

# Five Year Integrated M.Sc. Examination, 2017

Semester - II

Course: CH-1-2-1 (Old)

( Chemistry )

Time: Four Hours

Full Marks: 80

Questions are of value as indicated in the margin.

## Group-A

1. Answer *any ten* of the following: 10x2=20
- Explain Schottky defect with example.
  - Explain with suitable example how proton affinity can be determined by using Born-Haber cycle.
  - He<sub>2</sub> does not exist. - Explain.
  - State Bent's rule of isovalent hybridization.
  - Arrange the following carbanions according to increasing order of stability:  
 $\text{CH}_3^-$ ,  $\text{CH}_3\text{CH}_2^-$ ,  $(\text{CH}_3)_2\text{CH}^-$ , and  $(\text{CH}_3)_3\text{C}^-$
  - What type of bond cleavage generates free radicals?
  - Acetylacetone ( $\text{CH}_3\text{COCH}_2\text{COCH}_3$ ) forms stable enol. Explain
  - What is the basic difference between singlet and triplet carbenes?
  - Explain with examples, the intensive and extensive variables.
  - What are state functions? Do the state functions have exact differentials?
  - State with suitable example the laws of "Laplace and Lavoisier".
  - Show that pressure is a state function for a gas obeying  $(P + a/V^2)(V) = RT$ .

## Group-B

Answer *any two* questions.

2.
  - State Fajans' rules. 2
  - What do you understand by octahedral and tetrahedral holes? Show using figures. 2
  - What are polyhalides? Using VSEPR theory predict the structures of any two type of polyhalides of your choice. 1+2
  - Write a note on non-stoichiometric defect. 3
3.
  - What are the different products formed when B<sub>2</sub>H<sub>6</sub> is allowed to react with NH<sub>3</sub> at high temperature in 1:1 and 1:2 ratios? Hence establish the structure of the compounds. 2+2
  - Draw the molecular orbital energy level diagram of C<sub>2</sub> molecule. Comment on its magnetic property based on the diagram. 2+1
  - What are extrinsic semiconductors? What are the different types of extrinsic semiconductors? Give examples. 3
4.
  - Draw the molecular orbital energy level diagram of HF molecule. 2
  - Write down a method for the synthesis of S<sub>4</sub>N<sub>4</sub>. Discuss about its structure and bonding. State one interesting property of the compound. 1+2+1
  - Construct the Born-Haber cycle for the formation of NaCl from Na(s) and Cl<sub>2</sub>(g). Hence find out the lattice energy of NaCl. Given: Heat of formation of NaCl = 414 kJmole<sup>-1</sup>, Heat of sublimation of Na = 109 kJmole<sup>-1</sup>, Ionisation energy of Na = 494 kJmole<sup>-1</sup>, Bond dissociation energy of Cl<sub>2</sub> = 121 kJmole<sup>-1</sup> and Electron affinity of Cl<sub>2</sub> = -347 kJmole<sup>-1</sup>. 2+2

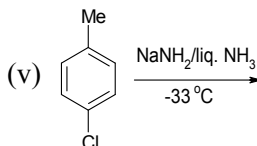
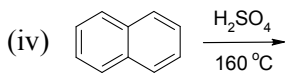
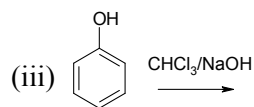
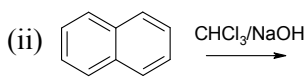
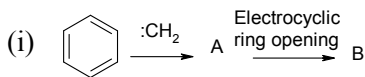
P.T.O.

( 2 )

**Group-C**

Answer *any two* questions.

5. a) Write the structure of the products in the following reactions



6. a) Write notes on: 3x3
- Keto-enol tautomerism
  - Primary Kinetic Isotope Effect
  - Neopentyl rearrangement
- b) Why benzyl cation ( $C_6H_5CH_2^+$ ) is more stable than methyl cation ( $CH_3^+$ )? 1
7. a) How benzyne intermediate can be generated? 4
- b) How this intermediate can be trapped? 4
- c) Write the structure of the self-trapping product of benzyne. 2

**Group-D**

Answer *any two* questions.

8. a) Show that pressure is a state function for a gas obeying  $(P + \frac{a}{V^2})(V) = RT$ . 2
- b) What are reversible and irreversible processes? Show that the magnitude of the work involved during expansion will be the maximum, if the process is quasi-static or reversible. 1+3
- c) One mole of an ideal gas is heated at constant pressure from 0 °C to 200 °C.
- Calculate work done.
  - If the gas were expanded isothermally & reversibly at 0 °C from 1 atm to some other pressure  $P_t$ , what must be the final pressure if the maximum work is equal to the work involved in (a). 2+2
9. a) Derive the thermodynamic relationship,  $PV^\gamma = \text{constant}$  for an adiabatic change in volume of an ideal gas, where symbols have their own meaning. 3
- b) Derive the relationship between heat capacities of a gas,  $C_p - C_v = \frac{TV\alpha^2}{\kappa_T}$ , where  $\alpha$  and  $\kappa_T$  are the expansion co-efficient and thermal compressibility factor, respectively. Hence show that the difference between these heat capacities for an ideal gas is equal to 'R', the gas constant. 3+1
- c) 20 g of  $N_2$  at 300 K is compressed reversibly and adiabatically from 20 litres to 10 litres. Calculate the final temperature, q, w,  $\Delta U$ . [Given  $C_v = 5 \text{ cal mol}^{-1}$ ]. 3
10. a) What is the Joule-Thomson's experiment? Show that it is an iso-enthalpic process and hence derive the expression for the Joule Thomson's co-efficient ( $\mu_{JT}$ ) for a van der Waals' gas. 1+3
- b) What are the differences between "Bond Energy" and "Dissociation Energy"? When these two will have the same value? 1+1
- c) Define the term "Heat of neutralization". The heat of neutralization of a strong acid by a strong base is 13.70 kcal, whereas the heat of neutralization of acetic acid by a strong base is 12.60 kcal. Calculate the molar heat of dissociation of acetic acid. 1+3