FIRST B. SC. EXAMINATION, 2017

(2nd Semester)

CHEMISTRY (HONOURS)

PAPER - III

Time : Twohours Full Marks : 50

Use a separate answerscript for each Group

GROUP - A

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

   a) i) Classify each of the following as either intensive or extensive property :
   surface tension, enthalpy, molar specific heat, inversion temperature.

   ii) State, with proper reasons, whether the following statements are true or false :

   x) $\int_1^2 dQ = \Delta Q$ y) $C_p = C_v + R$ 2+2

   b) For a closed system show that

$$C_p - C_v = P\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

   where the terms have their usual meaning. Explain the physical significance of the two terms on R.H.S., specially in case of a gaseous system. 4

c) i) Prove that Joule-Thomson expansion is an isoenthalpic process.

ii) At 300°C and at pressures of 0-50 atm, the Joule-Thomson coefficient of $N_2(g)$ can be represented by the equation

$$\mu = \{0 \cdot 0150 - 2 \cdot 50 \times 10^{-4} (P/atm)\}$$

Assuming the equation to be temperature independent near 300°C, find out the temperature drop which may be exprected on Joule-Thomson expansion of the gas from 50 to 10 atm. 2+2

d) 2 mol of an ideal gas at 1 atm. and 27°C is heated at constant pressure until the final temp. is 77°C. For the gas, $C_{v,m}$ = 7·50 + 3·0 × 10^{-3}T Cal.$mol^{-1}K^{-1}$. Calculate W, ΔU, ΔH & Q for the process. 4

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

a) i) Show that for a reversible adiabatic expansion or compression of an ideal gas, $T^{\gamma}P^{1-\gamma}$ = constant, where the symbols have their susual meaning.

ii) 2 mol. of an ideal gas having $C_{v,m} = \frac{3}{2}R$ and initially at 27°C and 100 kPa, is compressed adiabatically using a constant pressure equal to the final pressure until the temperature of the gas reaches 327°C. Calculate the

iii) Polarity : C-Cl, Ba-Cl, Br-Cl, Cl-Cl

c) Using dipole moment data comment on the structure of $CO_2(\mu = 0 \cdot 0\ D)$ and $SO_2(\mu = 1 \cdot 63\ D)$. 2

8. a) Define MO. Write down the conditions of MO construction from AOs. Assign the Ground state Electronic Configuration of CO and explain its coordinating ability to metal ion. $1+1\frac{1}{2}+2\frac{1}{2}$

b) Using MO theory explain the magnetic property of B_2. 2

c) Bond dissociation energy of $N_2 > N_2^+$ and that of $O_2 < O_2^+$. Explain. 1

GROUP - B

3. a) Draw the important conformations (about $C_2 - C_3$) and the energy profile diagram of n-butane. What is the requirement for a molecule to show conformational variability? $1\frac{1}{2} + \frac{1}{2}$

   b) Write any two methods of racemisation of active α-phenylethyl chloride. 2

   c) Draw the most stable conformer in sawhorse structure of 2R, 3R-butane diol and convert it to the corresponding Fischer projection. 1

   d) Systematically assign symmetry elements of 1-chloroallene. 1

   e) Draw the R-configured Flying-Wedge structure of a compound containing an asymmetric carbon attached with the following groups :

   C_6H_5, $C(CH_3)_3$, CHO and CH_2CH_2OH 1

4. Answer ***any three*** questions : $1\frac{1}{2} \times 3$

   a) Compare the dipole moments with justification of the *meso*-and *active*-stilbene dichloride (PhCHClCHClPh).

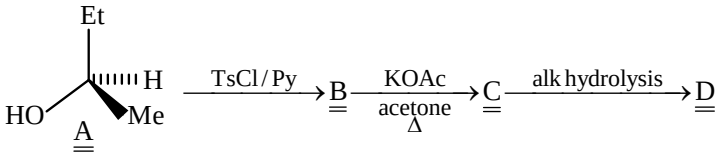
   b) Explain why active 2, 3-butanediol enhances the conductivity of boric acid more than does its *meso*-isomer.

   c) What happens when *threo*-1-bromo- 1, 2–diphenylpropane is reacted with sodium hydroxide ? Comment on the stereoelectronic requirement of this reaction.

   d) Give an explanation of the following observation :

   'Hydrolysis of active $C_6H_5CH(CH_3)Cl$ in 80% aq. acetone occurs with 98% recemisation whereas that of active $C_6H_{13}CH(CH_3)Cl$ under similar solvent condition proceeds with 34% racemisation'.

5. a) Write the structure of the products ($\underline{B} - \underline{D}$) of each step with proper stereochemical outcome, and comment on the relationship between the sign of specific rotations of $\underline{A}$ and $\underline{D}$. Write the name of the mechanistic pathway (abbreviated) of the second step. $2\frac{1}{2}$



   b) Predict the product(s) with mechanism and proper stereochemical outcome, of the following reactions :

      i) erythro-3-Bromo-2-butanol on reaction with HBr.

      ii) (R)-1-Phenylethanol on reaction with thionyl chloride in petroleum ether. $1\frac{1}{2} \times 2$

GROUP - C

Answer ***any two*** questions

6. a) Write down Born-Lande equation and explain the meaning of the symbols used. Calculate Lattice Energy of NaCl.

[Given : $\Delta H_f = -381 \cdot 2$ kJ mol^{-1} ; $\Delta H_s = 108 \cdot 4$ kJ mol^{-1} ; I = 495·4 kJ mol^{-1} ; $\Delta H_d = 120 \cdot 9$ kJ mol^{-1} ; E = –348·6 kJ mol^{-1}] 2+2

b) Calculate limiting r_+/r_- ratio for coordination number 4 in Tetrahedral geometry. 2

c) Experimental dipole moment of HCl is 1·03 D and the bond distance is 1·275 Å . Calculate % ionic character of the bond. 2

(Given, electronic charge $= 4 \cdot 8 \times 10^{-10}$ esu)

7. a) Define Hybridisation. Account on the qualitative relation between hybridization and structure of the molecules. Also determine hybridization of Xe in XeF_4. 1+2+1

b) Arrange in ascending order of following compounds according to the prescribed properties (any two) : 1×2

i) Acidity : Al_2O_3, P_2O_5, Cl_2O_7, SO_3

ii) Ionic size : O_2, O_2^-, O_2^+, O_2^{2-}

final pressure, Q, W, ΔU and ΔH for the transformation. 2+3

b) One mol of an ideal gas ($C_{v,m}$ = 12·6 J $K^{-1}mol^{-1}$) undergoes the following reversible cycle :

State I (1 atm, 273K) $\xrightarrow{\text{Isochoric heating}}$ State II (546 K)

State II (546 K) $\xrightarrow{\text{Adiabatic expansion}}$ State III (273 K)

State III (273 K) $\xrightarrow{\text{Isothermal compression}}$ State I

i) Depict the cycle in a V vs. T diagram

ii) Depict the cycle in a P vs. V diagram

iii) Calculate Q, W, ΔU and ΔH for each step. 1+1+3