2022

(November)

CHEMISTRY

(Elective/Honours)

[Part—A (Theory)]

(Chem-EH-301)

(Inorganic-III, Organic-III and Physical-III)

Marks : 56

Time : 3 hours

The figures in the margin indicate full marks for the questions

SECTION—I

(Inorganic—III)

(*Marks* : 18)

1. *(a)* Explain the anomalous behaviour of lithium from the other members of its group. 2

(b) Be and Mg show similar chemical and physical properties. Explain. 1½

(c) Write one method of preparation and one use of boric acid. Draw its structure. 2

(d) What is inert pair effect? Explain with example. 1½

(e) Write chemical reaction when—

(i) KI is treated with copper sulphate;

(ii) I_2 is treated with sodium thiosulphate. 2

OR

2. (a) Explain the term ionization enthalpy. What are the factors that affect the ionization enthalpy. 2

(b) What is catenation? Explain why in group 14 of the periodic table, the tendency for catenation decreases down the group. 2

(c) How is hydrazine prepared? How does it react with $KMnO_4$? (Write balanced chemical equation.) 1½

(d) Explain why—

(i) $[PF_6]^-$ exists but $[NF_6]^-$ does not exist;

(ii) H_2O is amphoteric while H_2S is slightly acidic in nature. 1+1=2

(e) Write one method of preparation of lithium aluminium hydride and give one chemical reaction to show the reducing property of lithium aluminium hydride. 1½

3. (a) Giving reason for your answer, explain why do transition elements and many of their compounds act as good catalysts. 1½

(b) Write one method of preparation of nickel tetracarbonyl and write the action of heat on it. 2

(c) What is meant by actinide contraction? What is its cause? Explain why actinides exhibit greater multiplicity of oxidation states as compared to lanthanide elements. 2

(d) Write one method of preparation and one use of UF_6. 1½

(e) Explain which one among the following metal ions does not form coloured compounds and explain their magnetic behaviour when placed in a magnetic field :

Cu^{+2}, Cr^{+3} and Zn^{2+} 2

OR

4. *(a)* Explain giving reason for your answer why the second and third rows of transition elements resemble each other more closely than that with the first row transition elements. 2

(b) The transition elements are not as good reducing agent as the groups 1, 2 and 13. Explain. 1½

(c) How does the basic character of $Ln(OH)_3$ vary with increasing atomic number of Ln? Ln stands for lanthanum and other lanthanide elements. Give reason for your answer. 1½

(d) Write down the balanced chemical reaction when an aqueous solution of KI is treated with an acidified $K_2Cr_2O_7$ solution. 1

(e) Why is it difficult to separate the lanthanide elements from their mixture? Describe one method for their separation. 1+2

(Continued)

SECTION—II

(Organic–III)

(*Marks* : 19)

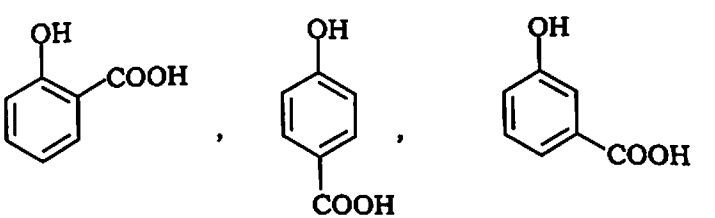
5. *(a)* Explain why—

(i) organolithium compounds are more reactive than organomagnesium compounds;

(ii) absolutely dry condition is required in the preparation of Grignard reagents;

(iii) carboxylic acids have higher boiling points than alcohols of comparable molecular weight. 1½×3=4½

(b) Arrange the following carboxylic acids in increasing order of their acid strength. Justify your answer with appropriate reasons : 3



(Turn Over)

(c) Write the tautomeric forms of ethylacetoacetate. 1

(d) How is cinnamic acid synthesised from diethylmalonate? 1

OR

6. (a) Explain with mechanism how the following compounds can be prepared from the given starting materials : 1½×3=4½

