2012

Part: I

Part: II

Part I *(Answer all questions)*

Question: 1

a. Fill in the blanks by choosing the appropriate word/words from those given in the brackets:

(Raoult's, Arrhenus, lateral, sodium, magnesium, negative, positive, non-ideal, ideal, iron, copper, van't Hoff, s.p , ethanol, ethanoic acid, methanoic acid, methanol, propanoic acid.)   [5]

   i.   For a spontaneous change to take place, the ΔS of the system should be _____ and ΔG of the system should be _____.

Answer:

   ii.   Hydrolysis of methyl propanoate gives _____ and _____.

Answer:

   iii.   Solutions which strictly obey_____law are called _____solutions..

Answer:

   iv. π bonds are formed by the _____overlap of _____orbitals.

Answer:

   v.   Zinc can displace_____from CuSO4 solutions, but cannot displace_____ from MgSO4 solution.

Answer:

b. Complete the following statements by selecting the **correct alternative** from the choices given: [5]

   1.   The quantity of electricity required to deposit 1-15g of sodium from molten NaCl (Na = 23, Cl = 35.5) is:

      1 F

      0.5 F

      0.05 F

      1.5 F

   2.   When acetic acid is reacted with calcium hydroxide and the product is distilled dry, the compound formed is:

      Calcium acetate

      Acetone

      Acetaldehyde

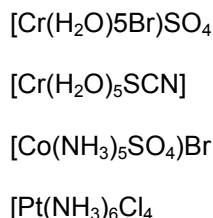   Acetic anhydride

3. The [OH] concentration of a weak base is given by:

$$ck_b$$

$$\sqrt{ck_b}$$

$$\sqrt{K_{b/c}}$$

$$\sqrt{Kb}$$

4. In a plot of log k vs 1/T, the slope is:

-Ea/2.303

Ea/2.303 R

Ea 2.303

-4 Ea/2.303 R

5. Among the following coordination compounds, the one giving a white precipitate with $BaCl_2$ solution is:

$[Cr(H_2O)5Br)SO_4$

$[Cr(H_2O)_5SCN]$

$[Co(NH_3)_5SO_4)Br$

$[Pt(NH_3)_6Cl_4$

c. Answer the following questions: [5]

i.   A solution X is prepared by dissolving three moles of glucose in one litre of water and a solution Y is prepared by dissolving 1.5 moles of sodium chloride in one litre of water. Will the osmotic pressure of X be higher, lower or equal to that of Y? Give a reason for your answer.

Answer:
Osmotic pressure of the two solutions X and Y will be same. Because osmotic pressure is a colligative property which depends on the number of particles present in the solution. Glucose is non-electrolyte.
∴ Value of I for Glucose = 1
Value of I for NaCl = 2
Now for Glucose, π = I x cRT
= 1 x 3 RT / 1000 = 3RT / 1000
For NaCl π = I x cRT
= 2 x 1.5 RT / 1000 = 3RT / 1000

ii. Give one example (equation) of a homogeneously catalyzed reaction and name the catalyst.

Answer:
Catalysts in solution with the reactants usually provide fast reaction paths by allowing reactants to form an unstable intermediate that quickly decomposes into products. For example, the substitution reaction

$$CH_3CH_2OH(g) + HCl(g) \xrightarrow{H_2SO_4} CH_3CH_2Cl + H_2O(l)$$
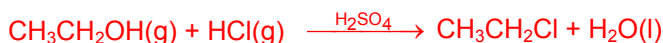
is catalyzed by acid because the ethanol is converted into unstable $CH_3CH_2OH_2^+$, which quickly reacts with Cl^- to produce the products.

iii. Write the formula of the product formed when formaldehyde reacts with ammonia and name the product.

