3/EH–23 (iii) (Syllabus–2015)

2017

(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

(c) Arrange the following elements in increasing order of their electro-negativities : 1

Li, K, Be, Cs

OR

2. (a) Explain with reasons the following observations : 1½+1½=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

3. (a) Comment on the following statement : 2

"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? 2

(c) Write a method of preparation of potassium ferrocyanide, $K_4Fe(CN)_6$ and its reaction with copper sulphate solution. 2

OR

4. (a) Write the actions of (i) $K_2Cr_2O_7$ on $FeSO_4$ in the presence of dil. H_2SO_4 and (ii) $KMnO_4$ on oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) acidified with dil. H_2SO_4. 2

(b) What is meant by lanthanide contraction? Write the consequences of lanthanide contraction. 3

(c) Write the general electronic configurations of lanthanides and actinides. 1

5. (a) What is a ligand? Give one example of multidentate ligand with its structure. 2

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

(c) Draw the geometrical isomers of $Cr(NH_3)_3Cl_3$ and name them as per IUPAC nomenclature. 3

OR

6. *(a)* Comment on the statement, "While *trans*-$[Co(en)_2Cl_2]^+$ is optically inactive the complex $[Co(en)_3]^{+3}$ is optically active". Write the structures for the optical isomers. 3

(b) Draw the crystal-field splitting diagrams for octahedral and tetrahedral complexes.

Explain why crystal-field stabilization energy (CFSE) of an octahedral complex is higher than that of a tetrahedral complex. 3

SECTION—II

(Organic)

(*Marks* : 19)

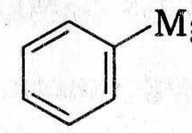
7. *(a)* Explain why carboxylic acids have higher boiling points than alcohols of similar molecular weight. 1½

(b) Arrange the following acids in order of increasing acidity with appropriate reasons : 1½

ICH_2COOH, $BrCH_2COOH$,
$ClCH_2COOH$, FCH_2COOH

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

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

(ii)  $\xrightarrow{O=C=O} ? \xrightarrow{H_2O/H^+} ?$

(d) Write the tautomeric forms of diethyl malonate. 1

(e) Starting from diethyl malonate how are the following compounds synthesized?

(i) Malonyl urea 1

(ii) Succinic acid 1½

OR

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

$R-\overset{\overset{O}{\|}}{C}-Cl$, $R-\overset{\overset{O}{\|}}{C}-NH_2$, $R-\overset{\overset{O}{\|}}{C}-OR'$

$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$

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

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

(i) $CH_3Li + H_2C\overset{O}{\diagup\!\diagdown}CHCH_3 \longrightarrow ?$

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

(ii) $CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + CH_3MgI \longrightarrow ?$

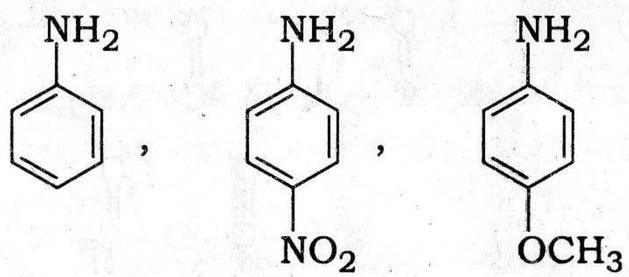
(d) Complete the following reactions : ½+1+½+½=2½

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{Pyridine}]{SOCl_2} A \xrightarrow{2\bar{C}H_2-\overset{+}{N}\equiv N} B$$

$$\xrightarrow{\text{Wolff rearrangement}} C \xrightarrow[Ag_2O]{H_2O} D$$

(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

(c) What happens when—

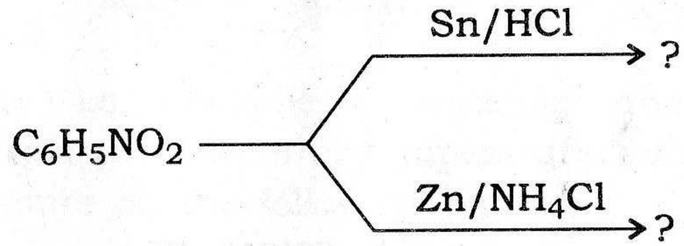
(i) aniline is treated with a mixture of $NaNO_2$ and HCl at 273 K;