(i) Ethanoic acid from ethyl-magnesium iodide

(ii) Benzamide from benzoic acid

(iii) Ethylmethyl ketone from ethyl-acetoacetate

(b) Complete the following reactions with mechanism : 2½×2=5

(i) $C_6H_5C{\equiv}\ddot{N} \xrightarrow{H^+/H_2O} ? \xrightarrow{H^+/H_2O} ?$

(ii) $CH_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}OH + LiAlH_4 \longrightarrow ?$

(Continued)

7. (a) Explain with mechanism how a primary amine is synthesised by Gabriel phthalimide method. Why cannot this method be used for the synthesis of tertiary amines? 2+1=3

(b) "Aryldiazonium compounds are more stable than alkyldiazonium compounds." Explain. 1½

(c) Explain the following reactions with suitable examples and mechanism : 2½×2=5

(i) Sandmeyer reaction

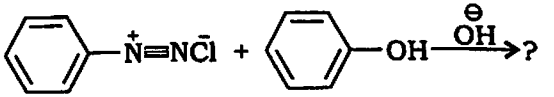
(ii) Carbylamine reaction

OR

8. (a) Complete the following reactions with mechanism : 1½×3=4½

(i) $CH_3CH_2NO_2 + CH_3{-}\overset{O}{\overset{\|}{C}}{-}H \xrightarrow[H_2O]{OH^{\ominus}} ?$

(ii) $C_6H_5\ddot{N}H_2 + CH_3{-}\overset{O}{\overset{\|}{C}}{-}Cl \xrightarrow{\text{Pyridine}} ?$

(iii) 

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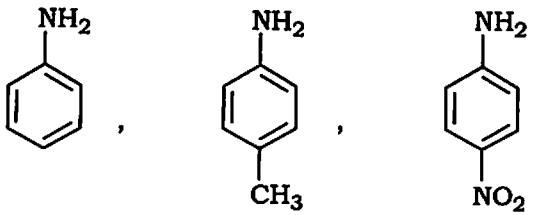
(b) "Nitration of aniline gives a significant amount of the meta product." Explain. 2

(c) Arrange the following compounds in order of their increasing basic strength. Justify your answer with appropriate reasons : 3



SECTION—III

(Physical—III)

(*Marks* : 19)

9. (a) Derive the van't Hoff equation in terms of K_p. 3

(b) What are homogeneous and heterogeneous equilibria? 1+1=2

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

(d) For the reaction

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

the values of enthalpy change and free energy change are –68·32 and –56·69 kcal respectively at 25 °C. Calculate the value of the entropy change at 30 °C. 2

OR

10. (a) Derive Clausius-Clapeyron equation. What are its applications? 3

(b) Show that— 1½+1½=3

(i) $\left(\frac{\partial G}{\partial P}\right)_T = V$

(ii) $\left(\frac{\partial A}{\partial T}\right)_V = -S$

(c) State Le Chatelier's principle and discuss the effects of temperature on the reaction.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(s)$; $\Delta H = -92{\cdot}38$ kJ 1+1=2

(d) The equilibrium constant K_c for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

is 800 at 527 °C. Calculate the equilibrium constant for the reaction

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$

at the same temperature. 2

11. (a) State Raoult's law and Henry's law. 1+1=2

(b) What are colligative properties? Show that osmotic pressure is a colligative property. 1+2=3

(c) Define the following : 1+1=2

(i) Tyndall effect

(ii) Gold number

(d) The coagulation of 110 ml of a colloidal solution of gold is completely prevented by addition of 0·20 g of starch to it after adding 1 ml of 10% NaCl solution. Find the gold number of starch. 2

(Continued)

OR

12. (a) Derive the relation between elevation in boiling point and molecular mass of a solute. 3

(b) Write a note on reverse osmosis and give its applications. 2

(c) Classify colloids on the basis of physical state of dispersed phase and dispersion medium. 2

(d) Describe the Bredig's arc method for preparation of colloidal solution. 2

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