Odd Semester, 2020

(Held in March, 2021)

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

UNIT—I

(Inorganic)

(*Marks* : 18)

1. *(a)* Explain why the *s*-block elements do not exhibit variable valencies. 1

(b) Account for the facts that "Although beryllium and aluminium belong to different groups in the periodic table, they resemble each other closely". 2

(c) Write down one method of preparation and one use of the following compounds : 1½×2=3

(i) Boric acid

(ii) Sodium thiosulphate

OR

2. *(a)* What is catenation? Give reason why on going down the group the tendency for catenation decreases. 2

(b) Give one method of preparation and one use of $LiAlH_4$. 2

(c) What is inert pair effect? Give a reason why on moving down the group the lower oxidation state of group 13 elements becomes more stable. 2

3. *(a)* Give a reason why the second and third row transition elements resemble each other more closely than they resemble the first row transition elements. 1½

(b) Write a method of preparation of potassium ferrocyanide and its reaction with copper sulphate solution. 2

(c) What is lanthanide contraction? What are the consequences of lanthanide contraction? 2½

OR

4. *(a)* Write one method of preparation of $K_2Cr_2O_7$. Also write the action of $K_2Cr_2O_7$ on $FeSO_4$ in presence of dil. H_2SO_4. 2

(b) Explain the separation of lanthanide on the basis of ion-exchange method. 3

(c) What are transuranic elements? 1

5. *(a)* What is a chelating ligand? Write down the application of chelate formation. 2½

(b) Give the IUPAC nomenclature of the following : ½×2=1

(i) $[Cu(NH_3)_4]SO_4$

(ii) $[NH_4]_3[Cr(NCS)_6]$

(c) Draw the geometrical isomers of $[Cr(NH_3)_4Cl_2]^+$ and name them as per IUPAC nomenclature. 2½

OR

6. *(a)* Write down the important postulate of Werner's theory of coordination compounds. 2

(b) Explain using valence bond theory why $[Fe(H_2O)_6]^{2+}$ ion is paramagnetic but $[Fe(CN)_6]^{4-}$ ion is low spin diamagnetic complex. 3

(c) Calculate the effective atomic number of Fe in $Fe(CO)_5$. 1

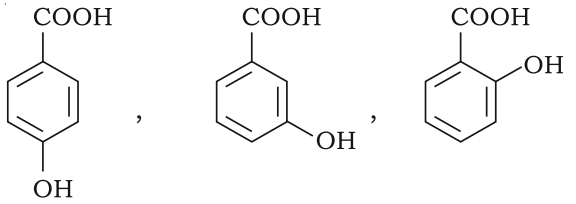
UNIT—II

(Organic)

(*Marks* : 19)

7. *(a)* Give the mechanism of acid hydrolysis of an alkyl cyanide into carboxylic acid. 2

(b) Arrange the following in order of increasing acidity giving reasons : 2

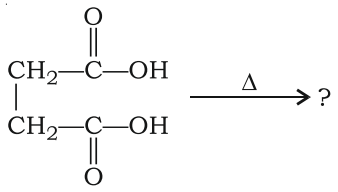


(c) Discuss the acid-catalysed tautomerisation of ethyl acetoacetate. 1½

(d) Complete the following reactions :

(i) $CH_3—\overset{\overset{O}{\|}}{C}—OH \xrightarrow{PCl_5} ? \xrightarrow{NH_3} ? \xrightarrow{LiAlH_4} ?$ 1½

(ii) $C_4H_9Br + 2Li \xrightarrow{\text{dry ether}} ? \xrightarrow[(2)\ H^+/H_2O]{(1)\ HCHO} B$ 1½

(iii)  1

OR

8. *(a)* Write two points to distinguish between resonance and tautomerism. 2

(b) Discuss the factors affecting the reactivity of carboxylic acid derivatives with nucleophilic reagents. 2

