2013

Part I (Answer all questions)

Question: 1

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

(Zero, first, second, increased, decreased, anode, cathode, inactive, active, potassium cyanide, internal, external, dependent, independent, red, benzoic acid, benzoin, common ion effect, salt hydrolysis, alkali, potassium hydroxide.) [5]

i. In a galvanic cell, electrons flow from _____to _____through the connecting wires.

Answer:

ii. Racemic mixtures are optically _____ because of _____ compensation.

Answer:

iii. Half life period of a _____ order reaction is _____ of the concentration of the reactant.

Answer:

iv. Benzaldehyde when treated with an alcoholic solution of _____ forms_____.

Answer:

v. Solubility of calcium oxalate is _____ in the presence of ammonium oxalate because of _____.

Answer:

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

1. The compound which is optically active is:

   1 - butanol

   2 - butanol

   1 - propanol

   2 – methyl – 1 - propanol

2. The salt which will not hydrolyse in aqueous solution is:

   Copper sulphate

   Sodium sulphate

   Potassium cyanide

   Sodium carbonate

3. Copper has the face centred cubic structure. The coordination number of each ion is

   4

   12

   14

   8

4. For the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the unit of equilibrium constant is:

   L mol^{-1}

   J mol^{-1}

   Mol L^{-1}

   $[L\ mol^{-1}]^2$

5. The deficiency of vitamin D causes:

   Rickets

   Gout

   Scurvy

   Night blindness

c. Answer the following questions: [5]

i. Two metallic elements A and B have the following standard oxidation potentials :
A = 0.40v, B = 0.80v. What would you expect if element A was added to an aqueous salt solution of element B? Give a reason for your answer.

Answer:

A gets reduced due to higher electrode potential and B gets oxidized.

ii. Two moles of NH_3 are introduced into one litre flask in which it dissociates at high temperature as follows:
$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$. Determine Kc, if at equilibrium 1 mole of NH_3 remains.

Answer:

$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$.

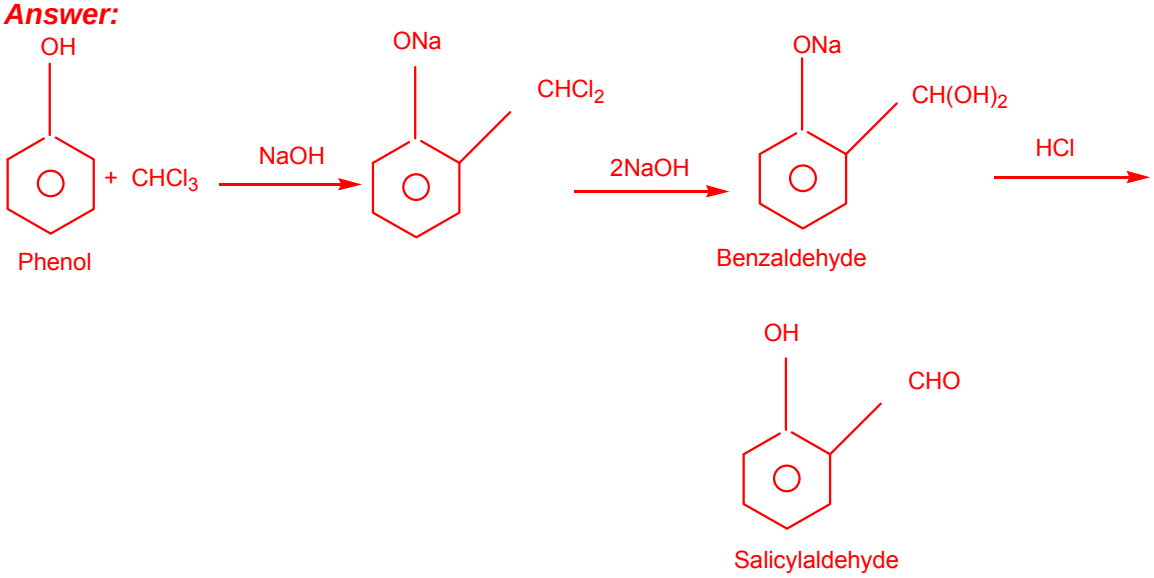
2 0 0

$\frac{2-2\times0.5}{1}$ $\frac{0.5}{1}$ $\frac{3\times0.5}{1}$

$= 1.6875\ mol^2 / l^2$.

iii. Give balanced equation for the preparation of salicylaldehyde from phenol.