Answer:
Urotropine (hexamethylene tetramine) is formed when formaldehyde reacts with ammonia

$6HCHO + 4NH_3 \cdot (CH_2)_6N_4 + 6H_2O$

iv. If the ionization (dissociation) constant of acetic acid is k_a, what will be the pH of a solution containing equal concentrations of acetic acid and sodium acetate:

Answer:
We know that

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$pH = pK_a + \log \frac{[CH_3 COONa]}{[CH_3 COOH]}$$

[As given: concentration of salt and acid is same]
$pH = pK_a + \log 1$
$pH = pK_a$

v. What is the electronic configuration of chromium atom (Z=24)? Give a reason for your answer.

Answer:
In the world of quantum numbers, different elements are shown as having different electron configurations. For chromium (Cr) one would predict it would have the configuration: (Z=24): [Ar] 4s2 3d4. However, in experiments, it shows an actual electron configuration of: Cr (Z=24): [Ar] 4s1 3d5.

d. Match the following:

i. Nernst equation	a. Water
ii. Lactic acid	b. Constant volume
iii. Amphiprotic solvent	c. Ammonia
iv. Lewis base	d. Optical isomers
v. Isochoric process	e. Electrochemical cells

Answer:
i. (e)   ii (d)   iii (a) iv (c) v (b)

Part II *(Answer six questions choosing two from section A, two from section B. And two from section C)*

Section A *(Answer any two questions)*

_____

Question: 2

a.

i. A solution of urea in water has a boiling point of 100.18^0C. Calculate the freezing point of the solution. (K_1 for water is 1.86 K kg mol^{-1} and K_b for water is 0.512 K kg mol^{-1}). [2]

Answer:
Calculation of molality of the solution:
$100.18^0C + 273 = 373.18$ K
$100^0C + 273 = 373$ K
$\Delta T_b = 373.18 - 373$ K
$= 0.18$ K
$\Delta T_b = K_b \times m$
$m = \dfrac{\Delta T_b}{K_b} = \dfrac{0.18}{0.512}$
$= 0.351$ m
Calculation of freezing point:
$\Delta T_f = K_f \times m$
$= 1.86 \times 0.351$
$= 0.652$ K
$\Delta T_f = T_f - \Delta T_f$
$= 273$ K $- 0.652$ K
$= 272.348$ K

$T_f = -0.652\ ^0C.$

ii. A solution of lactose containing 8.45 g of lactose of 100g of water has a vapor pressure of 4.559 mm of Hg. Calculate the molecular weight of lactose. [2]

Answer:
Vapour pressure of solvent (P0) = 4.579 mm
Vapor pressure of solution (P) = 4.559 mm
Mass of solution (ω) = 8.45 g
Mass of solvent (W) = 100g
Molecular mass of solvent H_2O (M) = 18
Molecular mass of solute (M') = ?
According to Raoult's law
$M' = \dfrac{8.45 \times 18 \times 4.579}{100 \times 0.02}$

$\dfrac{P^0 - P}{P^0} = \dfrac{\omega M}{W.M'}$

$\dfrac{4.579 - 4.559}{4.579} = \dfrac{8.45 \times 18}{100 \times M'}$

M' = 348.232
Hence, Molecular Mass of lactose = 348.232

b.

i. The molecular weight of H_2S is more than that of H_2O, but H_2S is a gas and H_2O is a liquid. Explain. [3]

_____

_____

Answer:
This is because of the intermolecular hydrogen bonding present in H_2O but not in H_2S due to the low electronegativities of sulphur as compare to oxygen.

    ii.   When potassium cyanide reacts with water, will the resulting solution be acidic, alkaline or neutral? Justify your answer.   [2]

Answer:
$KCN + H_2O \rightarrow KOH + HCN$
Resulting solution will be basic (weakly) due to the formation of strong base KOH and weak acid HCN.

  c.   What is the hybridization of the carbon atom in ethyne molecule? What is the H-C-H bond angle? *(**)*   [1]

Answer:

Question: 3

a.
i.   State the second law of thermodynamics in terms of the entropy of the universe. *(**)*   [1]

