

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

2 0 1 7

(October)

CHEMISTRY

(Elective/Honours)

(**General Chemistry-III**)

(Chem-EH-301)

Marks : 56

Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

SECTION—I

(**Inorganic**)

(Marks : 18)

1. (a) Write two important characteristics of alkali metals. 1

(b) Account for the facts that—

(i) compounds in the +2 oxidation state of Pb are more stable than its compounds in the +4 oxidation state;

(ii) although beryllium and aluminium belong to different groups in the periodic table, they resemble each other closely.

2+2=4

(Turn Over)

(2)

- (c) Arrange the following elements in increasing order of their electro-negativities :

Li, K, Be, Cs

OR

2. (a) Explain with reasons the following observations : $1\frac{1}{2} + 1\frac{1}{2} = 3$

(i) CO_2 is a gas but SiO_2 is a high-melting solid.

(ii) NCl_3 is a better Lewis base than NF_3 .

- (b) Write one method of obtaining lithium aluminium hydride, LiAlH_4 and describe one chemical application of the compound as a reducing agent.

3. (a) Comment on the following statement :

"All transition metals are *d*-block elements but all *d*-block elements are not transition metals."

- (b) Write the probable oxidation states of manganese (Mn). Which of the oxidation states is most stable and why?

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(Continued)

(3)

- (c) Write a method of preparation of potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$ and its reaction with copper sulphate solution.

OR

4. (a) Write the actions of (i) $\text{K}_2\text{Cr}_2\text{O}_7$ on FeSO_4 in the presence of dil. H_2SO_4 and (ii) KMnO_4 on oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) acidified with dil. H_2SO_4 .

- (b) What is meant by lanthanide contraction? Write the consequences of lanthanide contraction.

- (c) Write the general electronic configurations of lanthanides and actinides.

5. (a) What is a ligand? Give one example of multidentate ligand with its structure.

- (b) Calculate the effective atomic number of Fe in $\text{Fe}(\text{CO})_5$.

- (c) Draw the geometrical isomers of $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$ and name them as per IUPAC nomenclature.

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(Turn Over)

(4)

OR

6. (a) Comment on the statement, "While $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is optically inactive the complex $[\text{Co}(\text{en})_3]^{+3}$ is optically active". Write the structures for the optical isomers. 3
- (b) Draw the crystal-field splitting diagrams for octahedral and tetrahedral complexes. 3
- Explain why crystal-field stabilization energy (CFSE) of an octahedral complex is higher than that of a tetrahedral complex.

SECTION—II

(Organic)

(Marks : 19)

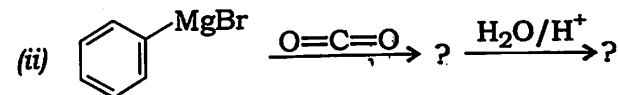
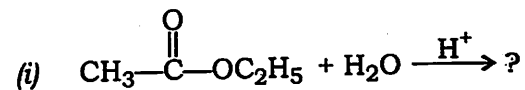
7. (a) Explain why carboxylic acids have higher boiling points than alcohols of similar molecular weight. $1\frac{1}{2}$
- (b) Arrange the following acids in order of increasing acidity with appropriate reasons : $1\frac{1}{2}$
- ICH_2COOH , BrCH_2COOH ,
 ClCH_2COOH , FCH_2COOH

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(5)

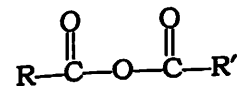
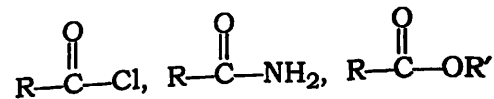
- (c) Complete the following reactions with mechanisms : $1\frac{1}{2} \times 2 = 3$



- (d) Write the tautomeric forms of diethyl malonate. 1
- (e) Starting from diethyl malonate how are the following compounds synthesized? 1
- (i) Malonyl urea 1
- (ii) Succinic acid $1\frac{1}{2}$

OR

8. (a) Explain the order of reactivity of the following acid derivatives in nucleophilic substitution reactions : 3



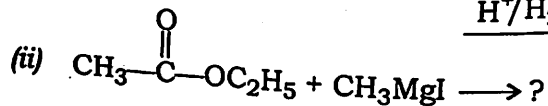
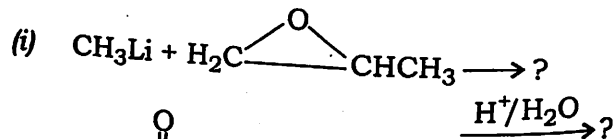
- (b) Why are organolithium compounds more reactive than Grignard reagents? 1

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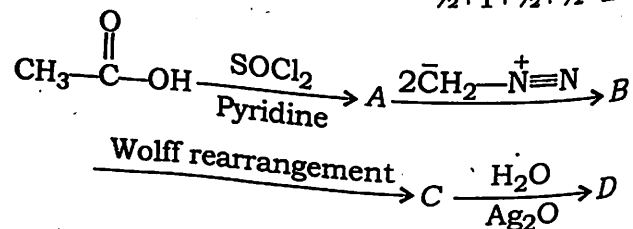
(6)

