QP Code : 20444

(Time : 2½ Hours) **(Total Marks : 75**

N.B : 1. **All** questions are **compulsory**.
2. **Figures** to the **right** indicate **full** marks.
3. Use of **logtable** / **non-programmable calculator** is **allowed**.
4. **Answer** to **both sections** should be written in separate **answer books** and submitted separately.

Physical Constants :

$N_A = 6.022 \times 10^{23}$ mo^{-1}	$h = 6.626 \times 10^{-34}$Js
F = 96500 C	$C = 3 \times 108$ ms^{-1}
R = 8.315 Jk^{-1} mol^{-1}	F = 19 a.m.u.
H = 1 a.m.u.	O = 16 a.m.u.
C = 12 am	1 amu = 1.66×10^{-27} kg

Section - I

1. Attempt **any three** of the following :

(A) Define Dipole moment. How is it used to : **5**
(i) identify cis and trans isomers.
(ii) determine geometry of CO_2 and SO_2.

(B) The frequency of separation between rotational lines of CO is $19.2 \times 10^2 m^{-1}$. Calculate the rotational constant and equilibrium internuclear distance for CO. **5**

(C) Explain the Rule of mutual exclusion using suitable example. **5**

(D) For an anharmonic oscillator, show that the frequencies of fundamental, first and second overtone bands are approximately in the ratio of 1 : 2 : 3. **5**

(E) Explain the different modes of stretching and leading bending vibrations. **5**

(F) The force constant of H - F bond is 9.2×10^2 Nm^{-1}. Calculate the vibrational frequency of the molecule. **5**

2. Attempt **any three** of the following :

(A) Derive an expression for emf of electrolyte concentration cell without transference reversible to cation. **5**

(B) What is meant by liquid junction potential? How does it arise ? How is it eliminated ? **5**

(C) Derive Nernst equation for emf of galvanic cell. **5**

(D) Device and derive an expression for emf of electrolyte concentration cell with transference reversible to anion. **5**

(E) Define ionic strength. Calculate the ionic strength of a solution containing 0.1m $CaCl_2$ and 0.05m NaCl. **5**

(f) For the cell Pt, Cl_2(g) (20 bar) | NaCl aq sdn. | Cl_2(g) (40 bar), Pt **5**

(i) Identify the type of cell.

(ii) Write the electrode reactions.

(iii) Calculate the E_{cell} at 298 K.

3. (A) Answer the following : **4**

Say whether the following statement is true of false :

(a) Hononuclear diatomic molecules have zero dipole moment.

(b) The molecules of Carbon tetrachloride are microwave active.

(c) Water molecule has three degrees of vibrational freedom.

(d) When the wavelength of the scattered radiation is same as that of incident radiation, stokes lines are obtained in Raman spectra.

OR

(A) Choose the correct answer : **4**

(p) Raman spectra _____.

(i) visible (ii) microwave (iii) uv

(q) When _____, Rayleigh scattering is conserved.

(i) $\lambda s > \lambda i$ (ii) $\lambda s = \lambda i$ (iii) $\lambda s < \lambda i$

(r) Methane has _____ dipole moment.

(i) 1.6 (ii) Zero (iii) 4.0

(s) Bond between atoms of higher masses vibrate at _____ frequency than the bands between lighter atoms.

(i) lower (ii) higher (iii) ten times more

3. (B) Say whether the following statement is **true** of **false** : **4**

(a) Liquid junction potential is minimized by using salt bridge.

(b) For chemical cell $E°_{cell} = 0$.

(c) In concentration cell, the two half cells are made up of different electrodes.

(d) Oxidation takes place at anode in galvanic cells.

OR

(B) Choose the correct answer :

(p) Saturated solution of _____ is used to prepare salt bridge. **4**

(i) NaCl (ii) NH_4HO_3 (iii) $BaCl_2$

(q) The activity of $AlCl_3$ is given by _____.