Answer:

    ii.   Calculate the maximum work that can be obtained from the given electrochemical cell constructed with two metals M and N. [$E^{o}M+2/M$ = -0.76 V, $E^{o}N+2/N$ =+0.34V. the cell reaction is $M + N^{+2} \rightarrow M^{+2} + N$ [3]

Answer:
$E^{o}_{cell} = E_R - E_L$
= 0.34 – (-0.76)
= 1.10 V
Max. work done = -nF E^{o}_{cell}
= -2 x 96500 x 1.10
= -212300 J
= -212.3 kJ

b.
i.   To precipitate group III cations NH_4Cl should be added to the solution before the addition of ammonium hydroxide. Explain why.   [2]

Answer:
$NH_4Cl \rightarrow NH_4^+ + Cl-$
$NH_4OH \rightarrow NH_4^+ + OH^-$
NH_4^+ ion present in both, create common ion effect which depress the concentration of OH- as a result ionic product will be increases as compare to solubility product and hence precipitate will formed.

    ii.   A study of chemical kinetics of the reaction A+B$\rightarrow$ products, gave the following data at 25^0C: [2]

Experiment	[A]	[B]	D[Products]/dt
1	1.0	0.15	4.20×10^{-6}
2	2.0	0.15	8.40×10^{-6}
3	1.0	0.20	5.60×10^{-6}

Find :
    (1) The order of reaction with respect to A.
    (2) The order of reaction with respect to B.
    (3) The rate law.

Answer:

Suppose the given reaction is of order p with regards to A and q with regards to B. the rate of formation of product can thus be written as:

$4.20 \times 10^{-6} = K[1.0]^p [0.15]^q$ ….(i)
$8.40 \times 10^{-6} = K[2.0]^p [0.15]^q$ ….(ii)
$5.60 \times 10^{-6} = K[1.0]^p [0.20]^q$ ….(iii)

Dividing equation (ii) by (i) we get

$$\frac{8.40 \times 10^{-6}}{4.20 \times 10^{-6}} = \left(\frac{2.0}{1.0}\right)^p$$

$$\frac{5.60 \times 10^{-6}}{4.20 \times 10^{-6}} = \left(\frac{0.20}{0.15}\right)^q$$

$$\frac{4}{3} = \left(\frac{4}{3}\right)^q$$

$\therefore$ q = 1

Hence (i) The order of reaction with regards to A is 1.
      (ii) The order of reaction with regards to B is 1.
      (iii) The rate Law can be written as

Rate = K [A] [B]

Question: 4

a.
i.   The central atom of methane and water is in the same state of hybridization, but the shapes of the two molecules are different. Discuss.   (**)   [2]

Answer:

ii.   The conductivity of 0.2 M KCl solution is 3×10^{-2} ohm^{-1} cm^{-1}. Calculate its molar conductance.
    [2]

Answer:
Molar Conductivity =

$$\Lambda_m = \frac{k \times 1000}{M}$$

Given k = 3×10^{-2} ohm^{-1} cm^{-1}, M = 0.2 M

$$\Lambda_m = \frac{3 \times 10^{-2} \times 1000}{0.2}$$

= 1.5×10^2 S cm^2 mol^{-1}

b.

_____

i. Draw the valence shell molecular orbital diagram of oxygen molecule and predict its magnetic nature.   (**)   [2]

ii. Calculate the solubility of lead chloride in water, if its solubility product is 1.7×10^{-5}. (Pb = 206, Cl = 35.5)   [2]

Answer:
Given : K_{sp} ($PbCl_2$) = 1.7×10^{-5}
($PbCl_2$) = $[Pb^{2+}]$ $[Cl^-]^2$
If solubility of $PbCl_2$ is S.
$1.7 \times 10^{-5} = S \times (2S)^2$
$\quad\quad = S \times 4S^2 = 4S^3$

$$S = \sqrt[3]{\frac{1.7 \times 10^{-5}}{4}} = 0.016$$

Molecular mass of $PbCl_2$ = 207 + 2 x 35.5 = 278
Solubility, S = 0.016 x 278
S = 4.448 gL^{-1}.

c. For a crystal of diamond, state: [2]

i. The hybridization of the carbon atom.