(c) Complete the following reactions : 1+1=2



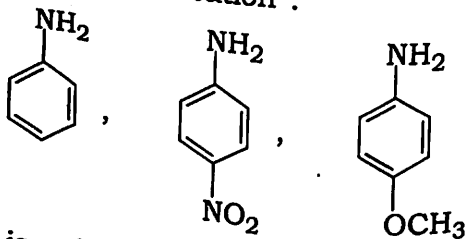
(d) Complete the following reactions :

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



(e) What happens when oxalic acid is heated with glycerol at 230 °C? Give chemical equation. 1

9. (a) Arrange the following aromatic amines in order of increasing basic strength with proper justification : 2



(b) How is primary amine synthesized by Gabriel phthalimide synthesis? 1½

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(7)

(c) What happens when—

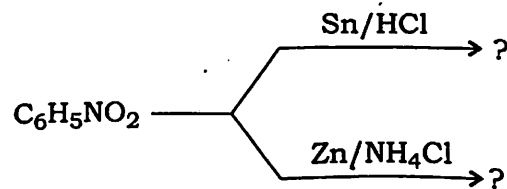
(i) aniline is treated with a mixture of NaNO_2 and HCl at 273 K;

(ii) methylamine is warmed with carbon disulphide in the presence of mercuric chloride?

Explain with mechanism. $1\frac{1}{2} + 1\frac{1}{2} = 3$

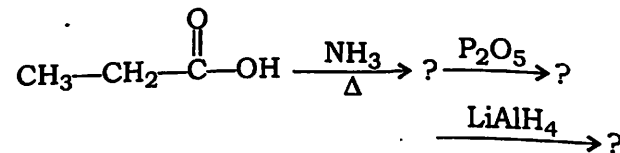
(d) Starting from an alkylhalide, how is nitroalkane prepared? 1

(e) Complete the following reactions : 1+1=2



OR

10. (a) Complete the following reactions : 1½



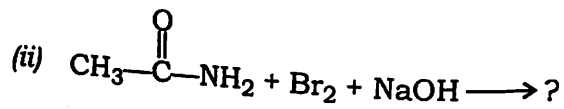
(b) Explain with chemical equations the reactions of primary, secondary and tertiary amines with HNO_2 . 3

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(Turn Over)

(8)

(c) Complete the following reactions with mechanisms : $1\frac{1}{2}+1\frac{1}{2}=3$



(d) How will you convert—

(i) aniline to chlorobenzene;

(ii) aniline to *o*-nitroaniline and *p*-nitroaniline? $1+1=2$

SECTION—III

(Physical)

(Marks : 19)

11. (a) Write an expression for the efficiency of a Carnot's engine. How can the efficiency of a heat engine be increased? 2

(b) Establish the relation : $2\frac{1}{2}$

$$dG = VdP - SdT$$

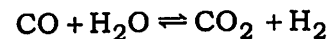
(c) Derive the relation between K_p and K_c . 3

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(9)

(d) The value of K_p for the reaction



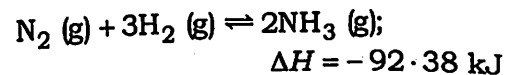
is 1.06×10^5 at $25^\circ C$. Calculate the standard state free energy change (ΔG°) of the reaction at $25^\circ C$. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$) 2

OR

12. (a) Derive the Clausius-Clapeyron equation for the equilibrium of the type

liquid \rightleftharpoons vapour 3

(b) State Le Chatelier's principle and discuss the effects of temperature and pressure on the following reaction : 3



(c) State the law of mass action. $1\frac{1}{2}$

(d) Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K . The molar heat of vaporization of ethanol is $39.84 \text{ kJ mol}^{-1}$. 2

13. (a) Derive an expression for the rate constant of a second-order reaction of the type $2A \rightarrow \text{Products}$. 3

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(Turn Over)

- (b) Discuss the effect of catalyst on the rate of a reaction. 2
- (c) What are colligative properties? Give examples. 2
- (d) 10 g of a substance is dissolved in 100 g of water at 25 °C. The vapour pressure of water is lowered from 17.5 mm to 17.2 mm. Calculate the molecular weight of the substance. 2½

OR

14. (a) State Henry's law. What are the limitations of Henry's law? 2
- (b) What is van't Hoff factor? What is the cause of abnormal molecular weights of solutes in solutions? 1+2=3
- (c) What is a zero-order reaction? Give examples. 2
- (d) The rate constant of a certain hydrolysis reaction is 2.3×10^{-2} lit mol⁻¹ S⁻¹ at 0 °C and 8.2×10^{-2} lit mol⁻¹ S⁻¹ at 15 °C. Find the activation energy of the reaction. 2½