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

Explain with mechanism. 1½+1½=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

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{NH_3} ? \xrightarrow{P_2O_5} ?$$

$$\xrightarrow{LiAlH_4} ?$$

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

(c) Complete the following reactions with mechanisms : 1½+1½=3

(i) $C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow ?$

(ii) $CH_3—\overset{\overset{O}{\|}}{C}—NH_2 + Br_2 + NaOH \longrightarrow ?$

(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 : 2½

$$dG = VdP - SdT$$

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

(d) The value of K_p for the reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

is $1 \cdot 06 \times 10^5$ at 25 °C. Calculate the standard state free energy change ($\Delta G°$) of the reaction at 25 °C. ($R = 8 \cdot 314\ JK^{-1}\ mol^{-1}$) 2

OR

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

liquid ⇌ vapour 3

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

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g);$$
$$\Delta H = -92 \cdot 38\ kJ$$

(c) State the law of mass action. 1½

(d) Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K. The molar heat of vaporization of ethanol is $39 \cdot 84\ kJ\ mol^{-1}$. 2

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

(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 $2 \cdot 3 \times 10^{-2}$ lit mol^{-1} S^{-1} at 0 °C and $8 \cdot 2 \times 10^{-2}$ lit mol^{-1} S^{-1} at 15 °C. Find the activation energy of the reaction. 2½

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2018

(October)

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(General Chemistry—III)

(Chem–EH–301)

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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 : 1½×2=3

(i) Boric acid

(ii) Sodium thiosulphate

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. 1½+½=2

(c) Give reasons for the following : 1×2=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

OR

4. *(a)* Write down the preparation of $K_2Cr_2O_7$ starting from chromite ore along with the chemical equations. Draw the structure of $Cr_2O_7^{2-}$. 2½

(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. 1½

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 $CoCl_3$, $3NH_3$ non-ionic according to this theory? 3

OR

6. *(a)* Give the IUPAC names of the following complexes : 1×2=2

(i) $[Co(NH_3)_4Cl_2]Cl$

(ii) $K_3[Al(C_2O_4)_3]$

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

(c) Identify the kind of isomerisms exhibited by the following isomers : ½×2=1

(i) $[Cr(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Cr(CN)_6]$

(ii) $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$

SECTION—II

(Organic)

(*Marks* : 19)

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

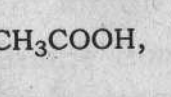
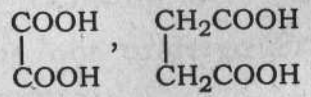
(b) Explain with chemical equations, what happens when acetic acid is—

(i) heated with phosphorous pentoxide;

(ii) treated with chlorine in the presence of red phosphorous;

(iii) reduced with lithium aluminium hydride. 1×3=3

(c) Arrange the following acids in order of increasing acidity. Explain with appropriate reasons : 1½

CH_3COOH,  , 

(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? 1½

(e) Write down the products in the following reactions : 1×2=2

(i) $CH_3-C\equiv N + CH_3MgI \longrightarrow ? \xrightarrow{H_2O/H^+} ?$

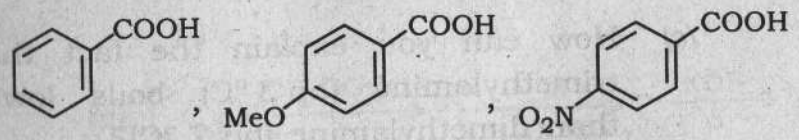
(ii) $CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5 + C_2H_5MgBr \longrightarrow ? \xrightarrow{H_2O/H^+} ?$

OR

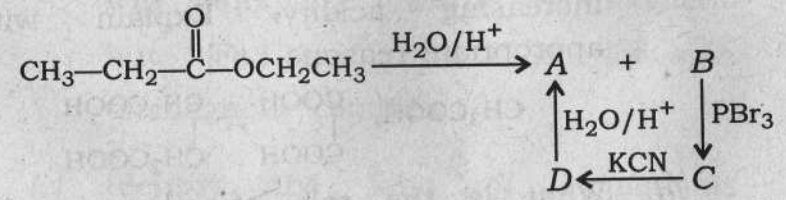
8. (a) Explain the mechanism of nucleophilic substitution in acid derivatives. Why are esters less reactive than acid chlorides? 2