(i) $27m^4\gamma^4$ (ii) $9m^4\gamma^4$ (iii) $8m^3\gamma^3$

(r) The relation between ionic strength μ and molality m for uni-univalent electrolyte is _____.

(i) $\mu = 2m$ (ii) $2\mu = m$ (iii) $\mu = m$

(s) Pt | Sn^{2+}, Sn^{4+} is _____ electrode.

(i) Redox (ii) Amalgam (iii) metal - metal ion

Section - II

4. Attempt **any three** of the following :

(A) Discuss the symmetry operations and assign the point group to BCl_3 molecule. **5**

(B) Explain C_{3V} and $C_{\infty V}$ point groups with a suitable example for each. **5**

(C) Explain the following symmetry elements with a suitable example for each. **5**

(a) Inversion centre, (b) Improper rotational axis.

(D) What is Walsh correlation diagram ? Draw a neat and labelled Walsh correlation diagram for linear and bent AH_2 type of molecule. **5**

(E) Draw a neat labelled molecular orbital diagram for H_2O molecule showing the distribution of electrons in various energy levels. Give its magnetic property. **5**

(F) Explain, the electrical properties of semiconductors and insulators on the basis of band theory. **5**

5. Attempt **any three** of the following :

(A) Prove that the packing density for face centered cubic (fcc) structure is 0.74. **5**

(B) For body centered cubic (bcc) structure, Calculate : **5**

(a) Number of atoms per unit cell (bcc)

(b) The lattice constant (a) if the atomic radius (r) is 124 pm.

(C)(a) Derive a relationship between lattice constant (a) and density of crystal material. **3**

(b) Calculate the density of a metal which crystallises in bcc structure with lattice constant 2.9×10^{-8}cm. Atomic weight of metal is 55.85 and Avogadro's number is 6.022×10^{23}. **2**

(D) Differentiate between Schottky defect and Frenkel defect. **5**

(E) Write a short note on Conventional superconductors. **5**

(F) Explain the terms : **5**

(a) Unit cell and lattice parameters.

(b) Ideal and Hard superconductors.

6. (A) Select and write the appropriate answer : **4**

(a) The order of energy of the molecular orbitals in triangular H_3^+ ion is _____.

(i) $3\sigma > 2\sigma = 1\sigma$ (ii) $3\sigma = 2\sigma > 1\sigma$ (iii) $3\sigma < 2\sigma = 1\sigma$

(b) Axis of symmetry present in H_2O molecule is _____.

(i) C_2 (ii) C_3 (iii) C_∞

(c) H_2 molecule belongs to _____ point group.

(i) $C_{\infty V}$ (ii) $D_{\infty h}$ (iii) C_{2h}

(d) When a pure crystal of germanium is doped with _____, p-type semiconductor is obtained.

(i) Ga (ii) As (iii) P

OR

(A) State whether the following statements are **true** or **false** : **4**

(p) The symmetry element identity is designated by symbol 'I'.

(q) On the basis of symmetry, the symbol 'e' represents a doubly degenerate orbital.

(r) BeH_2 molecule has linear geometry.

(s) The energy gap between the molecular orbitals increases as the number of overlapping atomic orbitals increases.

6. (B) Select and write the appropriate answer : **3**

(a) The number of atoms in simple cubic (sc) unit cell is _____.

(i) 1 (ii) 2 (iii) 4

(b) Point defect occurring due to presence of foreign atoms in crystal lattice is _____ defect.

(i) vacancy (ii) impurity (iii) interstitial (self)

(c) The number of five and six membered rings in C_{60} fullerene is _____ respectively.

(i) 4 and 5 (ii) 12 and 18 (iii) 12 and 20

OR

(B) State whether the following statement are **true** or **false** : **3**

(p) Lattice points signify the position of centre of particles and not the size.

(q) In silver halides, Schottky defect is predominant.

(r) High temperature super conductors require liquid helium for cooling.