Answer:
Hybridization of C-atom in diamond = sp^3

ii. The coordination number of each carbon atom.

Answer:
Co-ordination of C-atom of each C-atom = = 4

iii. The type of lattice in which it crystalise.

Answer:
The type of lattice = fcc

iv. The number of carbon atoms present per unit cell.

Answer:
The number of carbon atoms present per unit cell = 4

Section B *(Answer any two questions)*

Question: 5

a. Write the formulae of the following coordination compounds: [2]
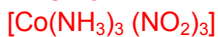i. Potassiumtetracyanonickel(0)

Answer:
$K_4[Ni(CN)_4]$

ii. Triamminetrinitrocobalt (III)

_____

Answer:
$[Co(NH_3)_3 (NO_2)_3]$

b. $[CoF_6]^{3-}$ is a coordination complex ion.   [2]

i.   What is the oxidation number of cobalt in the complex?

Answer:
Oxidation number of Cobalt = 3

ii.   How many unpaired electrons are there in the complex?

Answer:
No. of unpaired electron = 4

iii. State the magnetic behavior of the complex.

Answer:
Highly paramagnetic.

iv.   Give the I.U.P.A.C name of the complex.
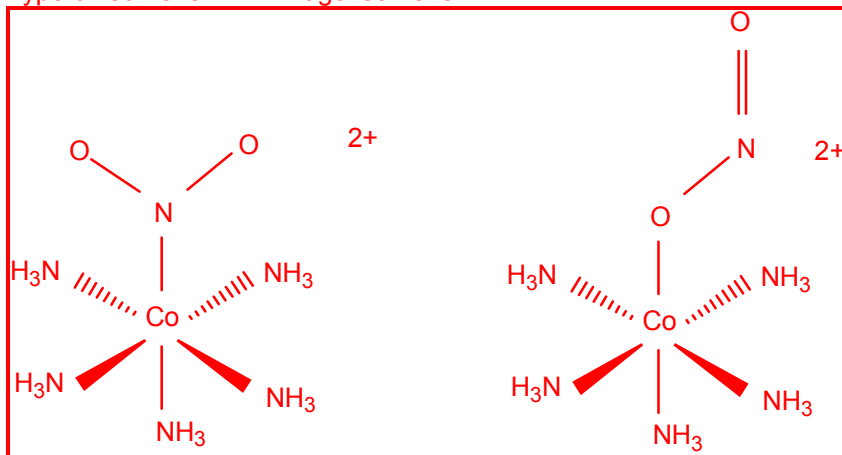
Answer:
Hexafluoridocobalt (III) ion.

c.   Draw the structural isomer of $[Co(NH_3)_5NO_2]Cl$ and name the type of isomerism.   [1]

Answer:
Structural isomer of $[Co(NH_3)_5NO_2]Cl_2 \leftrightarrow [Co(NH_3)_5ONO]Cl_2$
Type of isomerism = Linkage isomerism.
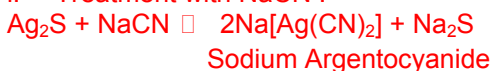

Question: 6

a.   Give the equations for the conversion of argentite (Ag_2S) to metallic silver.   [2]

Answer:
Conversion of argentite (Ag_2S) to Ag:
i.   Treatment with NaCN :
$Ag_2S + NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$
                    Sodium Argentocyanide

A current of hot air oxidizes Na_2S to Na_2SO_4

$Na_2S + 2O_2 \rightarrow Na_2SO_4$

ii. Precipitation of Silver:

$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Ag(CN)_2] + 2Ag\downarrow$

Sodium tetracyanozincate (II)
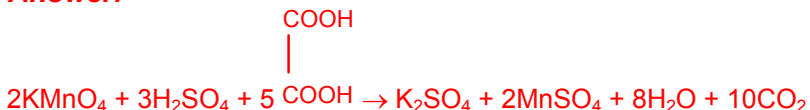
Silver thus obtained purified by electrolysis and deposited at cathode.