(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 : 1½



(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—

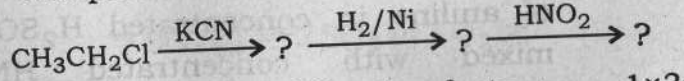
(i) $Br_2 - H_2O$;

(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

(Continued)

(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

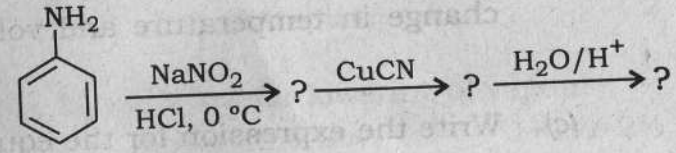
OR

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

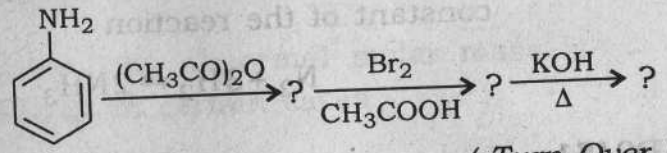
(b) What is Sandmeyer reaction? Give a plausible mechanism of the reaction with explanation using specific set of reagents. 1½

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

(i)



(ii)

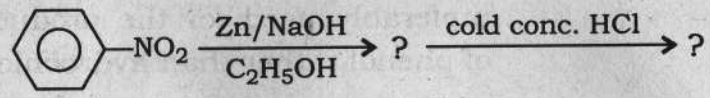


(Turn Over)

(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

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$ 1½

(d) Calculate K_c for the reaction

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

at 27 °C. K_p for the reaction is $3{\cdot}5\times10^{-23}$ atm at 27 °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

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 ($K_b = 0{\cdot}52$ K/m, molar mass of glucose = 180). 2½

★★★

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SECTION—I

(Inorganic)

(*Marks* : 18)

1. *(a)* Explain why the atomic and ionic radii of the alkaline-earth metals are lower as compared to alkali metals. How do they differ from alkali metals based on the above observation? 1½+1½=3

(b) How do the acidic and basic characters of oxides of the *s*- and *p*-block elements change on moving across a period and down the group? 3

OR

2. *(a)* 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

(b) Give one method of preparation and one use of the following compounds : 1½×2=3

(i) Potassium iodide

(ii) Lead tetraacetate

(c) Explain why phosphorus forms pentahalides but nitrogen does not form pentahalides. 1

3. *(a)* Give reasons for the following : 1½×2=3

(i) Cations of transition elements have a higher tendency to form complexes.

(ii) The second and the third rows of transition elements resemble each other more closely than they resemble the first row transition elements.

(b) What is lanthanide contraction? Explain the cause of lanthanide contraction. 3

(Continued)

OR

4. *(a)* What are transuranic elements? Write down the preparation of the first transuranic element. 2

(b) Explain the separation of lanthanides by ion-exchange method. 3

(c) What is the number of ions per mole of the complex $CoCl_3 \cdot 5NH_3$ in aqueous solution? 1

5. *(a)* What is meant by effective atomic number? Calculate the effective atomic number of cobalt in $[Co(NH_3)_6]^{3+}$. (Atomic number of cobalt = 27) 1+1=2

(b) Give the IUPAC nomenclature of the following : ½×3=1½

(i) $[Ag(NH_3)_2]Cl$

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

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

(c) What is chelating ligand? Write down the applications of chelate formation. 2½

OR

6. *(a)* Give an example and draw the structure of an octahedral complex of the type $[M(aa)_3]$. What type of isomerism will it exhibit? 1½

(Turn Over)

(b) Using valence-bond theory, predict the structure and magnetic behaviour of $[Mn(CN)_6]^{4-}$ and also mention whether it is an outer or inner orbital complex and high-spin or low-spin complex. 2½

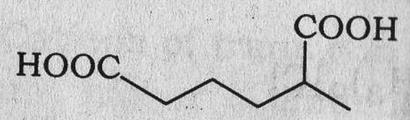
(c) What relationship exists between the crystal-field splitting energy (Δ_0) and pairing energy (P) in determining whether a given complex will be high spin or low spin? 2

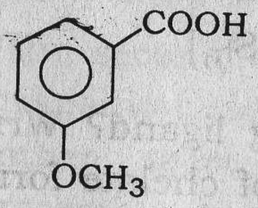
SECTION—II

(Organic)

