QP Code : **77104**

(2 ½ Hours) [ **Total Marks :75**

**N.B. :** (1) **All** questions are **compulsory**
(2) **Figures** to the **right** indicate **full** marks.
(3) Use of logarithmic table/ non-programmable calculator is allowed.
(4) Answers to both the sections should be written in separate answer books and tied together.

Physical Constants
$N=6.022 \times 10^{23}$
$k=1.38 \times 10^{-23} K^{-1}$
$F= 96500$ C
$R= 8.314$ J $mol^{-1}$ $K^{-1}$
$h= 6.626 \times 10^{-34}$ Js
$C= 3.0 \times 10^{8}$ $ms^{-1}$
$\pi = 3.142$

$$\frac{2.303\ RT}{F} = 0.0592 \text{ at } 298\ K$$

## SECTION -I

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

(A) (i) Define and explain the orgin of dipole moment. 2
(ii) Explain how dipole moment helps to identify ortho, meta and para isomers. 3

(B) (i) State and explain the rule of mutual exclusion with the help of $CO_2$ molecule 3
(ii) Mention the limitations of rotational spectra. 2

(C) What is meant by zero point energy? The force constant of HF bond is $970 Nm^{-1}$. Calculate the zero point energy. 5

(D) With respect to R-branch lines in vibrational rotational spectra, answer the following :- 5
(i) Derive the expression for its wave number.
(ii) State the expression for the spacing between two such successive lines.
(iii) Qualitatively sketch the R- branch lines for the first four transitions and name them.

(E) How does basic quantum theory explain the Raman effect? 5

(F) The frequency of separation of successive lines in the rotational spectrum of CO molecule is $382.4 m^{-1}$. Calculate the moment of inertia and the bond length. 5

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

(A) Find the emf of the following cell at 298 K. 5

$Al \mid Al^{3+}_{(a=0.02)} \| Cl^{-}_{(a=0.04)}, Cl_{2(g)} \mid Pt.$

$E^{\circ}_{Cl_2, Cl} = 1.36V$

$E^{\circ}_{Al+3/Al} = -166V$

(B) Derive an expression for emf of the following cell. 5

$$\ominus Ag_{(s)} \left| AgCl_{(s)}, \underset{a_1}{HCl} \right| \underset{a_2}{HCl}, AgCl_{(s)} \left| Ag^{\oplus} \right.$$

(C) Explain the origin of liquid junction potential. How is it eliminated? 5

(D) What are galvanic cells? Explain any four types of ion-specific electrodes with suitable example. 5

(E) Calculate the mean activity coefficient of 0.02m KCl in 0.002m $K_2SO_4$. The constant A=0.509 at 298 K for water. 5

(F) What are gas concentration cells? Derive an expression for emf of gas concentration cell reversible to cation. 5

3. (A) Choose the correct answer. 4

(a) In -plane bending vibrations are classified as _____.

(i) Rocking and Wagging

(ii) Scissering and Rocking

(iii) Scissoring and Wagging

(b) For Stoke's line_____.

(i) $\nu_i > \nu_s$

(ii) $\nu_i = \nu_s$

(iii) $\nu_i < \nu_s$

(c) In pure rotational spectra, B= ————

(i) $B = \frac{h}{8\pi Ic}$

(ii) $B = \frac{h}{8\pi^2 Ic}$

(iii) $B = \frac{h^2}{8\pi^2 Ic}$

(d) Total degrees of freedom in $CO_2$ molecule is_____.
(i) 9 (ii) 6 (iii) 5

**OR**

(A) State whether **True** or **False** : 4

(p) Bending vibration requires less energy than stretching vibration.
(q) The rotational constant B has lesser value for $^{12}C^{16}O$ than $^{13}C\ ^{16}O$.
(r) Homopolar molecules give rise to rotational spectra.
(s) The molecule of $BF_3$ has zero dipole moment.

