

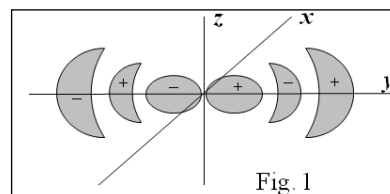
**NOTE: There are FIVE questions in all. Attempt all the questions. Start answering each question on a fresh page and answer all parts of the question together. Pencil should not be used. Symbols have usual meanings. Do not scribble on the question paper.**

**USEFUL DATA:**  $c = 3 \times 10^8$  m/s; Mass of electron =  $9.109 \times 10^{-31}$  kg;  $1 \text{ amu} = 1.66 \times 10^{-27}$  kg;  $a_0 = 0.529 \text{ \AA}$ ;  $h = 6.626 \times 10^{-34}$  Js;  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $R_H = 109677 \text{ cm}^{-1}$ ;  $1 \text{ bar} = 101.3 \text{ kPa}$

**Q. 01. (a)** When an electric discharge is passed through a particular sample of gaseous hydrogenic ion  $M^{2+}$ , it produces the electromagnetic spectrum corresponding to the lowest frequency in the Paschen series. What will be the energy (in Joule) required to produce  $M^{3+}$  ion from the above irradiated sample? [4]

**(b)** Looking at the hydrogenic orbital (Fig. 1), write your answer in tabular form in answer sheet.

No. of Radial Nodes	No. of Angular Nodes	Orbital

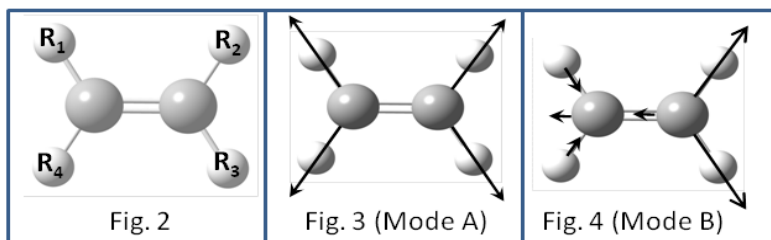


[3]

**(c)** Assume the carbon molecule  $C_{32}$  as a rigid sphere (having radius  $2.5 \text{ \AA}$ ) and the electrons of the molecule as being confined to the surface of the sphere. The wavelength of light necessary to cause a transition of an electron from state  $l$  to  $l+1$  is 127 nm. Calculate the value of  $l$ . [5]

**(d)** Write the ground state term for  $Fe^{3+}$  ion. [2]

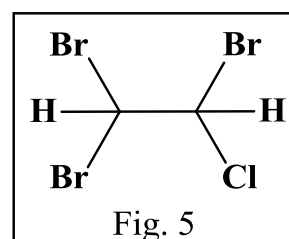
**Q. 02. (a)** Consider a substituted ethylene molecule having a general structure (Fig. 2). Comment on rotational activity in the microwave spectrum in one/two lines, for the molecules with (i)  $R_1=R_2=R_3=R_4=H$ , (ii)  $R_1=R_2=F$ ;  $R_3=R_4=H$ .



[3]

**(b)** Comment on the IR activity of the following two vibrational modes (Fig. 3: Mode A; Fig. 4: Mode B) with  $R_1=R_2=R_3=R_4=H$ : [Arrows on each atom represents relative movement of the atoms] [2]

**(c)** The compound 1,1,2-tribromo-2-chloroethane (Fig. 5) shows two doublets in proton NMR ( $^1H$  NMR) spectrum centered at  $\delta$  5.3 (lines p, q) and  $\delta$  5.5 (lines r, s) respectively, when run at 100 MHz. If sample is run in a 500 MHz NMR instrument and spectrum obtained in a frequency domain (frequency plotted on x-axis), how will the separation between the following lines vary? (i) Line p and line q; (ii) Line q and line r. Provide **ONE-LINE** explanation for each.

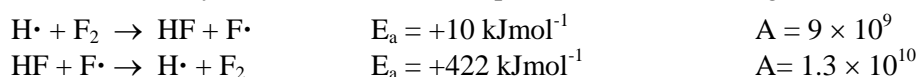


[3]

**(d)** The spectral transitions of  $HF_2^-$  in isolated alkali metal salts are listed here.

Determine the geometry of the anion.  $1550 \text{ cm}^{-1}$  (IR active),  $1200 \text{ cm}^{-1}$  (IR active), and  $675 \text{ cm}^{-1}$  (Raman active). [2]

**(e)** Consider the elementary reactions and their respective activation energies ( $E_a$ ) and Arrhenius constants (A)



(i) Calculate the equilibrium constant for the reversible reaction at  $127^\circ\text{C}$

(ii) Determine the Gibb's free energy change for the reversible reaction at  $127^\circ\text{C}$ . [4]