(Marks : 19)

7. (a) Name the following compounds according to IUPAC nomenclature : ½×2=1

(i) 

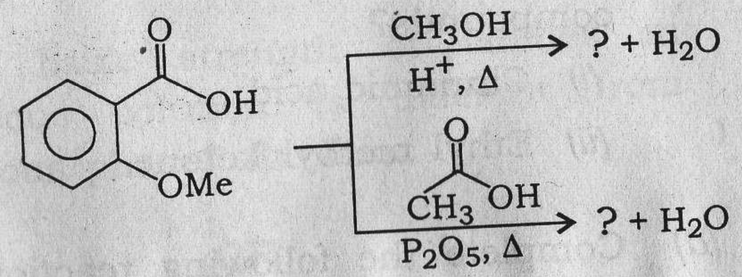
(ii) 

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

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

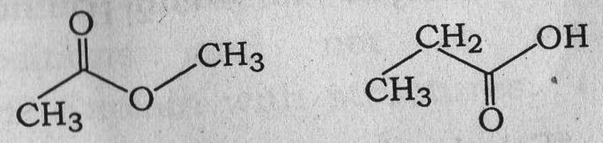
(Continued)

(c) Complete the following reactions with mechanisms : 2×2=4

(i) 

(ii) $CH_3Br \xrightarrow{2Li,\ Et_2O} ? \xrightarrow{CO_2} ? \xrightarrow{H_2O/H^+} ?$

(d) Why is Grignard reagent prepared under anhydrous conditions? 1½

(e) 

I *II*

Although *I* and *II* are isomers, the boiling point of *I* is lower than *II*. Explain. 1½

OR

8. (a) Discuss with an example the difference between tautomerism and resonance. 1½

(b) "Acid chlorides give a pungent smell in air." Explain. 1

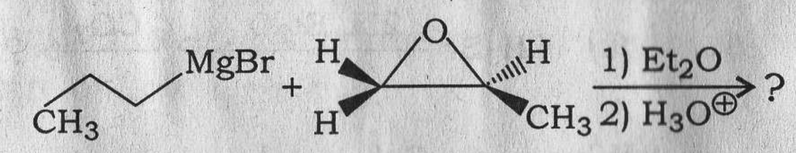
(Turn Over)

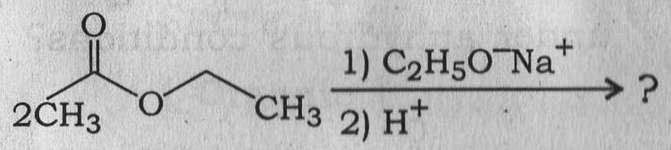
(c) Starting from ethylacetoacetate, how would you synthesize the following compounds? 1½×2=3

(i) Cinnamic acid

(ii) Ethyl methyl ketone

(d) Complete the following reactions with mechanisms : 2×2=4

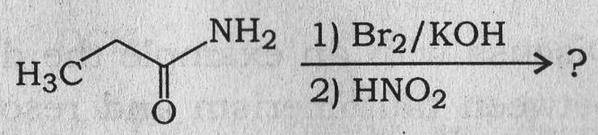
(i) 

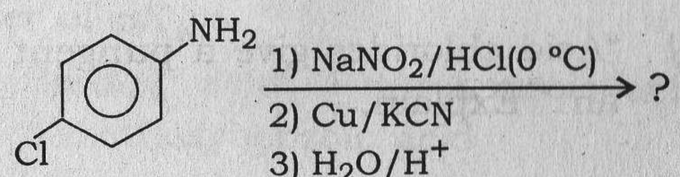
(ii) 

9. (a) "Ethylamine is soluble in water whereas aniline is not." Explain. 1½

(b) Why is it necessary to use concentrated H_2SO_4 in nitration of benzene? 1½

(c) Complete the following reactions : 2×2=4

(i) 

(ii) 

(d) Why is diazotization of aniline always carried out in ice-cold solution? 1

(e) "The basic strength of amines in aqueous solution is different from gaseous phase." Explain. 1½

OR

10. (a) Why is it difficult to prepare pure amines by ammonolysis of alkyl halides? 1½

