

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

2 0 1 8

(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) Explain why the s-block elements do not exhibit variable valencies. 1
- (b) What type of oxides will an element with atomic number 11 form? Write down the reaction of this metal oxide with water. 2
- (c) Write down one method of preparation and one use of the following compounds : $1\frac{1}{2} \times 2 = 3$
- (i) Boric acid
- (ii) Sodium thiosulphate

(2)

OR

2. (a) What is catenation? Give reasons why on going down the group, the tendency for catenation decreases. 2
- (b) Write down one method of preparation of AlCl_3 along with the balanced chemical equation and draw its structure. $1\frac{1}{2} + \frac{1}{2} = 2$
- (c) Give reasons for the following : $1 \times 2 = 2$
- (i) Sulphur can form SF_6 molecule but oxygen cannot form OF_6 molecule
- (ii) The electron affinity of fluorine is lower than that of chlorine
3. (a) Explain why transition elements show more oxidation states than other elements. 2
- (b) Give a reason why the radii of the elements of the third transition series are very similar to those of second transition series. 1
- (c) Give a method for the preparation of UF_6 . 1
- (d) Explain the separation of lanthanides on the basis of ion-exchange method. 2

(3)

OR

4. (a) Write down the preparation of $\text{K}_2\text{Cr}_2\text{O}_7$ starting from chromite ore along with the chemical equations. Draw the structure of $\text{Cr}_2\text{O}_7^{2-}$. $2\frac{1}{2}$
- (b) Mention two points of similarities and differences between lanthanides and actinides. 2
- (c) Give reasons why most of the *d*-block elements can act as catalyst. $1\frac{1}{2}$
5. (a) What is a chelating ligand? Write down two applications of chelate formation. $1+2=3$
- (b) Write down the important postulates of Werner's coordination theory. Why is the complex $\text{CoCl}_3 \cdot 3\text{NH}_3$ non-ionic according to this theory? 3

OR

6. (a) Give the IUPAC names of the following complexes : $1 \times 2 = 2$
- (i) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
- (ii) $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$

(4)

- (b) Explain using the valence bond theory why $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion is paramagnetic but $[\text{Fe}(\text{CN})_6]^{2-}$ ion is low-spin diamagnetic complex. 3
- (c) Identify the kind of isomerisms exhibited by the following isomers: $\frac{1}{2} \times 2 = 1$
- (i) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ and $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$
- (ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$

SECTION—II

(Organic)

(Marks : 19)

7. (a) How are carboxylic acids prepared from alkyl cyanides? Discuss with mechanism. $1\frac{1}{2}$
- (b) Explain with chemical equations, what happens when acetic acid is—
- (i) heated with phosphorous pentoxide;
- (ii) treated with chlorine in the presence of red phosphorous;
- (iii) reduced with lithium aluminium hydride. $1 \times 3 = 3$

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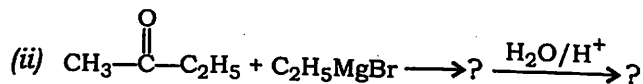
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(5)

- (c) Arrange the following acids in order of increasing acidity. Explain with appropriate reasons : $1\frac{1}{2}$

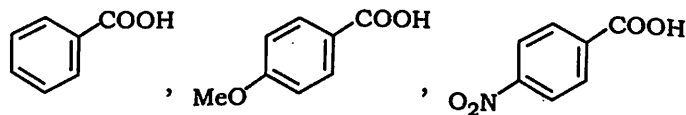


- (d) What is the role of ether in the preparation of Grignard reagent? Why is it important to use anhydrous condition in the preparation of Grignard reagent? $1\frac{1}{2}$
- (e) Write down the products in the following reactions : $1 \times 2 = 2$



OR

8. (a) Explain the mechanism of nucleophilic substitution in acid derivatives. Why are esters less reactive than acid chlorides? 2
- (b) (i) Explain the weak acidic and basic characters of amides. 1
- (ii) Arrange the following carboxylic acids in increasing order of acidity and explain with appropriate reasons : $1\frac{1}{2}$

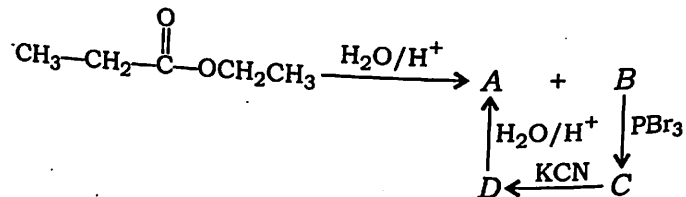


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(6)

