2022

(November)

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)* Differentiate between oxides of Li and Na by giving reaction of respective element with O_2. Also write the reaction of the metal oxides with water. 1½

   (b) Comment on the following : 1½+1½=3

   (i) The second ionisation of enthalpy of group II elements is lower than the first ionisation enthalpy.

(ii) Both Be and Al show similar properties.

(c) Write one method of preparation of lithium aluminium hydride, $LiAlH_4$ and mention one of its uses. 1½

OR

2. (a) Discuss the trend of basicity exhibited by the oxides and hydroxides of Group–13 elements. 1½

(b) Explain the following : 1½+1½=3

(i) Fluorine does not form oxyacids

(ii) Pb^{4+} is less stable than Pb^{2+} ion in compound formation

(c) Give one method of preparation of boric acid and mention one of its uses. 1½

3. (a) Why does Mn exhibit the highest oxidation state among the first transition series elements? 1½

(b) Explain with reason— 1½+1½=3

(i) Zn and Zn^{2+} are not considered as transition element or ion;

(ii) Cl^{4+} is more stable than Ce^{3+} ion.

(c) Write down one method of preparation of nickel tetracarbonyl and draw its structure. 1½

OR

4. (a) Write the electronic configuration of actinide with atomic number 92. Name the element. 1

(b) Explain the following facts : 1½+1½=3

(i) Actinides exhibit greater multiplicity of oxidation states compared to lanthanides.

(ii) The atomic radii of lanthanides progressively decrease from cerium to lutetium.

(c) Discuss how can the difficulties of seperation of lanthanides be overcome by ion-exchange method. 2

5. (a) What is EAN? Calculate the EAN of $[Cu(CN)_4]^{3-}$. 2

(b) Give the IUPAC name of

$[Co(NH_3)_2(H_2O)ClBr(ONO)]$ 1

(c) Draw the isomer of $[Co(NH_3)_3Cl_3]$. 1

(d) Give the hydration isomer of $CrCl_3 \cdot 6H_2O$. Give the reaction with $AgNO_3$. 2

OR

6. (a) Depict the splitting of *d*-orbitals in octahedral field. Explain the reason why splitting of *d*-orbitals in tetrahedral and octahedral fields are inverse of one another. 1+1=2

(b) Account for the following facts :

(i) According to crystal field theory, complexes of Ti^{3+} are coloured while complexes of Sc^{3+} are colourless.

(ii) According to valence bond theory, $[Fe(CN)_6]^{4-}$ is diamagnetic whereas $[Fe(H_2O)_6]^{2+}$ is paramagnetic. 1½+1½=3

(c) Define weak field ligands and strong field ligands. 1

SECTION—II

(Organic)

(*Marks* : 19)

7. (a) How are carboxylic acids prepared from alkyl cyanides? Discuss with mechanism. 1½

(b) Arrange the following in decreasing order of pK_a : 1½

Benzoic acid, 4-nitrobenzoic acid, 4-methoxybenzoic acid

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

(i) $CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + H_2O \xrightarrow{H^+} ?$

(ii) $C_6H_5MgBr \xrightarrow{CO_2} ? \xrightarrow{H_2O/H^+} ?$

(d) How can acetyl chloride be converted into—

(i) acetamide;

(ii) acetic anhydride? 1+1=2

(e) Why is Grignard reagent prepared under anhydrous condition? 1½

8. *(a)* Write down the products in the following reactions : 1×2=2

(i) $CH_3—C\equiv N + C_2H_5MgI \rightarrow ?$

$$\xrightarrow{H_2O/H^+} ?$$

(ii) $CH_3—\overset{\overset{O}{\|}}{C}—CH_3 + CH_3MgBr \rightarrow ?$

$$\xrightarrow{H_3O^+} ?$$

(b) Starting from ethyl acetoacetate, how are the following compounds synthesized? 1½×2=3