Answer:



iv. If the half life period for a first order reaction is 69.3 seconds, what is the value of its rate constant?

Answer:

Given : $t_{1/2}$ = 69.3s, K = ?

$$K = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{69.3}$$

K = 0.01

v. Define cryascopic constant.

Answer:

Cryoscopic constant is defined as the depression in freezing point for 1 molal solution i.e a solution containing 1 gm mol of solute dissolved in 1000g of solvent.

d. Match the following:

i. Colligative property	a. Polysaccharide
ii. Nicol prism	b. Osmotic pressure
iii. Activation energy	c. Aldol condensation
iv. Starch	d. Polarimeter
v. Acetaldehyde	e. Arrhenius equation

Answer:

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. Ethylene glycol is used as an antifreeze agent. Calculate the amount of ethylene glycol to be added to 4kg of water to prevent it from freezing at -6. [3]

Answer:

Given: ΔT_f = -60c, w = 4kg, w' = ?

$$w' = \frac{\Delta T_f \times w \times M}{K_f \times 1000}$$

$$= \frac{6 \times 4 \times 62}{1.85 \times 1000}$$

w' = 0.8kg = 800 kg.

.

ii. The freezing point of a solution containing 0.3 gms of acetic acid in 30gms of benzene is lowered by 0.45 K. calculate the Van't Hoff factor. [2]

(at. Wt. of C = 12, H = 1, O = 16, K_f for benzene = 5.12 K kg mole^{-1}).

Answer:

We know that $\Delta T_f = I K_f m$

Where i represents Van't Hoff factor,

$$\text{molarlity , } m = \frac{w \times 1000}{M \times W}$$

$$m = \frac{0.3 \times 1000}{60 \times 30}$$

$$\text{Now, } i = \frac{\Delta T_f}{K_f \times m}$$

$$\frac{0.45}{5.12 \times 0.17}$$

= 0.517.

b. Name the low or principle confirmed by the following observations:

i. . When water is added to 0.01M aqueous solution of acetic acid the number of hydrogen ions increase. [2]

Answer:

Ostald's dilution law.

ii. When 96500 coulombs of electricity is passed through acidulated water, 5.6 litres of oxygen at s.t.p is liberated at the anode. [1]

Answer:

Faraday I Law of electrolysis.

c. Arrange Ag, Cr and Hg metals in the increasing order of reducing power. Given:

$E^o_{Ag^+/Ag} = 0.80\,V \quad E^o_{cr^{+3}/cr} = -0.74\,V \quad E^o_{Hg^{+2}/Hg} = +0.79\,V$ [1]

Answer:

$E^o_{Ag^+/Ag} < E^o_{Hg} < E^o_{Cr^{3+}/Cr}$

d. In a first order reaction, 10% of the reactant is consumed in 25 minutes. Calculate:

i. The half life of the reaction.

Answer:

For Ist order reaction,

$$K = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$= \frac{2.303}{25} \log \frac{100}{100-10}$$

$$= \frac{2.303}{25} \text{ x } 0.0457$$

K = 0.004

Now Half life,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.004}$$

$t_{½}$ = 173.25 min.

ii. The time required for completing 17% of the reaction.

Answer:

$$K = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$0.004 = \frac{2.303}{t} \log \frac{100}{100^{-17}}$$

$$\frac{2.303}{0.004} \text{x} 0.0806$$

= 46.40 min.