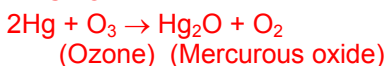b. Give balanced equations for the following reactions: [3]

i. Acidified potassium permanganate and oxalic acid.

Answer:

$$2KMnO_4 + 3H_2SO_4 + 5 \begin{array}{c} COOH \\ | \\ COOH \end{array} \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

ii. Ozone and mercury.

Answer:

$2Hg + O_3 \rightarrow Hg_2O + O_2$

(Ozone) (Mercurous oxide)

iii. Action of heat on a mixture of sodium chloride and concentrated sulphuric acid.

 Answer:

$NaCl + H_2SO_4 \text{ (conc.)} \xrightarrow{\text{Heat}} NaHSO_4 + HCl$

Question 7

a. Explain why transition metals form complex compounds.   [2]

Answer:

Transition metals form a large number of complex compounds due to the following reasons:
 i. Availability of vacant d-orbitals of suitable energy to accommodate lone pairs donated by ligands.
 ii. Small size and High Nuclear charge.

b.

Answer:

i. What tis the hybridization of the chlorine atom in CIF_3 molecule?
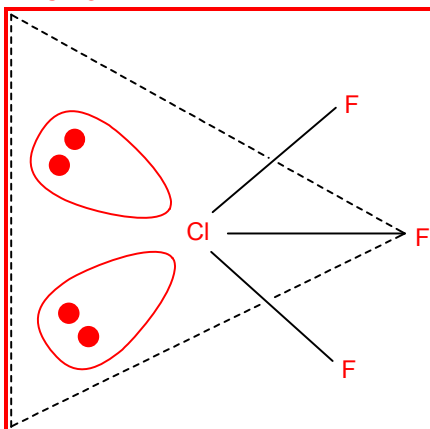
Answer:

Sp^3d hybridization.

ii.   Draw the structure of the molecule and state its geometry.   [2]

_____

Answer:

T-shaped ClF$_3$
Geometry of ClF$_3$ is T-shaped and formed by sp3d hybridization of the central atom X in its first excited state.

c. Name the inert gases used for: [1]

i. Filling sodium vapor lamps.

Answer:
Argon (Ar)

ii. Obtaining light of different colours in neon signs.

Answer:
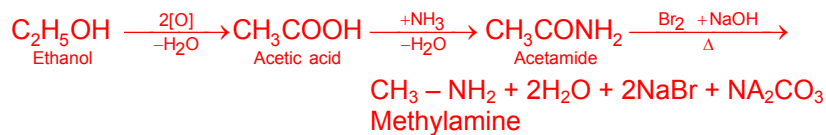Neon (Ne)

Section C *(Answer any two questions)*

Question: 8

a. How can the following conversions be brought about:

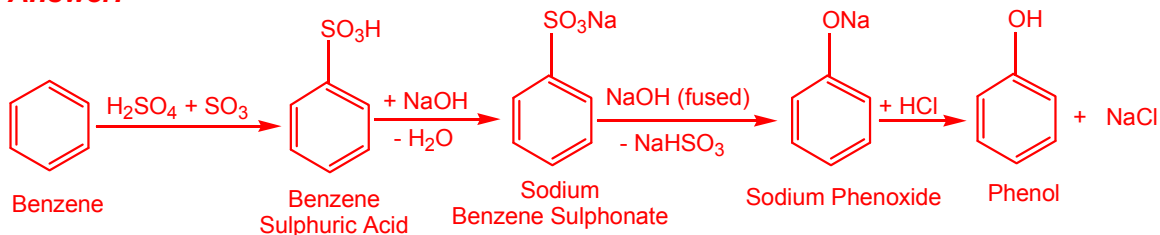i. Ethanol to methylamine.   [3]