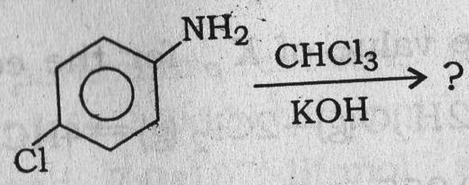
(b) Why does $-NO_2$ group increase the electrophilic character at *ortho-* and *para*-positions and not at *meta*-position? Explain with structures. 1½

(c) How will you make the following conversions? 1½×2=3

(i) Benzene to aniline

(ii) Aniline to *p*-hydroxyazobenzene

(d) Complete the following reaction : 2



(e) Give reason why aryl diazonium ions are more stable than alkyl diazonium ions. 1½

SECTION—III

(Physical)

(*Marks* : 19)

11. *(a)* Derive the expression for entropy change of an ideal gas in terms of temperature and volume change. 3

(b) Calculate the efficiency of a Carnot's engine working between the temperatures 110 °C and 25 °C. 2

(c) State Le Chatelier's principle and discuss the effect of pressure on the reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$ 2

(d) State and explain the 'law of mass action'. 2½

OR

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

(b) State Trouton's rule. 1½

(c) The value of K_p for the equilibrium

$$2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$$

is 0·035 atm at 400 °C when the partial pressure is expressed in atmosphere. Calculate the value of K_c for the same reaction. 2

(*Continued*)

(d) Derive van't Hoff equation for temperature dependence of equilibrium constant in terms of K_c. 3

13. *(a)* Distinguish between order and molecularity of a reaction. 2

(b) Derive an expression for the rate constant of a first-order reaction. Show that the half-life of a first-order reaction is independent of the initial concentration of the reactant. 2+1=3

(c) What do you understand by lowering and relative lowering of vapour pressure? 1+1=2

(d) A solution containing 4 g of a non-volatile organic solute per 100 ml solution was found to have an osmotic pressure equal to 500 cm of mercury at 27 °C. Calculate the molecular weight of the solute. 2½

OR

14. *(a)* 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 $R = 1{\cdot}98$ cal $mol^{-1}deg^{-1}$) 2½

(*Turn Over*)

(b) The differential form of the rate of a reaction is

$$\frac{dx}{dt} = k(a-x)^2$$

Obtain the integrated form of the rate equation. 3

(c) Define boiling point of a liquid. Why is boiling point of a solvent less than that of its solution? 1+1=2

(d) Explain reverse osmosis. 2

★ ★ ★

2019

(October)

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)* Account for the fact that "compounds in the +2 oxidation state of lead are more stable than its compounds in +4 oxidation state". 2

(b) Define ionization potential. What are the factors on which ionization potential depends upon? 1+1=2

(c) Give one method of preparation and one use of boric acid. 1+1=2

OR

2. *(a)* Why has lithium a greater tendency to form covalent compounds than other elements in group 1? 1½

(b) What happens when sodium thiosulphate is treated with a solution of ferric chloride? 1½

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

(i) Lead tetraacetate

(ii) Potassium iodide

3. *(a)* Give reasons why most of the *d*-block elements behaves as catalyst. 1½

(b) Write down the analytical differences between $KMnO_4$ and $K_2Cr_2O_7$ in various mediums. 1½

(c) Explain the separation of Lanthanides on the basis of ion exchange method. 3

OR

4. *(a)* Explain why transition elements show variable oxidation states than other elements. 2

(b) Give one similarity and dissimilarity between lanthanoids and actinoids. 2

(c) Write one method of preparation and one use of potassium ferricyanide. 2

5. *(a)* Give the IUPAC names of the following : 1×3=3

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

(ii) $Na_3[Co(NO_2)_6]$

(iii) $[Pt(NH_3)_4][PtCl_4]$

(b) Using effective atomic number (EAN) rules, calculate the EAN value of Fe in $[Fe(CN)_6]^{4-}$. 2

(c) Write down the ionization isomers of $[Cr(NH_3)_5(SO_4)]Br$. 1

OR

6. *(a)* What is an ambidentate ligand? Giving example, show how it differs from a bidentate ligand. 2

(b) Explain hydrate isomerism by using a suitable example. 2

(c) Draw the geometrical isomers of $[CoCl_2(en)_2]^+$ and indicate which isomer is optically active. 2

SECTION—II

(Organic)

