Cu}^{2+} / \mathrm{Cu}\right)=0.34 \mathrm{~V}
\end{aligned}
$$

(d) Consider the reaction :

$$
\mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})
$$

Derive the expression relating $K_{p}$ and degree of dissociation $\alpha$. Given : At $250^{\circ} \mathrm{C}$ and $1 \mathrm{~atm}, K_{p}$ for the above reaction is 1.78 . Calculate $\alpha$.

## SECTION B

Q5. (a) Draw the structures and d-orbital splitting diagrams of (i) $\left[\mathrm{NiCl}_{4}\right]^{2-}$, and (ii) $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$. 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 $\left[\mathrm{Cr}(\mathrm{CO})_{6}\right]$ and $\left[\mathrm{PtCl}_{3}\left(\mathrm{C}_{2} \mathrm{H}_{4}\right)\right]^{-}$, 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 $\left[\mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}\left(\mathrm{CO}_{2}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{R}\right)\right]\right.$. 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.
(c) The $\Delta_{0}$ value for $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ is $21,000 \mathrm{~cm}^{-1}$. For this metal ion, the value of pairing energy is $28,000 \mathrm{~cm}^{-1}$. Decide the spin-state of the complex. Briefly justify your answer.

Q7. (a) Draw the solid-state structure of $\mathrm{Co}_{2}(\mathrm{CO})_{8}$ and show valence-electron count around Co atom.
(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.
(c) Consider the complex $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}_{2}\right]^{+}$. Draw the structures of possible geometrical isomers.
(d) Draw the structure of ferrocene. Showing the number of electrons contributed, count the number of valence-electrons around the Fe atom.

Q8. (a) Comment on the consequences of 'Lanthanide Contraction'.
(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?
(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.
(d) What do you understand by quantum yield ? Discuss high and low values of quantum yield by taking suitable examples.