(c) Why are alkyl lithium more reactive than Grignard reagent? 1

(d) How would you synthesize—

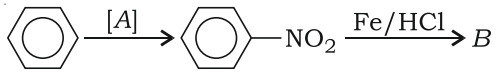
(i) a secondary alcohol from Grignard reagent;

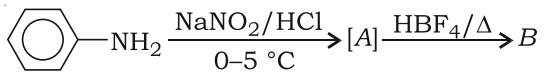
(ii) a ketone from alkyl lithium;

(iii) cinnamic acid from diethylmalonate? 1½×3=4½

9. *(a)* Discuss with mechanism the preparation of ethylamine by Gabriel phthalimide synthesis. 3

(b) Predict the reagents and products of the following reactions : 1×2=2

(i) 

(ii) 

(c) How will you convert—

(i) aniline to chlorobenzene;

(ii) aniline to *p*-nitroaniline? 1½×2=3

(d) Explain the acidic nature of nitromethane. 1½

OR

10. *(a)* Explain the following reactions with mechanism : 2×2=4

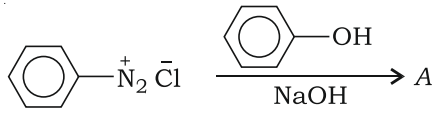
(i) Carbylamine reaction

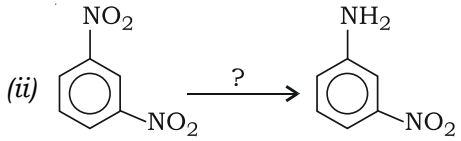
(ii) Sandmeyer reaction

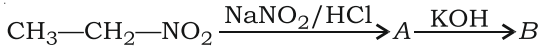
(b) Between *n*-butylamine and propanoic acid, which one will have higher boiling point and why? 1½

(c) Explain why nitration of aniline also gives *m*-nitroaniline. 1

(d) Identify the products/reagents in the following reactions : 1×3=3

(i) 

(ii) 

(iii) 

UNIT—III

(Physical)

(*Marks* : 19)

11. *(a)* Derive the Clausius-Clapeyron equation applicable to vaporization equilibria between a liquid and vapour phase. 3½

(b) Calculate the efficiency of a steam engine that operates between temperatures of 100 °C and 35 °C at 1 atm. 2

(c) Derive a relationship between K_P and K_C. 2

(d) State and explain the law of mass action. 2

OR

12. *(a)* Derive the Gibbs-Helmholtz equation. 3

(b) The equilibrium constant K_P for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is $1{\cdot}64 \times 10^{-4}$ atm. at 400 °C. What will be the equilibrium constant at 500 °C if the heat of reaction in this temperature range is −105185·8J?
(Given, $R = 8{\cdot}314\ J\ K^{-1}\ mol^{-1}$) 2

(c) Derive an expression for entropy change of an ideal gas when the temperature changes from T_1 to T_2 and volume changes from V_1 to V_2. 2½

(d) State Trouton's rule. 2

13. *(a)* State Henry's law. What are its limitations? 2

(b) Derive an expression for the rate constant of a first-order reaction of the type

$A \rightarrow$ products

Show that the half-life period of a first-order rection is independent of initial concentration. 2½+1=3½

(c) A solution containing 2·44 g of a solute dissolved in 75 g of water boiled at 100·413 °C. Calculate the molar mass of the solute.
(K_b for water = $0{\cdot}52\ K\ kg\ mol^{-1}$) 2½

(d) What are pseudounimolecular reactions? Explain with examples. 2

OR

14. *(a)* Derive a relation between the lowering of vapour pressure and osmotic pressure of a solution. 2

(b) Discuss the effect of catalyst on the rate of a reaction. 2

(c) In a first-order reaction, it takes a reactant 40·5 minutes to be 25% decomposed. Calculate the rate constant of the reaction. 2½

(d) What is the cause of abnormal molecular weights of solutes in solutions? 2

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