

**3/EH-23 (iii) (Syllabus-2015)**

**2019**

**( October )**

**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) Account for the fact that "compounds in the +2 oxidation state of lead are more stable than its compounds in +4 oxidation state". 2
- (b) Define ionization potential. What are the factors on which ionization potential depends upon? 1+1=2
- (c) Give one method of preparation and one use of boric acid. 1+1=2

( 2 )

OR

2. (a) Why has lithium a greater tendency to form covalent compounds than other elements in group 1?  $1\frac{1}{2}$
- (b) What happens when sodium thiosulphate is treated with a solution of ferric chloride?  $1\frac{1}{2}$
- (c) Write one method of preparation and one use of the following compounds :  $1\frac{1}{2}+1\frac{1}{2}=3$
- (i) Lead tetraacetate
- (ii) Potassium iodide
3. (a) Give reasons why most of the *d*-block elements behaves as catalyst.  $1\frac{1}{2}$
- (b) Write down the analytical differences between  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  in various mediums.  $1\frac{1}{2}$
- (c) Explain the separation of Lanthanides on the basis of ion exchange method. 3

OR

4. (a) Explain why transition elements show variable oxidation states than other elements. 2

( Continued )

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( 3 )

- (b) Give one similarity and dissimilarity between lanthanoids and actinoids. 2
- (c) Write one method of preparation and one use of potassium ferricyanide. 2
5. (a) Give the IUPAC names of the following :  $1\times 3=3$
- (i)  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
- (ii)  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$
- (iii)  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$
- (b) Using effective atomic number (EAN) rules, calculate the EAN value of Fe in  $[\text{Fe}(\text{CN})_6]^{4-}$ . 2
- (c) Write down the ionization isomers of  $[\text{Cr}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$ . 1

OR

6. (a) What is an ambidentate ligand? Giving example, show how it differs from a bidentate ligand. 2

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( Turn Over )

( 4 )

- (b) Explain hydrate isomerism by using a suitable example. 2
- (c) Draw the geometrical isomers of  $[\text{CoCl}_2(\text{en})_2]^+$  and indicate which isomer is optically active. 2

SECTION—II

( Organic )

( Marks : 19 )

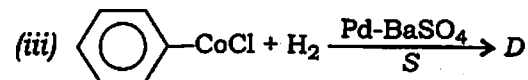
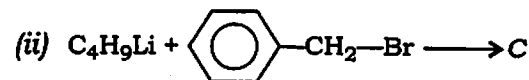
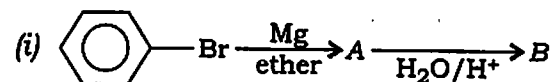
7. (a) Discuss the effect of electronegative elements on the acidity of aliphatic carboxylic acids with suitable examples.  $1\frac{1}{2}$
- (b) Write the preparation of  $\text{H}-\text{COOH}$  from oxalic acid. 1
- (c) How can acetyl chloride be converted into—  
(i) acetamide;  
(ii) acetic anhydride? 2
- (d) Synthesise the following, using a suitable Grignard reagent : 2
- (i)  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
- (ii) A secondary alcohol

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( Continued )

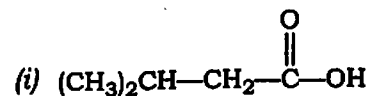
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- (e) Complete the following reactions : 3



OR

8. (a) Synthesise the following compounds from malonic ester (any one) : 2



(ii) Crotonic acid

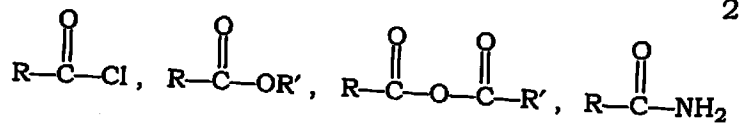
- (b) Explain why dry ether is used in the preparation of Grignard reagents. 1
- (c) How will you convert the following? 2
- (i) Ethanoic acid into methyl acetate
- (ii) Ethanoic acid into ethanamide

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( Turn Over )

( 6 )

- (d) Arrange the relative reactivity of the following carboxylic acid derivatives towards nucleophilic substitution with justification :



2

- (e) Write the different tautomeric forms of ethyl acetoacetate.

1

- (f) Write the preparation of citric acid from glycerol.

1½

9. (a) Why cannot aryl amines be prepared by Gabriel phthalimide synthesis?

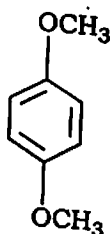
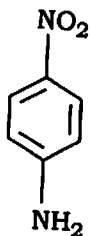
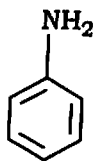
1

- (b) Outline the synthetic route of aniline from benzene.