Question: 3

a. Explain giving reasons why (Give equations in support of your answer):

i. A solution of NH_4Cl and NH_4OH acts as a buffer. [2]

Answer:

A solution of NH_4Cl and NH_4OH acts as a base buffer as it resist the change in its pH on adding small amount of an acid or a base.

ii. Cu is precipitated as CuS while Zn is not precipitated when H_2S is passed through an acidic solution of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ respectively. [2]

Answer:

In case of $Cu(NO_3)_2$ the ionic product will exceed from solubility product while in case of $Zn(NO_3)_2$. Solubility producer exceed from ionic product. Hence, Zn is not precipitated when H_2S is passed through the solution.

b.

i. What is Schottky defect in a solid? [1]

Answer:

Schottky defect arises when some of the Lattice point in a crystal are unoccupied due to missing of equal number of cation and anion.

ii. A bcc element (atomic mass 65) has a cell edge of 420 pm. Calculate the density in gms / cm^3. [3]

Answer:

Given: Z = 2, a = 420 pm = 420 x 10^{-10} cm., M = 65, d = ?

We have

$$d = \frac{Z \times M}{a^3 \times N^A}$$

$$= \frac{2 \times 65}{(420 \times 10^{-10})3 \times 6.022 \times 10^{23}}$$

d = 2.91g cm^{-3}.

c. The rate of the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is given by:

Rate = 1.7 x 10-19 $[H_2]$ $[I_2]$ at 25^0C.

The rate of decomposition of gaseous HI to H_2 and I_2 is given by:

Rate = 2.4 x 10-21 $[HI]^2$ at 25^0C.

Calculate the equilibrium constant for the formation of HI from H_2 and I_2 at 25^0C.

Answer:

At equilibrium

$\because$ Rate of forward reaction = Rate of backward reaction.

$\therefore$ 1.7 x 10^{-19} $[H_2]$ $[I_2]$ $[HI]^2$

We know that,

$H_2 + I_2 \rightleftharpoons 2HI$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{1.7 \times 10^{-19}}{2.4 \times 10^{-21}}$$

$$K_c = \frac{1.7 \times 10^{-19} \times 10^{-21}}{2.4}$$

Question: 4

a.

i. Give Lewis definition for acids and bases. [1]

Answer:

Lewis defined an acid is an electron pair acceptor and base is an electron pair donor.

ii. The solubility of Ag_2CrO_4 at 25^0C is 8.0 x 10^{-5} moles / litre. Calculate its solubility product. [1]

Answer:

Solubility of Ag_2CrO_4 = 8.0 x 10^{-5} mol L^{-1}.

Ag_2CrO_4 = $2Ag^+ + Ag_2CrO_4^{--}$

8 x 10^{-5} 2 x 8 x 10^{-5} 8 x 10^{-5}

Ksp = $[Ag+]^2$ $[CrO_4^{--}]$

= 2048 x 10^{-15}

K_{sp} = 2.048 x 10^{-12}

$\therefore$ Solubility product of Ag_2CrO_4 = 2.048 x 10^{-12}.

b.

i. Define molar conductance of a solution. State its unit. How is it related to the specific conductance of a solution? [2]

Answer:

The conductance of that volume of solution which contains one mole of the solute and is placed between two parallel electrodes of 1cm apart and having sufficient area to hold the whole of the solution.

Its unit is S m^2 mol^{-1} (S.I) S cm^2 mol^{-1}. (C.G.S)

It is related with specific conductance

$$\Lambda_m = \frac{1000}{C} \times \Lambda_{sp}$$

ii. Calculate the value of Ecell at 298K for the following cell: [3]

Al | Al3+ (0.01M) | | Sn2+ (0.015M) | Sn

$E^o_{Al3+|A|}$ = 1.66 volt and $E^o_{Sn2+|Zn}$ = -0.14 volt.

