# 3/EH-23 (iii) (Syllabus-2019)

# (2)

# Odd Semester, 2020

(Held in March, 2021)

# **CHEMISTRY**

(Elective/Honours)

(Chem-EH-301)

## ( General Chemistry—III )

Marks: 56

Time: 3 hours

The figures in the margin indicate full marks for the questions

### SECTION—I

## (Inorganic)

( *Marks* : 18 )

- **1.** (a) Discuss the variation of atomic and ionic radii of an element across the period and down the group.
  - (b) Electron gain enthalpy of chlorine is higher than that of fluorine. Explain. 1½
  - (c) What is catenation? Explain the uniqueness of carbon to catenate.  $2\frac{1}{2}$

(d) Give one preparation and one use of lithium aluminum hydride.

#### OR

- **2.** (a) The oxidising character of elements increases and reducing character decreases as we move from left to right in a period. How would you explain this observation?
  - b) Arrange in decreasing order the acid strength of oxyacid of halogen of the type HOX (X = Cl, Br, I). Give reason to your answer and also indicate the Na salt of the above oxyacid used mainly as a disinfectant in the recent Covid-19 pandemic. 2+1=3
  - (c) Ionisation energies of C, N and O follow the order C < N > O. Explain. 2
  - (d) Give one method of preparation and one use of sodium thiosulphate. 2
- **3.** (a) Explain why most of the compound of transition metals are generally coloured.
  - (b) Lanthanides exhibit + 3 most common oxidation state whereas certain lanthanides also show + 2 and + 4 oxidation state. Explain.

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- (c) Actinides have greater tendency to form complexes than lanthanides. Explain. 1½
- (d) What happens when-
  - (i) Ni(CO)<sub>4</sub> is heated above 150 °C;
  - (ii) ferric salt reacts with potassium ferrocyanide?

(Write down the balance chemical reaction wherever necessary.)  $1\frac{1}{2}+1\frac{1}{2}=3$ 

### OR

- **4.** (a) What is lanthanide contraction and what are its consequences? 1+2=3
  - (b) In the 1st transition series, oxidation state increases from Sc<sup>+3</sup> to Mn<sup>+7</sup> and then decreases back from Mn<sup>+7</sup> to Zn<sup>2+</sup>. Give reason to your answer.
  - (c) What are transuranic elements? Give one example.
  - (d) What happens when—
    - (i) KMnO<sub>4</sub> is treated with KI solution in acidic medium;
    - (ii)  $UF_4$  is treated with  $F_2$ ?

(Write down the balance chemical reaction wherever necessary.)  $1\frac{1}{2}+1\frac{1}{2}=3$ 

### SECTION—II

## (Organic)

( Marks : 19 )

**5.** (a) How is acetic acid (CH<sub>3</sub>COOH) prepared from acetonitrile (CH<sub>3</sub>CN)? Write chemical equation and its mechanism.

1+1=2

- (b) Complete the following reactions:  $1\times3=3$ 
  - (i)  $CH_3COOH + CH_2N_2 \rightarrow ?$

- (c) What are organometallic compounds? Give a method for the preparation of Grignard reagent. Write chemical equation.  $\frac{1}{2}+1+\frac{1}{2}=2$
- (d) Starting from ethyl acetoacetate, how will you synthesize succinic acid? 2½

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### OR

**6.** (a) Arrange the following acids in order of increasing acidity. Explain with appropriate reasons: 1½

$$\begin{array}{c|cccc} \mathrm{CH}_2\mathrm{-COOH} & \mathrm{COOH} & \mathrm{COOH} \\ | & | & \mathrm{CH}_2\mathrm{-COOH} \\ \end{array} , \quad \begin{array}{c|cccc} \mathrm{COOH} \\ \mathrm{COOH} \end{array} , \quad \begin{array}{c|ccccc} \mathrm{COOH} \\ \mathrm{COOH} \end{array}$$

(b) Identify the products in the following reactions: 1+1=2

(i) 
$$CH_3 - C - C1 - \frac{NH_3}{\Lambda} ? - \frac{H_2O/H^{\oplus}}{}?$$

(ii) 
$$R - C - OH - SOCl_2 \rightarrow ? R'COOH \rightarrow ?$$

- (c) Differentiate between resonance and tautomerism. 2
- (d) Using a suitable Grignard reagent, prepare the following compounds: 1+1=2

(ii) CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>

- (e) Complete the following reactions: 1+1=2
  - (i)  $CH_3CH_2CH_2CH_2Li +$

$$CH_2$$
  $CH_2$   $H_2O$  ?