2

- (c) Arrange the following molecules in order of their increasing basic strength with proper justification :

2



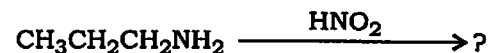
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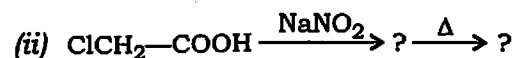
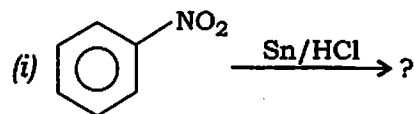
- (d) Complete the following reaction by writing a suitable mechanism :

2



- (e) Write the products of the following reactions :

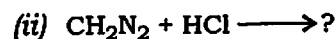
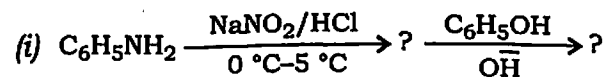
1+1½



OR

10. (a) Identify the products in the following reactions :

1½+1



- (b) Discuss the formation of different products on the treatment of methyl amine, dimethyl amine and trimethyl amine with  $\text{HNO}_2$ .

3

- (c) How will you prepare  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$  using diazomethane and ethanoic acid?

1

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( Turn Over )

( 8 )

- (d) Why is nitromethane acidic in nature? 1  
(e) Convert—  
(i) aniline into chlorobenzene;  
(ii) benzene diazonium chloride into cyanobenzene. 2

SECTION—III

( Physical )

( Marks : 19 )

11. (a) Derive an expression for the variation of Gibb's free energy with temperature and pressure. 3  
(b) Calculate the amount of heat supplied to a Carnot's cycle working between 368 K and 288 K if the maximum work obtained is 895 joules. 2  
(c) Give the thermodynamic derivation of the law of chemical equilibrium for a general reaction :  
$$aA + bB + \dots \rightleftharpoons lL + mM + \dots$$
  
(d) The equilibrium constant for the reaction  $H_2(g) + S(g) \rightleftharpoons H_2S(g)$  is 20.2 a.t.m. at 945 °C and 9.21 a.t.m. at 1065 °C. Calculate the heat of the reaction. 2

( 9 )

OR

12. (a) Differentiate between Gibb's free energy and Helmholtz free energy. 1½  
(b) One mole of an ideal mono-atomic gas expands reversibly from a volume of 10 dm<sup>3</sup> at a temperature of 298 K to a volume of 20 dm<sup>3</sup> at a temperature of 250 K. Assuming that  $C_V = \frac{3}{2}R$ . Calculate the entropy change for the process. 3  
(c) Derive van't Hoff equation for temperature dependence of equilibrium constant  $K_p$ . 3  
(d) At 473 K the equilibrium constant  $K_c$  for the decomposition of  $PCl_5$  is  $8.3 \times 10^{-3}$ . If the decomposition proceeds as  $PCl_5 \rightarrow PCl_3 + Cl_2$ , find  $K_p$  for the reaction. 2
13. (a) Derive the integrated rate law for a second-order reaction having one reacting species. 3  
(b) Why is the hydrolysis of an ester  $CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH$  Called a pseudounimolecular reaction though more than one kind of reactants are involved? 1½

( 10 )

- (c) What are colligative properties? Give examples. 2
- (d) A 0.5% aqueous solution of potassium chloride was found to freeze at  $-0.24^{\circ}\text{C}$ . Calculate the vant's Hoff factor. [Given  $K_f = 1.86 \text{ K kg mol}^{-1}$ ]. 3

OR

14. (a) From the following data, show that the decomposition of hydrogen peroxide in aqueous solution is a first-order reaction :

Time (min) :	0	15	30
V (ml) :	25.4	9.83	3.81

Where  $V$  is the volume of potassium permanganate required to decompose a definite volume of hydrogen peroxide. 2

- (b) The rate constant for the first-order reaction is

$$\log K (\text{s}^{-1}) = 14.34 - \frac{1.25 \times 10^4 K}{T}$$

Calculate the—

(i) actuation energy;

(ii) rate constant  $K$  at  $427^{\circ}\text{C}$ . 2½

( 11 )

- (c) What is reverse osmosis? What are its applications? 2
- (d) The freezing point of a solution containing 0.3 g of an organic compound in 30.0 g benzene is lowered by  $0.45^{\circ}\text{C}$ . Calculate the molecular weight of the compound. [Given  $K_f$  for benzene =  $5.12 \text{ K kg mol}^{-1}$ ]. 3

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