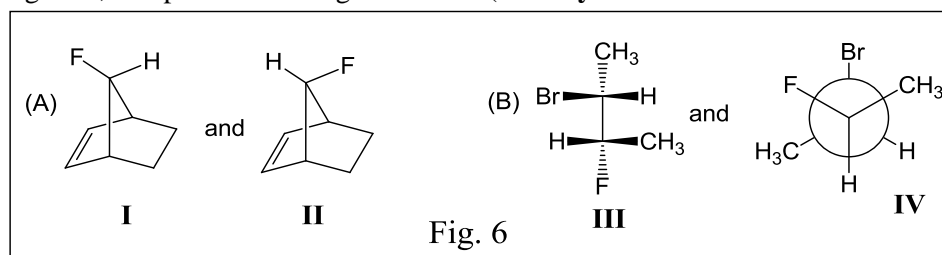
**Q. 03. (a)** Chemical reactions proceed by the initial loss or gain of an electron to a diatomic species ( $A_2$ ). Which of the molecules,  $F_2$  and  $C_2$  would you expect to be stabilized by (i) the addition of an electron to form an anion ( $A_2^-$ ), (ii) the removal of an electron to form a cation ( $A_2^+$ )? Justify your answer in **TWO LINES**. [2]

**(b)** Calculate the following parameters as mentioned in the given tabular format for the two complexes in **high spin states** of  $[Co(CO)_4]^-$  and  $[Co(NO_2)_6]^{4-}$ . (Write your answer in tabular form in answer sheet). [4]

Complexes	No. of unpaired electrons	Magnetic moments	Geometry	CFSE (in $\Delta_0$ ) (Ignore pairing energy)
$[Co(CO)_4]^-$				
$[Co(NO_2)_6]^{4-}$				

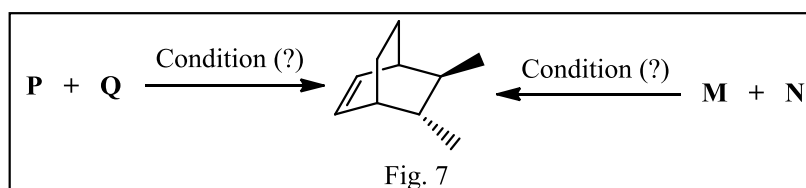
- (c) Show that the  $sp^2$  hybrid orbital  $(s + 2^{1/2}p_x)/3^{1/2}$  is normalized, where  $s$  and  $p_x$  are hydrogenic orbitals. [3]
- (d) Consider two octahedral complexes,  $[\text{Fe}(\text{NH}_3)_6]\text{Cl}_2$  and  $[\text{Cu}(\text{NH}_3)_6]\text{Cl}_2$ : (i) Which of the given complexes will have larger value of  $\Delta_0$ ? (ii) Which of the given complexes will show stronger Jahn Teller distortion? Justify your answer in **ONE LINE**. (iii) Specify the type of distortion (z-elongation and z-compression) and the order of d-orbital energies. [1+2+2]

**Q. 04 (a)** Based on figure 6, complete the table given below (**Write your answer in tabular form in answer sheet**). [4]



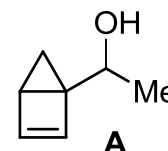
Stereochemical relationship between		In IV, absolute configuration (R/S) about	
I and II	III and IV	Front chiral carbon	Back chiral carbon

(b) For the following cycloaddition reaction (Fig. 7), identify structures of **P, Q, M, N** and reaction condition. [5]

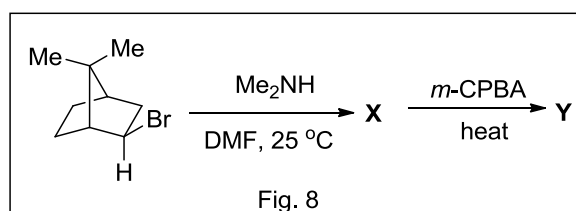


(c) The energy for 1,3-diaxial interaction between hydrogen and a substituent in a monosubstituted cyclohexane is 1.98 kJ/mol at 25 °C. Calculate the amount (number of moles) of axial and equatorial conformers present in five moles of the monosubstituted cyclohexane at 25 °C, considering the entropy change is negligible for the conformational interconversion. [5]

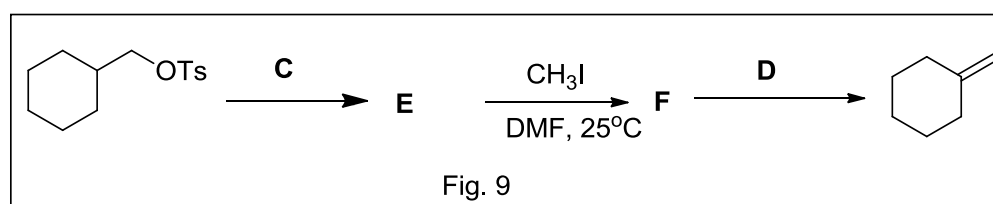
**Q. 05. (a)** An alcoholic compound **A** reacts with conc.  $\text{H}_2\text{SO}_4$  to produce a stable conjugated compound **B** ( $\text{C}_7\text{H}_8$ ) that possesses a permanent dipole-moment. Identify the structure compound **B**, propose a mechanism for its formation and provide reason for permanent dipole moment. [5]



(b) Write the structures of compounds **X** and **Y** obtained in the following transformation (Fig. 8) using an optically active halide. Also, comment on the optical activity of product **Y**. [5]



(c) Write the reaction conditions (**C & D**) and intermediate compounds (**E & F**) involved in the following transformation (Fig. 9). [4]



\*\*\*END\*\*\*