Answer:

$$C_2H_5OH \xrightarrow[-H_2O]{2[O]} CH_3COOH \xrightarrow[-H_2O]{+NH_3} CH_3CONH_2 \xrightarrow[\Delta]{Br_2 \ +NaOH}$$

Ethanol   Acetic acid   Acetamide

$$CH_3 - NH_2 + 2H_2O + 2NaBr + NA_2CO_3$$
Methylamine

ii. Benzene to phenol   [2]

_____

Answer:

Benzene → Benzene Sulphuric Acid → Sodium Benzene Sulphonate → Sodium Phenoxide → Phenol + NaCl

b. Complete the following reactions and name the reactions:

i. _____ $+ 3I_2 + 4KOH \rightarrow CHI_3 + CH_3COOK + 3KI + 3H_2O$ [3]

Answer:

$$CH_3 - \overset{\overset{\textstyle O}{\|}}{C} - CH_3 + 3I_2 + 4KOH \rightarrow CHI_3 + CH_3COOK + 3KI + 3H_2O$$

ii. $C_3H_7NH_2 + CHCl_3 + 3KOH \text{ (alc.)} \xrightarrow{\Delta}$ _____ $3KCl + 3H_2O$ [1]

Answer:

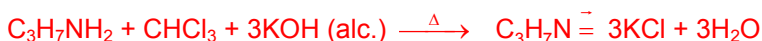$C_3H_7NH_2 + CHCl_3 + 3KOH \text{ (alc.)} \xrightarrow{\Delta}$ $C_3H_7N \bar{=}$ $3KCl + 3H_2O$
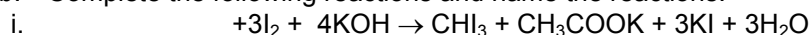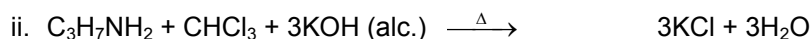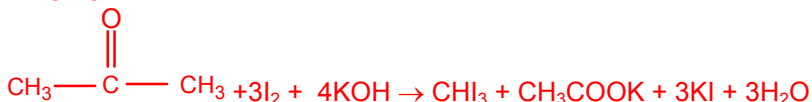
This is Carbylamine Reaction.

c. Name the type of polymerization (addition or condensation) and name the monomers in each of the following polymers: [2]

i. Protein

Answer:

Type of Polymerisation – Condensation
      Monomers - α-Amino acids

ii. Polyethylene

Answer:

Type of Polymerisation – Addition
      Monomers – Ethylene or Ethene

Question: 9

a.
i. What type of isomers are glucose and fructose? [1]

Answer:

Glucose and Fructose are functional (Structural) isomers.

ii. Name the functional group common to both glucose and fructose.

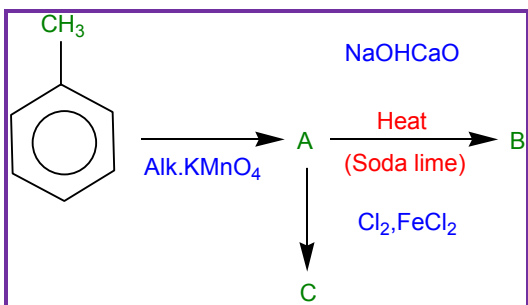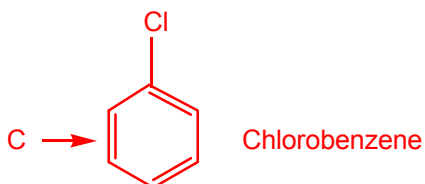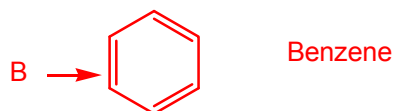**Answer:**

Hydroxyl Group – (-OH) common to both.

b.

   i. Identify the products A, B and C: [3]

Answer:

A → (COOH on benzene ring) Benzoic acid

B → (benzene ring) Benzene

C → (Cl on benzene ring) Chlorobenzene
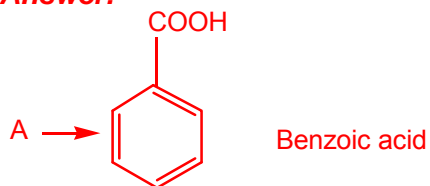
ii. Identify the reagents X, Y and Z.

$$C_2H_4Cl \xrightarrow{X} C_2H_4CN \xrightarrow{Y} C_2H_5CH_2NH_2 \xrightarrow{Z} C_2H_5CH_2NHCOCH_2$$

Answer:

$$C_2H_5Cl \xrightarrow[\text{KCN}]{(X)} C_2H_5CN \xrightarrow[\substack{\text{or Ni/H}_2}]{\substack{(Y)\\ C_2H_5OH,Na}} C_2H_5CH_2NH_2$$

(Z)
(CH$_3$CO)$_2$O

C$_2$H$_5$CH$_2$NH COCH$_3$

X = KCN, Y = C$_2$H$_5$OH, Na OR Ni / H$_2$, Z = (CH$_3$CO)$_2$O.
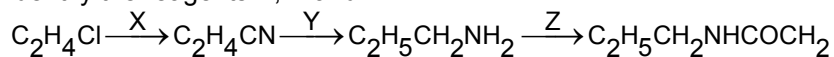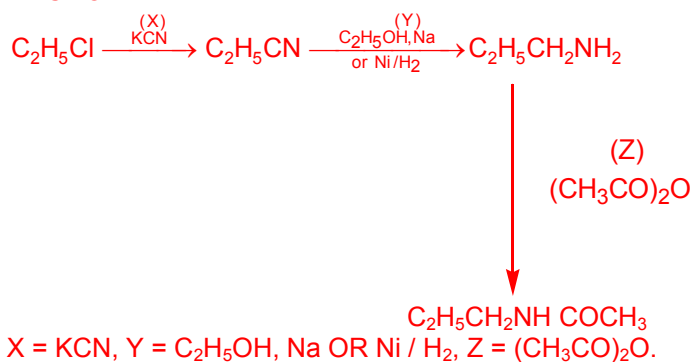
c. Give balanced equations for the following reactions: [3]

i. Benzaldehyde and Hydroxylamine.

Answer:

Benzaldehyde + Hydroxyl Amine → Benzaldoxime + H_2O

ii. Benzoic acid and phosphorus pentachloride.

Answer:

Benzoic Acid + Phosphorous Pentachloride → Benzoyl Chloride + $POCl_3$ + HCl

iii. I-butanol and Hydrogen chloride.

Answer:

I-butanol + HCl (Hydrozen Chloride) —$ZnCl_2$→ Chloro Butane

d. Give one good chemical test to distinguish between the following pairs of compounds: [3]
i. Methanal and ethanol

Answer:
Methanol and Ethanal: Ethanal when heated with I_2 and NaOH, it gives a yellow ppt of iodoform.

$CH_3CHO + 3I_2 + 4NaOH \rightarrow CHI_3 \downarrow HCOONa + 3NaI + 3H_2O$
Ethanal   Iodo form
                          (Yellow ppt)
$HCHO + 3I_2 + 4NaOH \rightarrow$ No Reaction
Methanol

ii. Urea and benzoic acid

Answer:
Urea on heating liberate NH_3 and white residue of biuret which gives violet colour with alkaline dilute $CuSO_4$ solution.
$NH_2CONH_2 + H_2NCONH_2 \xrightarrow[-NH_3]{\Delta} NH_2CONHCONH_2$

Urea   Biuret
$C_6H5COOH \xrightarrow{\Delta}$ No Reaction

_____

Question: 10

a. An aliphatic hydrocarbon A on treatment with sulphuric acid in the presence of $HgSO_4$ yields a liquid B with molecular formula C_2H_4O. B on oxidation with acidified potassium dichromate yields C which gives effervescence with sodium bicarbonate. C when treated with $SOCl_2$ gives D. when D reacts with ethanol it gives a sweet smelling liquid E. e is also formed when C reacts with ethanol in the presence of conc. H_2SO_4.