Answer:

Net cell reaction, $2Al + 3Sn^{2+} \rightarrow 2Al^{3+} + 3Sn$

Here n = 6,

Nernst Equation,

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Al^{3+}]^2}{[Sn^{2+}]^3}$$

$$= (E^o_R - E^o_L) - \frac{0.059}{n} \log \frac{[Al^{3+}]^2}{[Sn^{2+}]^3}$$

$$= (-0.14 + 1.66) - \frac{0.059}{6} \log \frac{[0.01]^2}{[0.015]^3}$$

$$= 1.52 - \frac{0.059}{6} \log 29.585$$

= 1.52 – 0.086789

c.

i. Calculate the degree of hydrolysis of 0.2 (M) solution acetate solution. [1]

(Hydrolysis constant of sodium acetate = 5.6 x 10^{-10} and ionic product of H_2O = 10-14 at 25^0C.

Answer:

Given: $k_w = 1 \times 10^{-14}$, c = 0.2 M, $k_b = 5.6 \times 10^{-10}$.

Degree of hydrolysis,

$$h = \sqrt{\frac{k_w}{c \times k_a}}$$

$$= \sqrt{\frac{1 \times 10^{-14}}{0.2 \times 5.6 \times 10^{-10}}}$$

$$= \sqrt{0.892 \times 10^{10}}$$

$$= 0.944 \times 10^5 = 9.44 \times 10^4$$

ii. Explain why high pressure is used in the manufacture of ammonia by Haber's process. State the law of principle used. [2]

Answer:
High pressure is used in the manufacture of ammonia by Haber's process because equilibrium shift in the direction in which less number of molecules exert lower pressure i.e in the forward direction. Le Chaterlier's principle used in the manufacture of ammonia by Haber's process.
According to Le-Chatelier Principle, if a system in equilibrium is subjected to change in temperature, presence or concentration of any components in the system, equilibrium automatically shifts in such a direction of the reaction so as to reduce the effect caused by that change.

Section B *(Answer any two questions)*

Question: 5

a. Give the IUPAC names of the following coordination compounds: [2]
i. $K_2[Zn(OH)_4]$

Answer:
Potassium tetrahydroxozincate (II)

ii. $[Co(NH_3)_5\ (CO_3)Cl]$

Answer:
Pentaammine carbonate cobalt (III) chloride.

b. For the complex ion $[Fe(CN)_6]^{3-}$ state: [3]

i. The geometry of the ion

Answer:
For $[Fe(CN)_6]^{3-}$ state:
Geometry – Octahedral.

ii. The magnetic property of the ion.

Answer:
Paramagnetic.

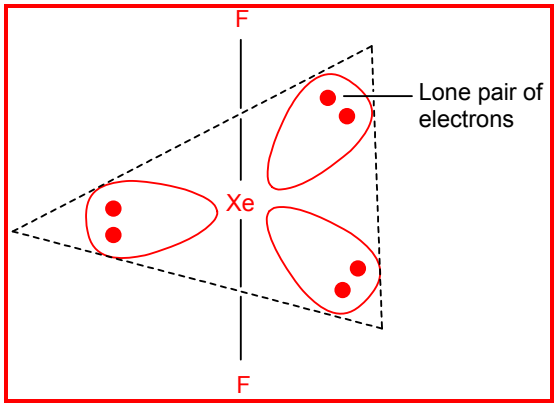
c. What type of structural isomers are $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$? give a chemical test to distinguish the isomers.

Answer:
They are ionization isomer.
$[Co(NH_3)_5Br]SO_4 + BaCl_2 \rightarrow$ White ppt.
$[Co(NH_3)_5SO_4]Br + BaCl_2 \rightarrow$ No ppt.

Question: 6

a. For the molecule
i. Draw the structure of the molecule indicating the lone pairs. [3]

Answer:



ii. State the hybridization of the central atom.

Answer:
Sp^3d hybridization.

iii. State the geometry of the molecule.

Answer:
Linear structure.

b. Give balanced equations for the following reactions: [2]

i. Fluorine treated with dilute sodium hydroxide solution.

Answer:
$2F_2 + 2NaOH \rightarrow 2NaF + H_2O + OF_2$
Fluorine dilute Sodium Fluoride Oxygen difluoride

ii. Hydrogen sulphide treated with concentrated sulphuric acid.