(*Marks* : 19)

7. (a) Discuss the effect of electronegative elements on the acidity of aliphatic carboxylic acids with suitable examples. 1½

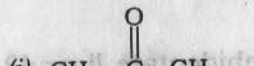
(b) Write the preparation of H—COOH from oxalic acid. 1

(c) How can acetyl chloride be converted into—

(i) acetamide;

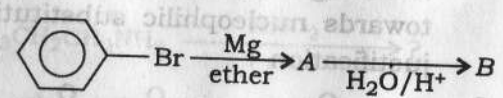
(ii) acetic anhydride? 2

(d) Synthesise the following, using a suitable Grignard reagent : 2

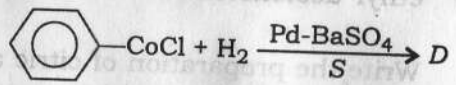
(i) 

(ii) A secondary alcohol

(e) Complete the following reactions : 3

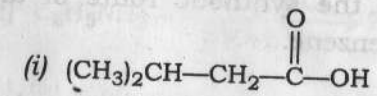
(i) 

(ii) 

(iii) 

OR

8. (a) Synthesise the following compounds from malonic ester (any *one*) : 2

(i) 

(ii) Crotonic acid

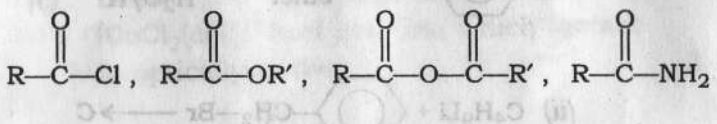
(b) Explain why dry ether is used in the preparation of Grignard reagents. 1

(c) How will you convert the following? 2

(i) Ethanoic acid into methyl acetate

(ii) Ethanoic acid into ethanamide

(d) Arrange the relative reactivity of the following carboxylic acid derivatives towards nucleophilic substitution with justification : 2



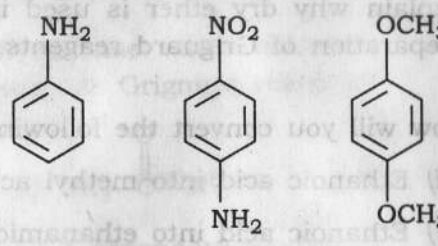
(e) Write the different tautomeric forms of ethyl acetoacetate. 1

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

9. (a) Why cannot aryl amines be prepared by Gabriel phthalimide synthesis? 1

(b) Outline the synthetic route of aniline from benzene. 2

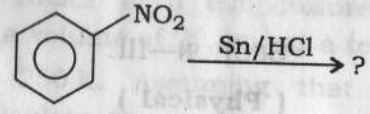
(c) Arrange the following molecules in order of their increasing basic strength with proper justification : 2



(d) Complete the following reaction by writing a suitable mechanism : 2

$$CH_3CH_2CH_2NH_2 \xrightarrow{HNO_2} ?$$

(e) Write the products of the following reactions : 1+1½

(i) 

(ii) $ClCH_2—COOH \xrightarrow{NaNO_2} ? \xrightarrow{\Delta} ?$

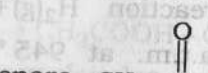
OR

10. (a) Identify the products in the following reactions : 1½+1

(i) $C_6H_5NH_2 \xrightarrow[0\,°C–5\,°C]{NaNO_2/HCl} ? \xrightarrow[\bar{O}H]{C_6H_5OH} ?$

(ii) $CH_2N_2 + HCl \longrightarrow ?$

(b) Discuss the formation of different products on the treatment of methyl amine, dimethyl amine and trimethyl amine with HNO_2. 3

(c) How will you prepare  using diazomethane and ethanoic acid? 1

(d) Why is nitromethane acidic in nature? 1

(e) Convert—

(i) aniline into chlorobenzene;

(ii) benzene diazonium chloride into cyanobenzene. 2

SECTION—III

(Physical)

(*Marks* : 19)

11. (a) Derive an expression for the variation of Gibb's free energy with temperature and pressure. 3

OR

12. (a) Differentiate between Gibb's free energy and Helmholtz free energy. 1½

(b) One mole of an ideal mono-atomic 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) Derive van't Hoff equation for temperature dependence of equilibrium constant K_p. 3

(d) At 473 K, th[illegible]