6. a) Is H-Cl bond covalent ? Explain your answer. 2

   b) Draw the structures of XeF_2, XeF_4 and XeF_6. Explain the difference in terms of VSEPR theory. 3

   c) Draw the hybrid orbitals of B-H-B motif using p_x function of B and 1s function of H. Arrange qualitatively in the energy axis. 3

FIRST B. SC. EXAMINATION, 2019

(2nd Semester, Old Syllabus)

CHEMISTRY (HONOURS)

PAPER - III

Time : Two hours Full Marks : 50

Use a separate answerscript for each Group.

GROUP - A

1. Answer ***any three*** :

   a) Classify the following as extensive or intensive properties :

   (i) heat capacity ; (ii) chemical potential, (iii) density, (iv) mole fraction.

   Adiabatic free expansion of an ideal gas must be isothermal : Justify / Criticize. 2+2

   b) For an ideal gas show that adiabatic curve is steeper than isothermal curve on a P-V indicator diagram.

   Find coefficient of volume expansion (α) and coefficient of compressibility (β) for an ideal gas at 298 and 1 atm. 2+2

   c) Show that $(\partial P/\partial T)_v = \alpha/\beta$, α = coefficient of volume expansion and β = coefficient of compressibility.

   84 g of nitrogen initially at 300 K and 10 atm pressure expands adiabatically against a constant pressure of 1 atm. Assuming ideal behaviour calculate the final temperatue. 2+2

d) For ideal gas one can always write ; $dU = C_v\, dT$: Justify/ criticize.

e) For a reversible polytropic process described by the general relation $PV^n = \text{Constant}$, show that for ideal gas

$$W = \frac{RT}{(n-1)}\left\{1-\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}\right\}. \qquad 4$$

2. Answer ***any one*** :

a) Show that for a reversible adiabatic change involving an ideal gas $TV^{\gamma-1} = \text{constant}$; where the symbols have their usual meaning.

One mole of a mono-atomic ideal gas at 300 K is compressed adiabatically and reversibly to one fourth of its original volume. What is the final temperature of the gas ? Also calculate ΔH. 3+2

b) Show that $C_P - C_V = [V - (\partial H/\partial P)_T](\partial P/\partial T)_V$.

Show that dP is an exact differential for the relation P(V-b)=RT 3+2

GROUP - B

3. a) Answer ***any two*** of the following questions :

i) "(*2R*, *3R*)-3-Bromo-2-butanol, on treatment with HBr produces racemic 2, 3-dibromobutane" – Justify the statement mechanistically.

GROUP - C

Answer ***any Two*** Questions

4. a) Draw the structures of CH_3^- and CF_3^+ and comment on the difference, if any. 2

b) Explain the bonding in Na metal and explain its conductivity. 2

c) Define dipole moment and comment on the dipole moment of the ozone. 2

d) Explain why two 's' orbitals cannot form a pi bond although two p-orbitals can form. 2

5. a) Calculate the electron affinity of chlorine from the Born-Haber cycle, given the following data : lattice energy = – 774 kJ/mole, I.P. of Na = 495 kJ/mole, heat of sublimation of Na = 108 kJ/mole, energy for bond dissociation of chlorine (Cl_2) = 240 kJ/mole, heat of formation of NaCl = 410 kJ/mole. 4

b) Predict the bond orders of $O_2^+, O_2^-, O_2^{2-}, O_2$ using MO theory. 2

c) The B-F bond energy in BF_3 is 646 kJ/mole but that of NF_3 is only 280 kJ/mole. Explain. 2

ii) Draw the conformers in Newman projection of *active* - 2, 3- butanediol, and comment on the most stable conformer with justification.

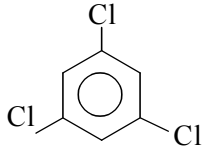
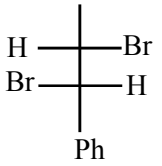
iii) An organic compound of molecular weight 100 has specific rotation + 120° (observed at 27°C and sodium D-line).

Its optical rotation, measured in a 10 cm cell is +1.2°. Calculate the molar concentration of the compound.

b) i) Draw the structure of an *R*-configured modecule in Fischer projection in which the asymmetric carbon is attached with the following four groups :

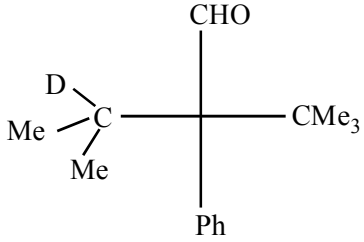
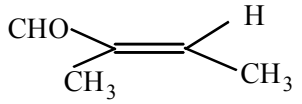
CH_2CD_3, $CH_2CH_2CH_3$, CHO & C ≡ N. 1

ii) Find out the symmetry elements present in the following molecules : 3

$H_2C = CH_2$;  ; 

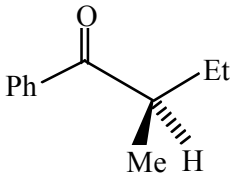
A **B** **C**

iii) Assign *R*/*S* or *E*/*Z* (as applicable) to the following examples : 2

 ; 

D **E**

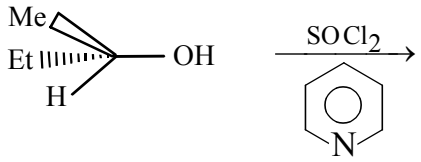
c) i) Optical rotation of a solution of enantiopure molecule **F** in the presence of catalytic amount of a base slowly changes to zero – Justify the observation. 2

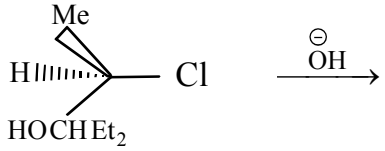


F

ii) Draw the wedge structure of L-2-aminobutyric acid. 1

d) Predict the product(s) with plausible mechanism ***(any two)*** : $1\frac{1}{2} \times 2$

i) 

ii) 

iii) *threo*-1-Bromo-1, 2-diphenylpropane $\xrightarrow{\ominus OH}$

(for this reaction, mechanism is not necessary).