Answer:
$H_2S + H_2SO_4 \rightarrow S + SO_2 + 2H_2O$
Hydrogen Sulphide Conc. Sulphur

iii. Potassium iodide treated with acidified potassium permanganate solution.

Answer:
$2KMnO_4 + 8H_2SO_4 + 10KI \rightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$
Pot Permanganate Conc. Iodide sulphur Sulphate

Question 7

a. In the extraction of zinc from zinc blende: [2]

i. Give an equation to show how zinc oxide is converted to zinc.

Answer:

$ZnO + C \rightarrow Zn + CO$

Zinc oxide Coke Zinc

ii How is impure zinc finally electro refined?

Answer:

In electrolytic methods, on passing electric current pure zinc is obtained at cathode using impure rod of zinc as anode and zinc sulphate as electrolyte.

b. Explain why:

i. Transition elements form coloured compounds.

Answer:

Transition elements form coloured compounds due to d-d transitions taking place between the splitted d-orbitals.

ii. Interhalogen compounds are more reactive than their constituent elements. [2]

Answer:

Interhalogen compounds are more reactive than their constituent elements because x-y bonds present in them are weaker than x-x and y-y bonds.

iii. Cu^{+} is diamagnetic but Cu^{2+} is paramagnetic. (Z = 29)

Answer:

Cu^{+} is diamagnetic due to $3d^{10}$ configuration it has no unpaired electrons while Cu^{2+} has $3d^{9}$ configuration and one unpaired electron.

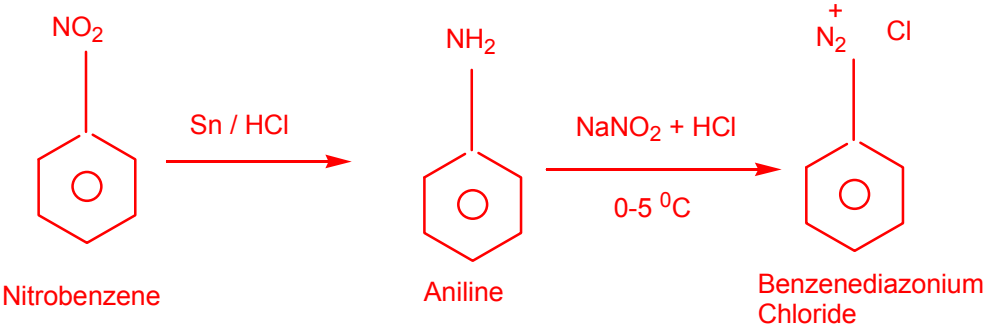
Section C *(Answer any two questions)*

Question: 8

a. How can the following conversions be brought about:

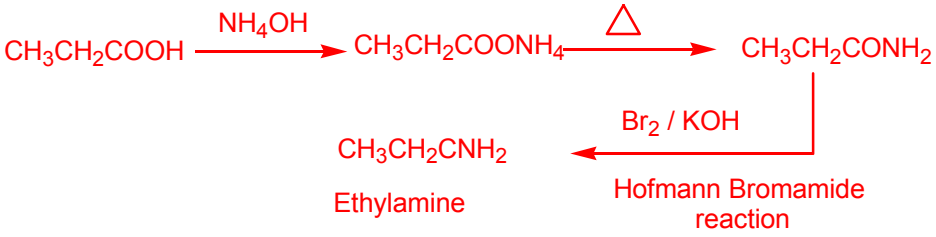
i. Nitro benzene to benzene diazoniumchloride. [3]

Answer:



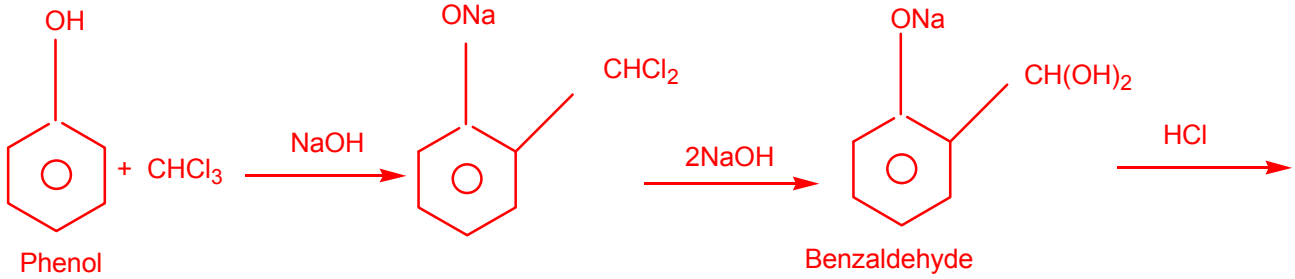
ii. Propanoic acid to ethylamine. [3]

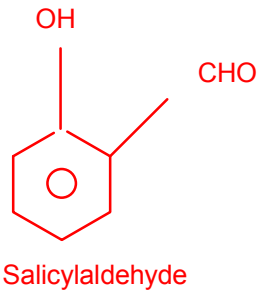
Answer:



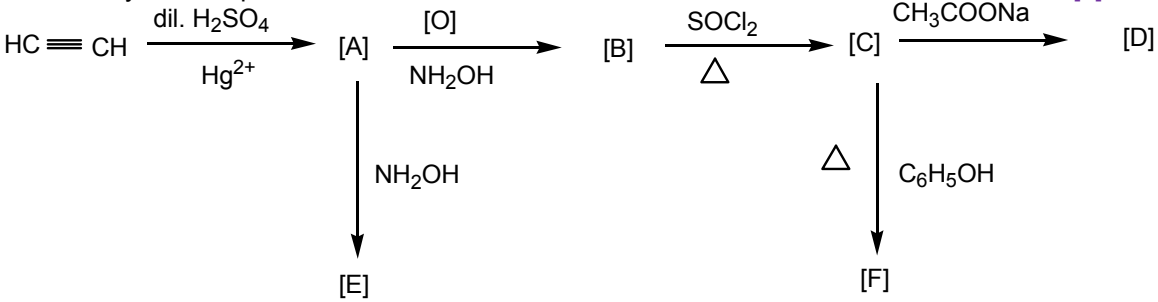
iii. Benzoic acid to benzaldehyde

Answer:

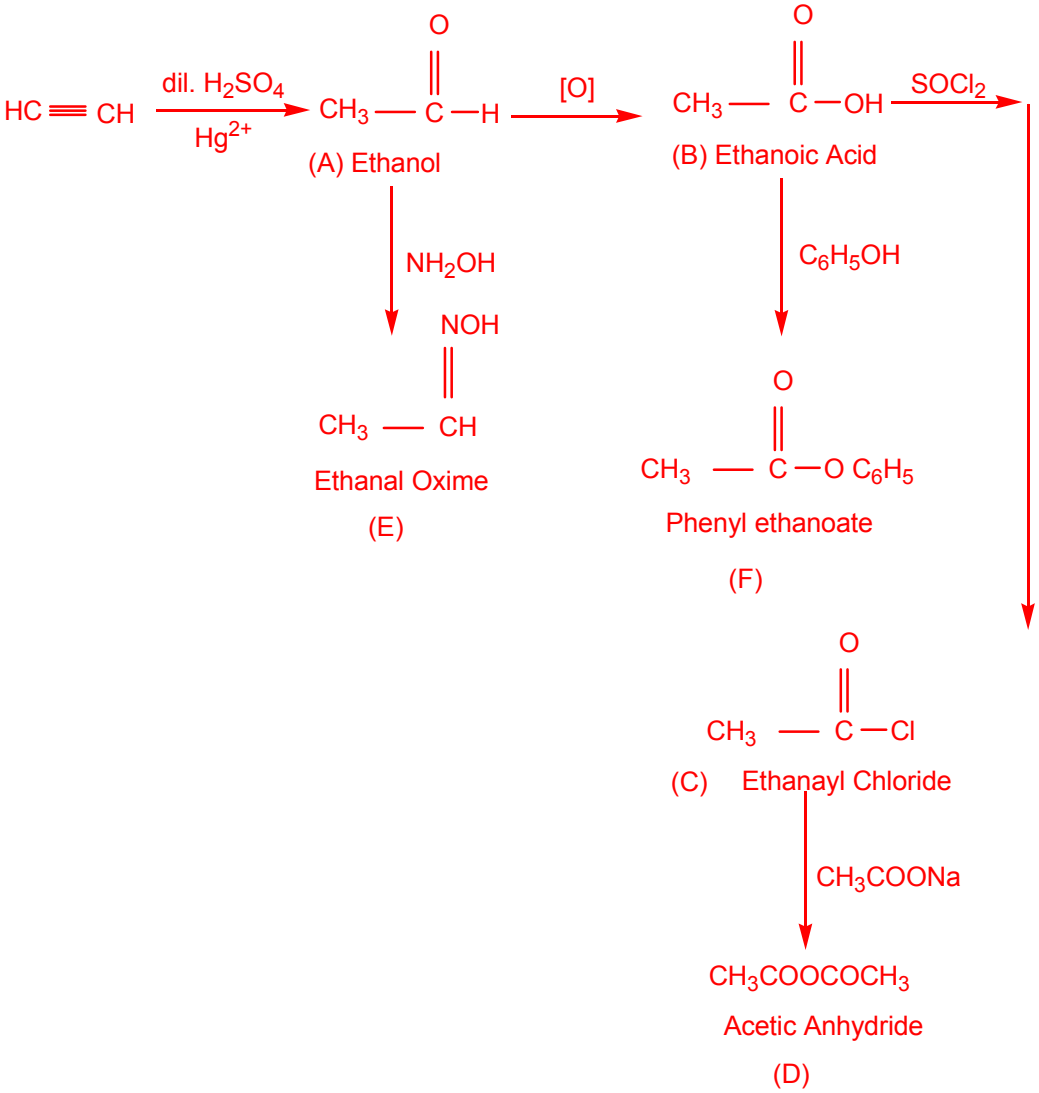




b. Identify the compounds A,B,C,D,E and F: [1]



Answer:



Question: 9

a. Write balanced chemical equations for the following reactions and name the reactions:

i. Acetamide is heated with bromine and sodium hydroxide solution. [3]

Answer:

$CH_3CONH_2 + Br_2 + 4KOH \rightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$

Acetamide methyl Amine

This reaction is known as Hoffmann bromamide degradation reaction.

ii. Benzaldehyde is treated with 50% sodium hydroxide solution.

Answer:

$C_6H_5CHO + C_6H_5CHO \xrightarrow{50\%\ NaOH} C_6H_5CH_2OH + C_6H_5COO\text{-}Na+$

Benzaldehyde Benzyl alcohol Sodium benzoate

This reaction is known as Cannizzaro reaction.

b. Give one chemical test to distinguish between the following pairs of compounds: [3]

i. Acetone and phenol.

Answer:

Phenol gives violet colour with neutral $FeCl_3$ while neutral $FeCl_3$ while acetone does not give this test.

$C_6H_5OH + FeCl_3 \rightarrow$ Violet colour

Phenol

ii. Fromic and Acetic acid

Answer:

Formic acid gives silver mirror test with Tollen's reagent while acetic acid does not give this test.

$HCOOH + 2[Ag(NH_3)_2OH] \rightarrow 2Ag + 2H_2O + CO_2 + 4NH_3$

Formic acid Tollen's reagent Silver mirror

$CH_3COOH + 2[Ag(NH_3)_2OH] \rightarrow$ No reaction

Acetic acid

c.

i. Name the type of isomerism exhibited by the following pairs of compounds:

1. $(C_2H_5)_2NH$ and $CH_3\text{-}NH\text{-}C_3H_3$

Answer:

$(C_2H_5)_2NH$ and $CH_3NH\ C_3H_7$ exhibit Metamerism.