(i) Cinnamic acid

(ii) Succinic acid

(c) How will you convert the following? 1+1=2

(i) Ethanoic acid into methylacetate

(ii) Ethanoic acid into ethanamide

(d) Write the preparation of citric acid from glycerol. 1½

(e) Write the tautomeric forms of diethylmalonate. 1

9. *(a)* α-H atom of nitroalkanes are acidic. Explain giving suitable examples. 1½

(b) Describe the Gabriel phthalimide syntheses. How will you prepare methylamine by this method? 1½

(c) Which will be more basic—ethyl amine or aniline? Explain. 1½

(d) How will you differentiate primary, secondary and tertiary amines by Hinsberg method? Give chemical equations. 2

(e) Complete the following reactions : 1×3=3

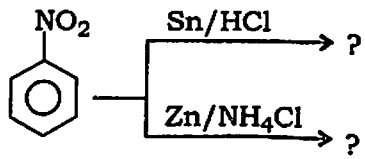
(i) $C_2H_5NH_2 + CH_3—\overset{\overset{O}{\|}}{C}—Cl \rightarrow ?$

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

(iii) $CH_3—\overset{\overset{O}{\|}}{C}—CH_3 + CH_3NH_2 \rightarrow ?$

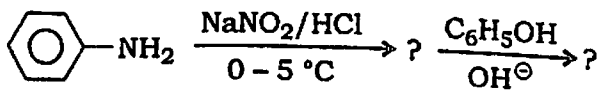
10. *(a)* How will you prepare ethylamine from propanamide? Write its mechanism. 1½

(b) Complete the following reaction : 1+1=2



(c) Primary, secondary and tertiary amines react differently with HNO_2. Explain giving chemical equations. 2

(d) Identify the products in the following reaction : 2



(e) How will you convert—

(i) aniline into chlorobenzene;

(ii) benzene diazonium chloride into cyanobenzene?

Give equations only. 1+1=2

SECTION—III

(Physical)

(*Marks* : 19)

11. *(a)* Derive an expression for entropy change of a gas when temperature changes from T_1 to T_2 and volume changes from V_1 to V_2. 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

$$aA + bB + \cdots \rightleftharpoons cC + dD + \cdots$$ 2½

(d) The value of equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 720 K is 48. What is the value of the equilibrium constant for the reaction $2HI \rightleftharpoons H_2 + I_2$? 2

OR

12. *(a)* Derive the Gibbs-Helmholtz equation. 2½

(b) One mole of an ideal monatomic gas expands reversibly from a volume of $10\ dm^3$ at a temperature of 298 K to a volume of $20\ dm^3$ at a temperature of 250 K. Assuming that $C_V = \frac{3}{2}R$, calculate the entropy change for the process. 3

(c) State and explain Le Chatelier's principle. 2

(d) At 473 K the equilibrium constant K_c for the decomposition of PCl_5 is $8{\cdot}3\times10^{-3}$. 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 two different reacting species. 3

(b) 50% of a first-order reaction is completed in 23 minutes. Calculate the time required to complete 90% of the reaction. 2

(Continued)

(c) State Henry's law. What are the limitations of Henry's law? 2

(d) A 0·5% aqueous solution of potassium chloride was found to freeze at $-0{\cdot}24\ ^\circ C$. Calculate the van't Hoff factor. [Given $K_f = 1{\cdot}86\ K\ kg\ mol^{-1}$] 2½

OR

14. *(a)* Show that the lowering of vapour pressure is directly related to osmotic pressure. 2½

(b) For a particular reaction, the rate constant k is $2{\cdot}8\times10^{-5}$ lit mol^{-1} sec^{-1} at 300 K and $7{\cdot}0\times10^{-1}$ lit mol^{-1} sec^{-1} at 400 K. Calculate the energy of activation for the reaction. [Given $R = 1{\cdot}38$ cal mol^{-1} deg^{-1}] 2½

(c) What is reverse osmosis? What are its applications? 2

(d) The freezing point of a solution containing 0·3 g of an organic solute in 30·0 g benzene is lowered by $0{\cdot}45\ ^\circ C$. Calculate the molecular weight of the organic solute. [Given K_f for benzene $= 5{\cdot}12\ K\ kg\ mol^{-1}$] 2½

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