i.   Identify A,B,C,D and E.   [4]
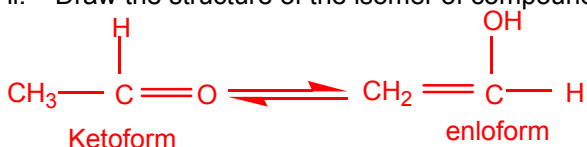
Answer:

$A \rightarrow C_2H_2$ $B \rightarrow CH_3CHO$
    Ethyne   Ethanal

$C \rightarrow CH_3COOH$ $D \rightarrow CH_3COCl$
    Ethanoic Acid   Ethanoyl chloride

$E \rightarrow CH_3COOC_2H_5$
    Ethyl Ethanoate

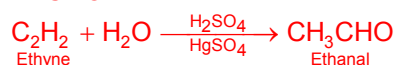ii. Draw the structure of the isomer of compound B.   [1]

$$CH_3-\overset{\displaystyle \overset{H}{|}}{C}=O \rightleftharpoons CH_2=\overset{\displaystyle \overset{OH}{|}}{C}-H$$

Ketoform   enloform

Answer:

iii. Write the balanced equation for the conversion of A to B.

Answer:

$$C_2H_2 + H_2O \xrightarrow[\text{HgSO}_4]{\text{H}_2\text{SO}_4} CH_3CHO$$
 Ethyne   Ethanal

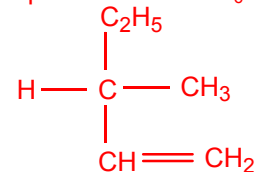b. The compound C_5H_{12} shows optical isomerism. Draw the structural formula of the compound and name it.   [1]
i.

Answer:
Optical isomer of C_6H_{12}

$$H-\overset{\displaystyle \overset{C_2H_5}{|}}{\underset{\displaystyle \underset{CH=CH_2}{|}}{C}}-CH_3$$

3 - methyl- pent 1 - enl

ii. Name any three types of isomerisms that the compounds with molecular formula C_4H_7Cl can give rise to. Also represent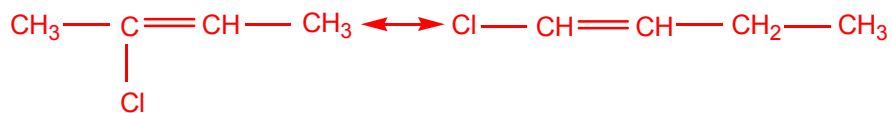 the structures of the compounds relevant to these isomers.   [3]

_____

Answer:
Compound with molecular formula C_4H_7Cl is

$CH_3 — CH = CH — CH_2 — Cl$

(I)

(1 - Chloro but - 2 - ene)

$CH_3 — C = CH — CH_3 \longleftrightarrow Cl — CH = CH — CH_2 — CH_3$

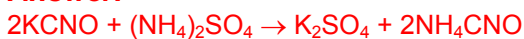$\quad\quad\quad\;\; |$

$\quad\quad\quad Cl$

(II) (III)

(2 - Chlorobut - 2 - ene) (1 - Chloro but -1 - ene)

c. Give equations to show what happens when a mixture of potassium cyanate and ammonium sulphate is strongly heated. Name the reaction. [2]

Answer:
$2KCNO + (NH_4)_2SO_4 \rightarrow K_2SO_4 + 2NH_4CNO$
Potassium Ammonium pot.   Ammonium
Cyanate   sulphate   sulphate   Cyanate

Ammonium cyanate on rearrangement gives urea.
$2NH_4CNO \rightarrow NH_2CONH_2$
Amm. Cyanate   Urea
This is wholer's synthesis of urea.

(**) Currently out of syllabus. Answer can be provided up on request