- (c) Complete the following reactions : 2



- (d) Starting from ethyl acetoacetate, how are the following compounds synthesized? 2

- (i) Cinnamic acid
(ii) Succinic acid

- (e) What happens when succinic acid is heated in a current of dry ammonia? Explain with chemical equations. 1

9. (a) Discuss the mechanism of Hofmann rearrangement. On the basis of this mechanism, explain why the reaction cannot be used to prepare secondary and tertiary amines. 2

- (b) Explain with chemical equations the reaction of aniline with—
(i) $\text{Br}_2\text{—H}_2\text{O}$;
(ii) benzoyl chloride. 1+1=2

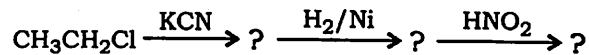
- (c) How can you explain the fact that trimethylamine (bp 3 °C) boils lower than dimethylamine (bp 7 °C)? 1

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(7)

- (d) Complete the following reactions : 1½



- (e) Account for the following facts : 1×3=3

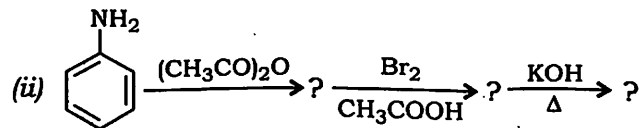
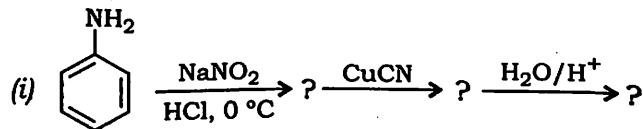
- (i) Aniline does not undergo Friedel-Crafts reaction
(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts
(iii) Benzene diazonium sulphate is preferably used for the production of phenol rather than hydrochloride

OR

10. (a) Explain through equations the Hinsberg method of differentiating primary, secondary and tertiary amines. 1½

- (b) What is Sandmeyer reaction? Give a plausible mechanism of the reaction with explanation using specific set of reagents. 1½

- (c) Complete the following reactions : 1½×2=3



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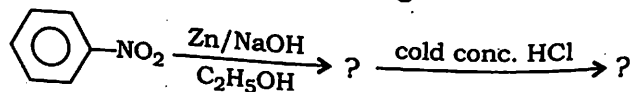
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(8)

(d) What would be the product if a solution of aniline in concentrated H_2SO_4 is mixed with concentrated HNO_3 ? Explain with equations. 1½

(e) (i) Explain why nitrobenzene undergoes electrophilic substitution with difficulty. 1

(ii) Complete the following reactions : 1



SECTION—III

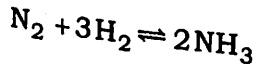
(Physical)

(Marks : 19)

11. (a) Derive Gibbs-Helmholtz equation. 3

(b) Obtain an expression for entropy change of an ideal gas with respect to change in temperature and volume. 3

(c) Write the expression for the equilibrium constant of the reaction 1½

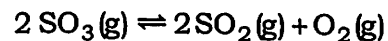


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(9)

(d) Calculate K_c for the reaction



at $27^\circ C$. K_p for the reaction is 3.5×10^{-23} atm at $27^\circ C$. 2

OR

12. (a) Derive van't Hoff equation for the temperature dependence of equilibrium constant. 3

(b) Show that $K_p = K_c (RT)^{\Delta n}$. 3

(c) For a heat engine, the source is at $500 K$ and the sink is at $300 K$. What is the efficiency of this engine? 2

(d) State Trouton's rule. 1½

13. (a) Define order and molecularity of a reaction with an example. 2+1=3

(b) What are pseudo-unimolecular reactions? Give examples. 2

(c) State Raoult's law for lowering of vapour pressure. Derive this law. 1+1½=2½

(d) Explain why abnormal molar mass is observed in certain cases. 2

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(Turn Over)

OR

14. (a) Derive the integrated rate equation of first-order reaction. 3
- (b) Write Arrhenius expression for the temperature-dependence of reaction rate and explain the terms involved. 2
- (c) Derive a relation between the osmotic pressure of a solution and molecular mass of the solute. 2
- (d) Find the boiling point of a solution containing 0.36 gm of glucose ($C_6H_{12}O_6$) dissolved in 100 gm of water ($K_b = 0.52 \text{ K/m}$, molar mass of glucose = 180). 2½