(ii) 
$$CH_2 + H_2N - C - NH_2 \xrightarrow{EtONa}$$
?

- 7. (a) Give the synthesis of propylamine by Gabriel phthalimide reaction with mechanism.
  - (b) Explain, giving examples, why the  $\alpha$ -H atom of nitro-alkanes is acidic. 1½
  - (c) How can you separate a mixture of  $1^{\circ}$ ,  $2^{\circ}$  and  $3^{\circ}$  amines? Give chemical equations.  $1\frac{1}{2}$
  - (d) Which of the following pairs of compounds is more basic? Give reasons: 1½×2=3

(i) 
$$CH_3CH_2NH_2$$
 and  $\bigcirc$   $NH_2$ 

(ii) 
$$CH_3$$
— $O_2N$ — $NH_2$  and  $O_2N$ — $NH_2$ 

(e) Complete the following reactions: 2

(i) 
$$\langle \bigcirc \rangle$$
-NH<sub>2</sub>-Br<sub>2</sub>/H<sub>2</sub>O  $\rightarrow$ ?

(ii)  $CH_3NH_2 + CHCl_3 + KOH \rightarrow ?$ 

### OR

- **8.** (a) Nitration of aniline produces *m*-nitroaniline as major product even though the amino group is *o* and *p*-directing. Explain giving equations. 1½
  - (b) How will you prepare ethanamine from propanamide? Write its mechanism. 2
  - (c) Identify the products in the following reactions:

$$\begin{array}{c|c}
O \\
C \\
C \\
OH \\
\hline
\begin{array}{c}
(i) & NH_3 \\
(ii) & \Delta
\end{array}$$

$$\begin{array}{c}
Br_2/KOH \\
\hline
\begin{array}{c}
O+5 \circ C
\end{array}$$

$$\begin{array}{c}
CuCN/KCN
\end{array}$$

- (d) How will you carry out the following conversions?  $1\frac{1}{2}\times2=3$ 
  - (i) Nitrobenzene to benzene
  - (ii) Aniline to p-hydroxyazobenzene

(e) Amines have higher boiling points than the hydrocarbons of corresponding molecular mass. Explain.

SECTION—III

### (Physical)

( Marks: 19)

- **9.** (a) State Carnot's theorem and write an expression for the efficiency of the Carnot's engine. 1+1=2
  - (b) Derive an expression for variation of free energy with temperature and pressure.
  - (c) Derive the relation between  $K_p$  and  $K_c$ .  $2\frac{1}{2}$
  - (d) The value of  $K_p$  for the reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

is  $1.06 \times 10^5$  at 25 °C. Calcualte the standard state free energy change  $(\Delta G^\circ)$  of the reaction at 25 °C.  $(R = 8.314 \, \text{JK}^{-1} \, \text{mol}^{-1})$ 

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OR

- **10.** (a) Derive Gibbs-Helmholtz equation.
  - (b) State Le Chatelier's principle and discuss the effects of temperature and pressure on the following reaction: 1+2=3  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$   $\Delta H = -92 \cdot 38 \text{ kJ}$
  - (c) State and explain the law of mass action.
  - (d) Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K. The molar heat of vaporisation of ethanol is 39.84 kJ mol<sup>-1</sup>.
- **11.** (a) Explain the phenomenon of osmosis. 2
  - (b) What is van't Hoff factor? What is the cause of abnormal molecular weights of solutes in solution? 1+2=3
  - (c) Explain Brownian movement. 2
  - (d) A solution of  $12.5 \,\mathrm{g}$  of non-volatile solute in 170 g of water gave boiling point elevation of  $0.63 \,\mathrm{K}$ . Calculate the molar mass of the solute.  $(K_b = 0.52)$

OR

- **12.** (a) What are colloids? What are the differences between lyophilic and lyophobic colloids? 1+2=3
  - (b) Explain the phenomenon of Tyndall effect in colloids.

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- (c) State Henry's law. What are its limitations?
- (d) At 298 K, the vapour pressure of ether is 442 mm of Hg. When 6·1 g of a substance was dissolved in 50 g of ether, the vapoure pressure fell to 410 mm. Calculate the molecular weight of the substance. (Molecular weight of ehter = 74)

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