

**FIRST B. SC. EXAMINATION, 2017**

( 1st Semester )

**CHEMISTRY ( HONOURS )**

**PAPER - II**

Time : Two hours

Full Marks : 50

Use a separate answerscript for each group.

**GROUP - A**

1. Answer *any three* questions : 3×3
- a) Draw 'Z' vs. 'P' plot for a fixed mass of methane gas at a particular temperature which is lesser than its *Boyle temperature*. How will you explain this experimental finding ?
  - b) Define *critical state* of non-ideal gas. What will be the value of 'Z' for a non-ideal *van der Waals* gas ? Use the expressions of its critical constants.
  - c) A *van der Waals* gas cannot be liquefied above 32.3°C by increasing pressure and minimum pressure required to liquefy the gas at that temperature is 48.2 *atm*. Find the radius of the gas molecule.
  - d) What is *limiting density* ? How will you determine molar mass of non-ideal gas using it ?

[ Turn over

[ 2 ]

2. a) Define *saturated vapor pressure* of a liquid ? Why does the boiling point of liquid rise with increase of pressure ?  
3
- b) What are *cohesion* and *adhesion* forces ? Under what condition, the work of adhesion between solid and liquid is equal to the work of cohesion of the liquid ? 3

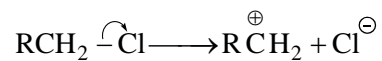
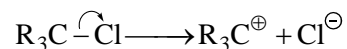
Or

Find the change in surface energy when two identical Hg droplets of diameter 2 mm merged isothermally to form 1 drop (surface tension of Hg = 49 mN.m<sup>-1</sup>).

- c) "Highly viscous liquids are less volatile" – justify or criticize. 2

### GROUP - B

3. a) Assuming that R<sub>3</sub>CCl and RCH<sub>2</sub>Cl have comparable free energies, which one of the following two reactions will occur more rapidly ? Use an energy profile diagram to explain your answer. Predict a structure for the transition state in each reaction. 3



[ 5 ]

6. What do you mean by atomic radii ? What are the techniques available to measure atomic radii ? Compare two types of atomic radii and explain how these two are related to the bond distance ?  
1+1+2+1
7. What is electron affinity ? How is it different from electronegativity ? How the electronegativity is related to the metallic character of an atom ? Comment on the feasibility of formation of M<sup>-</sup> in the light of electron affinity (where M is Na/K).  
1+1+1 $\frac{1}{2}$ +1 $\frac{1}{2}$

[ 4 ]

- e) With the help of  $\pi$ -MO picture of allyl cation, explain that its end carbons will react with a nucleophile. 2

### GROUP - C

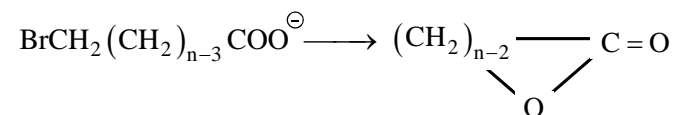
Answer question no. 4 and *any two* from the rest

4. i) Why do noble gases show very high ionization potential values? 1×6
- ii) What is the basis of measuring electronegativity by *Mulliken* scale?
- iii) What is lanthanide contraction?
- iv) Why the electron affinity of chlorine is greater than fluorine?
- v) What is the relation between ionic radii and effective nuclear charge?
- vi) Between  $\text{Cu}^+$  and  $\text{Cu}^{++}$  which one has greater ionization potential value?
5. Between Calcium and Zinc, which one has greater ionization potential and why? What are the anomalies observed in the case of Ga and Tl from the usual periodic trend of ionization potential of Gr-13 elements? Discuss with reasons.

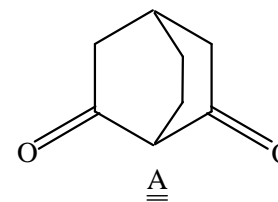
$$2\frac{1}{2} + 2\frac{1}{2}$$

[ 3 ]

- b) The relative rate constants at 50°C for the following reaction were found to be 21.7,  $1.5 \times 10^6$  and 1.0 when values of n were 3, 5 and 8, respectively. Explain the observation. 3



- c) Justify the following statements :
- i) While pentan-2, 4-dione is readily soluble in aqueous NaOH, the formally similar 1, 3-diketone A is insoluble in it. 3



- ii) Cyclopropanone forms a readily isolable hydrate.  $1\frac{1}{2}$
- ii) The ground state of  $:\text{C}(\text{OMe})_2$  is singlet.  $1\frac{1}{2}$
- d) Comment on the relation between  $\text{pK}_a$  of trichloroacetic acid (in water) and the  $\Delta G^\ominus$  for its ionisation in water. Explain that trichloroacetic acid is a stronger acid than acetic acid, though the enthalpy change for the ionisation in water remains approximately the same for the two acids. 3

[ Turn over