(B) Choose the correct answer :-

(a) The value of E°cell in concentration cells is
(i) Zero
(ii) Positive
(iii) Negative

(b) $Pb|PbSO_4, SO_4^{2-}$ is reversible to _____
(i) Cation
(ii) anion
(iii) both

(c) The expression for the activity of uni-trivalent electrolyte is_____
(i) $4\ m^4r^4$
(ii) $27m^4r^4$
(iii) $27m^3r^3$

(d) $^{\ominus}Ag \mid \underset{(a_1)}{AgNO_3} \parallel \underset{(a_2)}{AgNO_3} \mid Ag^{\oplus}$ is an example of
(i) electrode concentration cell
(ii) chemical cell
(iii) Electrolyte concentration cell

**OR**

(B) State whether **True** or **False** : 4

(p) The activity of $CaCl_2$ (m=0.5, r = 0.9) is 0.3645.
(q) Saturated calomel elestrode is an example of redox electrode
(r) When metals are dipped into their salt solutions they enter the solution in form of cations, This is known as electronation
(s) The polarity of cathode in galvanic cells is positive.



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## SECTION -II

4. Attempt **any three** of the following :-
   (A) Give an account of the following with suitable examples. **5**
   (i) principal axis and subsidiary axes (ii) Identity.
   (B) Discuss the point groups assigned to diatomic linear molecules. **5**
   (C) Explain the symmetry elements and assign a point group in $NH_3$ molecule with neat diagrams. **5**
   (D) Draw a neat labelled MO diagram for $BeH_2$ molecule. Give its structure and magnetic property. **5**
   (E) Write the wave equations for the formation of molecular orbitals in $H_2O$ molecule. (MO diagram not expected). **5**
   (F) What is doping? Explain n-type semiconductor with suitable diagrams. **5**

5. Attempt **any three** of the following -
   (A) What are Lattice Parameters? Derive a relationship between lattice constant (a) of a cubic crystal and density of the crystal material. **5**
   (B) Show that packing density for body centered cubic (bcc) lattice is 0.68. **5**
   (C) For a face centered cubic (fcc) lattice. Calculate - **5**
   (i) Number of atoms per unit cell (fcc)
   (ii) Atomic radii (r) of a metal with unit length of 3.9 A°, crystallizing in fcc lattice.
   (D) Metal has fcc structure and its atomic radii is 138 pm. Calculate the lattice constant (a) and density of the metal. Molar (M) of metal is 195 and Avogadros number (N) is $6.022 \times 10^{23}\ mol^{-1}$. **5**
   (E) With suitable example, explain Schottky defect in ionic solids. **5**
   (F) Explain the terms : **5**
   (i) Superconducting Transition temperature (Tc)
   (ii) Meissner's Effect

6. (A) Select and write the most appropriate answer. **4**
   (a) The angle of rotation for $C_3$ axis is _____.
   (i) 180° (ii) 120° (iii) 60°

   (b) Centre of inversion is absent in _____molecule
   (i) $SF_6$ (ii) HCN (iii) $C_6H_6$



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(c) $BCl_3$ molecule belongs to _____point group.
(i) $D_{\infty h}$ (ii) $C_{2h}$ (iii) $D_{3h}$

(d) Water molecule is not _____ molecule.
(i) angular (ii) linear (iii) triatomic

**OR**

(A) State whether the following statements are **True** or **False** :
(p) Electrical conductivity of metal increases with rise in temperature. **4**
(q) The collection of very closely spaced energy levels is called energy band.
(r) The semiconductor obtained by heating an insulator is called intrinsic semiconductor.
(s) $H_3^+$ ion molecule can be described by a three center three electron bond.

(B) Select and write the appropriate answer.
(a) The number of atoms in simple cubic (sc) unit cell is____. **3**
(i) 1 (ii) 2 (iii) 4

(b) Frenkel defect occurs in _____.
(i) alkali halides
(ii) silver halides
(iii) alkaline earth oxides

(c) High temperature superconductors (HTSC) require____for cooling.
(i) liquid Helium
(ii) liquid Hydrogen
(iii) liquid Nitrogen

**OR**

(B) State whether the following statements are **True** or **False** : **3**
(p) The atomic packing factor (APF) for hexagonal close packed lattice is 0.74
(q) In Frenkel defect, missing atom occupies an interstitial position between the lattice points.
(r) The carbon atoms in Fullerene are $sp^3$ hybridised.

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