<div align="center">

2½ Hours   **Total Marks:75**

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NB:
1. All questions are compulsory.
2. Figures to the right indicate full marks.
3. Use of logarithmic table / non- programmable calculator is allowed.
4. Answer to the two sections should be written in separate answer books and tied together.

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Section I

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Physical constants:

A	0.509 at 298 K for water
N	6.022×10^{23}
F	96500 C
R	$8.314 \; J \; K^{-1} \; mol^{-1}$
h	$6.626 \times 10^{-34} \; J \; s$
c	$3 \times 10^8 \; m \; s^{-1}$
2.303 RT/F	0.0592 at 298 K
π	3.142
Mass of electron	$9.109 \times 10^{-31} \; kg$
1 a m u	$1.66 \times 10^{-27} \; kg$

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

A. What is the origin of dipole moment? How does it explain the structure of BF_3 and NH_3 ?   **5**

B. Explain how the presence of isotopes affects rotational spectra?   **5**

C. Derive the expression for P - branch lines in rotational spectra. Qualitatively sketch the first four P- branch lines and name them.   **5**

D. Explain the Rule of Mutual Exclusion with the help of CO_2 molecule.   **5**

E. For a diatomic molecule as a perfect rotor , the frequency difference between successive lines in rotational spectra is $8.86 \times 10^2 \; m^{-1}$. Calculate the rotational constant, moment of inertia and frequency of first absorption in rotational spectra.   **5**

F. Calculate the zero point energy and the force constant of a molecule whose reduced mass is 1.2×10^{-27} kg.The wave number of the origin of and in IR spectra is $3700 \times 10^2 \; m^{-1.}$ **5**

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

A. Derive an expression for emf of electrolyte concentration cell with   **5**
transference ,reversible to cation.

B. What are gas concentration cells? Derive an expression for e m f of gas   **5**
concentration cell reversible to anion.

C. What are the different types of ion selective electrodes? Explain any two of   **5**
them.

D. Explain the origin of liquid junction potential. How is it eliminated?   **5**

E. Calculate the mean activity coefficient of 0.01m KCl in 0.001m K_2SO_4.   **5**

F. Calculate the emf of the following cell: **5**
I Pt,H_2 I HCl   ‖   HCl. I H_2, Pt.
1atm. m=0.1.   m=0.2.   1atm.
r=0.798. r =.768

3.A. State **true** or **false** for the following: **4**

a. Homonuclear molecules show zero dipole moment.

b. The CO_2 molecule posses six modes of vibrations.

c. Raman spectra is observed using infra red radiations.

d. Rotational constant B is directly proportional to moment of inertia.

<div align="center">OR</div>

3.A. Choose the **correct** answer: **4**

p. When Raman shift is _____, stokes line is observed
    (Positive/Negative)

q. _____ has zero dipole moment.
    (CO_2/SO_2)

r. _____ is microwave active.
    ($CHCl_3$/ C_6H_6)

s. Molecules which exhibit change in _____ show IR spectra.
    (dipole moment/polarisation)

3.B . State **true** or **false** for the following: **4**

a. Chemical cell is made of two half cell using different electrodes.

b. In the electrolyte concentration cell ,the two half cells contain same
electrolyte with different concentrations.

c. NaCl is used in preparation of salt bridge.

d. Magnitude of liquid junction potential independent of relative speed of ions of the electrolyte.

<div align="center">OR</div>

3.B. Match the following: **4**

p.	$Al_2(SO_4)_3$.(m=0.01)	(i)	μ =0.15
q.	$CaCl_2$. (m =0.1)	(ii)	μ =0. 3
r.	$ZnCl_2$. (m = 0.5)	(iii)	μ= 1.5
s.	NaCl. (m = 0.01)	(iv)	μ= 0.01
		(v)	μ=1.25

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SECTION II

4. Answer **any three** of the following:-

A. Explain the terms, 'Proper rotational axis' and 'Vertical plane of symmetry' with suitable example.   **5**

B. Explain the C_{3v} and $C_{\infty v}$ point groups, giving a suitable example for each.   **5**

C. Discuss the symmetry operations and assign the point group to BCl_3 molecule.   **5**

D. Draw a neat labelled molecular orbital diagram for BeH_2 molecule showing the distribution of electrons in various energy levels. Predict its magnetic property.   **5**

E. What is Walsh Correlation diagram? Draw a neat and labelled Walsh Correlation diagram for a linear and bent AH_2 type of molecule.   **5**

F. What is extrinsic semiconductor? Explain the n-type semiconductor.   **5**

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

A. Show that packing density for body centered cubic lattice is 68%.   **5**

B. For hexagonal close pack structure, calculate -   **5**
  (i) Number of atoms per unit cell.
  (ii) Length of unit cell, if atomic radius (r) is 205 pm.

C. Define lattice parameters. Derive a relationship between lattice constant and density of the crystal material.   **5**

D. Explain Schottky defect with suitable example.   **5**

E. Write a short note on High Temperature Superconductors (HTSC)   **5**

F. Explain the following:-   **5**
  (i) Different types of point defects found in crystals.
  (ii) Superconducting Transition Temperature (Tc)

6. Answer the following:

A. Select and write the appropriate answer.   **4**

  a. The operation that leaves the molecule unchanged is called _____ .
    (i) centre of symmetry   (ii) identity   (iii) centre of gravity

  b. $D_{\infty h}$ point group is assigned to _____ molecule.
    (i) H_2 (ii) HCl   (iii) H_2O

  c. The shape of H_3^+ ion is _____.
    (i) linear   (ii) 'T' shaped   (iii) triangular

  d. The p-type semiconductor is obtained, when Si is doped with _____.
    (i) As   (ii) Sb   (iii) Al

OR

A. State whether the following statements are **true** or **false**.　　　　　　　　　　**4**

   p. Improper axis of rotation is denoted by the symbol S_n .

   q. Trans dichloroethylene molecule has C_{2v} point group.

   r. The ground state electronic configuration of H_2O molecule is $(\sigma_s)^2(\sigma_z)^2$

   s. The collection of very closely spaced energy levels is called energy band.

B. Select and write the appropriate answer.　　　　　　　　　　**3**

   a. A point in crystal lattice signifies _____ of particles.

     (i) size　　　　　　　　(ii) volume　　　　　　　(iii) position of centre.

   b. Frenkel defect occurs in ionic crystals with _____radius ratio.

     (i) low　　　　　　　　(ii) high　　　　　　　(iii) almost equal to 1.

   c. The effect of ejecting out the flux lines of magnetic field is known as _____.

     (i) Meissner's effect　　　(ii) Doppler effect　　　(iii) line effect.

<p align="center">**OR**</p>

B. State whether the following statements are **true** or **false**.　　　　　　　　　　**3**

   p. Void spaces in face centered cubic unit cell is 26%.

   q. Frenkel defects do not affect the density of the ionic crystal.

   r. Conventional superconductors require liquid nitrogen for cooling.

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