## Ex/B.Sc/CHEM/H/12/IV/A/2019 (Old)

# FIRST B.Sc. Examination, 2019

(2nd Semester, Old Syllabus)

## CHEMISTRY (HONOURS)

## PAPER - IV

Time: Two hours Full Marks: 50

Use a separate answer script for each group.

#### GROUP-A

1. Answer *any four* questions:

- $2\times4$
- a) State and explain the first law of thermo-chemistry or law of Lavoisier and Laplace.
- b) Explain what do you mean by enthalpy of combustion.
- c) The Enthalpy of combustion of ethyl alcohol and acetic acid are -325.1 and -209.5 KCal<sup>mol-1</sup>. Calculate the heat change in the reaction:

$$C_2H_5OH(l) + O_2(g) = CH_3COOH(l) + H_2O(l)$$

- d) The heat of neutralization of HCN by NaOH is -2.9KCal mol<sup>-</sup>. Calculate the heat of ionization of HCN, given that the heat of neutralization of H<sup>+</sup> by OH<sup>-</sup> is -13.8 KCal mol<sup>-</sup>
- e) Calculate the enthaply of formation of cane sugar form the follwings data:

[ Turn over

 $CH_{3}CH = CH - CH_{2}CI \xrightarrow{\text{NaOEt in} \atop \text{EtOH}} C + \mathbf{D} \frac{\text{NaOEt in}}{\text{EtOH}} CH_{3} - CH - CH = CH_{2}$  CI  $\mathbf{A} \qquad \qquad \mathbf{B}$   $1 \frac{1}{2} + 1 \frac{1}{2}$ 

e) Show the mechanism of sodium metal - induced polymerisation of isoprene ( ). 3

#### GROUP-C

- 4. a) Calculate the pH of  $100 \, \text{mL} \, 0.1 \, (\text{N})$  acetic solition when (i)  $00 \, \text{mL}$ , (ii)  $99 \, \text{ml}$  and (iii)  $100 \, \text{mL}$  and (iv)  $101 \, \text{mL}$  of  $0.1 \, (\text{N}) \, \text{NaOH}$  is added to it. [Given:  $K_a = 1.8 \times 10^{-5}$ ] 6
  - b) How can you separate Cu<sup>2+</sup> and Cd<sup>2+</sup> from their mixture
    ? Discuss and give reactions.
  - c) What do you mean by buffer solution? Discuss mechanism of buffer action.
  - d) What is the basis of selection of an indicator in acid-base titration?
  - e) Can Fe<sup>3+</sup> and Mg<sup>2+</sup> be separeted quantitatively as hydroxide from solution that is 0.10 M with respect to each cation? Consider a precipitation to be quantitative when all but 1 part in 10000 of the ion has been removed from solution.

[given:  $K_{sp}$  of  $Fe(OH)_3 = 2.0 \times 10^{-39}$  and  $Mg(OH)_2 = 7.1 \times 10^{-12}$ ]

- i)  $C(s) + O_2(g) = CO_2(g)$ ,  $\Delta H = -94.0 \text{ KCal}$
- ii)  $2H_2(g) + O_2(g) = 2H_2O(l)$ ,  $\Delta H = -136.0$ KCal
- iii)  $C_{12}H_{22}O_{11}(s) + 12O_2(g) = 12CO_2(g) = 11H_2O(l)$

 $\Delta H = -1350.0$ KCal

## 2. Answer *any three* questions:

 $3\times3$ 

- a) Compute the limiting ratio of radius of cation and anion in body centred ionic cubic crystal.
- b) Calculate the percent void space in a face centred cubic system.
- c) Prove that  $\frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{l}\right)^2 + \left(\frac{l}{c}\right)^2$ . Where the terms bear usual significance in a crystal system.
- d) i) Calculate the Miller indices of the two feces having the intercepts with the three axes as.
  - $\left(\frac{1}{2}a,2b,\infty c\right)$  and (2a,3b,4c), where a, b, c are unit length along three axes.
  - ii) Which is the plane of closest packing in face centred cubic structure?

### **GROUP-B**

- 3. a) Predict the product of the following reactions and give plausible mechanism in each case (any *three*). 2×3
  - i)  $(CH_3)_3C-C \equiv C-H \xrightarrow{1\% HgSO_4} \frac{1\% GSO_4}{20\% H_2SO_4, 60-80^0C}$
  - ii)  $erythro CH_3CHBrCHBrCH_3 \xrightarrow{NaI \text{ in} \atop EtOH}$
  - iii)  $Me_zCHCH_2NMe_z \xrightarrow{(I)H_2O_2} (II)150^0C$
  - iv)  $\frac{I_2,C_6H_5COOAg}{\text{anhyd. CCl}_4 \text{ reflux}}$
  - b) Draw Hofmann and Saytzeff tranition states of  $E_2$  reaction of Me<sub>2</sub>CH CHBrMe in the presence of NaOR. Explain how the ratio of the products changes with the size of the R group.  $2\frac{1}{2}$
  - c) Identify the most successful route for the following reactions and justify your answer.  $2\frac{1}{2}$

$$OH \xrightarrow[route-I]{H^{\oplus}} \longleftrightarrow NaOEt in EtOH \\ route-II$$

d) At low NaOEt concentration, both the following chloro compounds **A** and **B** give the same products **C** and **D** in the same ratio. Write the structures of **C** and **D** and account for the result.