FIRST B.SC. EXAMINATION, 2018

(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) Specific heat ; (ii) critical volume. 1

   Show that with increase in no. of steps the magnitude of work of expansion increases and reaches maximum where the process becomes reversible. Consider isothermal expansion of ideal gas. 3

   Or,

   From the following data find the effect to temperature on ΔH of the reaction $A_2(g)+2B_2(g) \rightarrow 2AB_2(g)$; Given

   $C_p[A_2(g)] = 32{\cdot}0 + 1{\cdot}04 \times 10^{-2}T$;

   $C_p[B_2(g)] = 45{\cdot}2 + 2{\cdot}06 \times 10^{-2}T$ and

   $C_p[AB_2(g)] = 61{\cdot}2 + 2{\cdot}58 \times 10^{-2}T$ 3

b) The Work involved in an adiabatic expansion of a gas is independent of path – Justify/Criticize. 2

Show that for a gas obeying the van der Waals equation of state, $\alpha/\beta = R/V - b$; where α =coefficient of volume expansion and β = coefficient of compressibility. 2

Or,

Show that (P, V, T) cyclic rule is obeyed for ideal gas. 2

c) Define enthalpy of neutralization. 2

Or,

Show that for ideal gas adiabatic curve is steeper than isothermal curve on P-V diagram. 2

Enthalpies of neutralization of HCl and acetic acid by NaOH are –57.32kj mol^{-1} and –55.43kj mol^{-1}, respectively at 25°C. Find the enthalpy of ionization of acetic acid. 2

d) For a reversible polytropic process described by the general relation PV^n= Constant, show that for an ideal gas, $W = \frac{RT_1}{(n-1)}\left\{1-\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}\right\}$.

(Symols have usual meanings.) 4

6. a) Calculate limiting radius ratio (r^+/r^-) to CsCl type ionic lattice of 8 : 8 cation-to-anion ratio. 3

b) Draw the MO diagram of O_2. Explain (i) the bond length sequence as $O_2 < O_2^- < O_2^{2-}$; (ii) magnetic property of O_2. 2+2

c) Draw the molecular structure of XeF_6 and discuss its salient feature. 2

GROUP - B

3. a) i) Iodide induced debromination of *meso*-2,3–dibromobutane is faster than that of the active isomer.–account for the statement. 2

ii) Diastereomer of 3-bromo–2,3–diphenylpropanoic acid undergoes elimination in the presence of base affording the products of different molecular formulae.– explain. 2

iii) An optically active compound (2 gm) is dissolved in 100 ml water, and the solution shows optical rotation :– 8.4^{o}, when measured in a 20 cm long polarimeter tube. Predict the rotation if 3 gm of the same compound is dissolved in 100 ml water, and the optical rotation is measured using a 30cm long polarimeter tube. 2

b) Answer ***any two*** of the following questions : $1\frac{1}{2}\times2$

i) Draw the important conformations and energy profile diagram of 2-methylbutane about C_2–C_3 bond.

ii) Write one method of resolution of racemic $PhCHOHCH_3$.

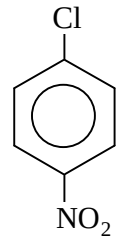
iii) Discuss on the dipole moment of 1,2–dibromoethane.

c) What is meant by conformer ? Draw the conformers of *2S, 3R*- dichlorobutane in Newman projection, and comment on their relative stability. Stereoisomeric relationship and chirality. 3

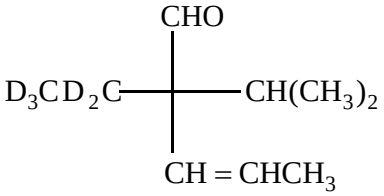
d) Find out the symmetry element(s) present in the following melecules (***any two***) : 1×2

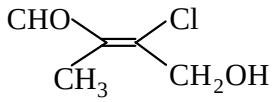
i) *threo*-$PhCHCH_3CHCH_3Ph$ (in Fischer projection).

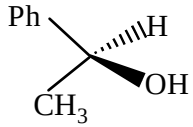
ii) $H_2C = C = CH_2$,

iii) 

e) Assign *R*/*S* or *E*/*Z* (as applicable) to the following molecules : 3

i) 

ii) 

iii) 

GROUP - C

Answer ***any two*** questions

4. a) Define lattice energy. Explain the factors which influence Lattice Energy. Following data are given : atomisation enthalpy of Mg, 1.48 kJ ; 1st IE of Mg, 738 kJ ; 2nd IE of Mg, 1451 kJ ; atomisation enthalpy of Cl_2, 244 kJ; electron affinity of Cl_2, – 698 kJ, Lattice enthalpy, –2526 kJ. Calculate ΔH_f. 5

   b) Explain the following : $1\frac{1}{2} \times 2$

      i) Dipole moment order of HX follows

      H-F > H-Cl > H-Br > H-I

      ii) NH_3 has larger dipole moment (1.46D) than NF_3 (0.24D)

5. a) What are the conditions to construct hybrid functions ? Why BeH_2 is linear while BH_3 is angular ? 3

   b) What are the drawbacks of VSEPR model to explain the structure of the molecules ? Give examples. 3

   c) Construct MOs obtained by the mixing of two 1s functions of two H atoms and one p_x function of B atom in BH_2 unit. 2

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

   a) Show that for a reversible adiabatic change involving an ideal gas PV^{γ} =Constant; where the symbols have their usual meaning.

   One mole of an ideal gas at 300K and 1atm is allowed to expand freely twice its initial volume under adiabatic condition. Find the final temperature and pressure. 3+2

   b) Show that, $C_p - C_v = \left[P + \left(\delta U / \delta V\right)_T\right]\left(\delta V / \delta T\right)_p$

   Isothernal free expansion of an ideal gas must be adiabatic. Justify/Criticize. 3+2