2. I-butanol and 2 methyl-1-propanol [2]

Answer:

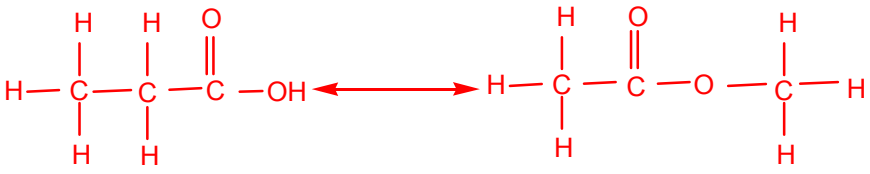
1-butanol and 2-methyl-1-propanol exhibit structural chain isomerism.

ii. Name the type of isomerism that the compound with molecular formula $C_3H_6O_2$ exhibits. Represent the isomers. [2]

Answer:

C_3H6O_2

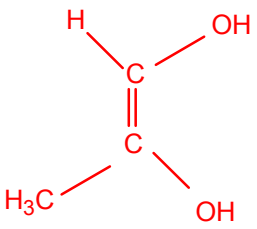
1. Functional isomerism: The isomers will be



Acetic Acid Methyl Acetate

These isomers exhibit functional group isomerism.

2. Geometrical isomerism: The isomers will be



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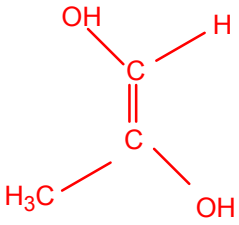


cis form

Trans form

Question: 10

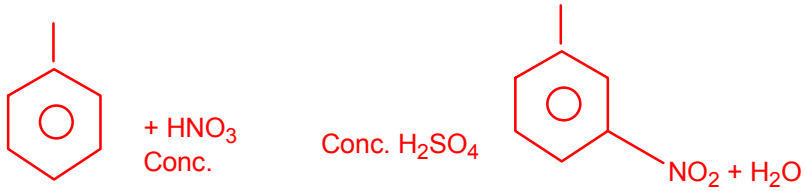
a. Write balanced equation for the following reactions: [4]

i. Oxalic acid is treated with acidified potassium permanganate solution.

Answer:

ii. Benzoic acid is treated with a mixture of concentrated nitric acid and concentrated sulphuric acid.

Answer:

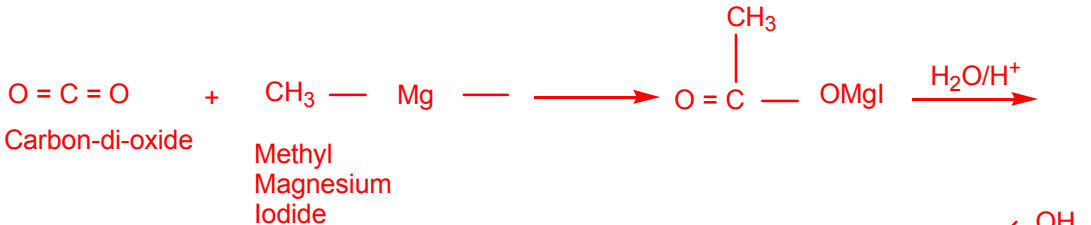


Benzoic Acid

m-nitro Benzoic Acid

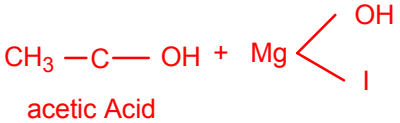
iii. Methyl magnesium iodide is treated with carbon dioxide and the product hydrolysed in acidic medium.

Answer:



Carbon-di-oxide

Methyl Magnesium Iodide



acetic Acid

Hydroxy Magnesium Iodide

iv. Ethylacetate is treated with ammonia.

Answer:

$CH_3COOC_2H_5 + NH_3 \rightarrow CH_3CONH_2 + C_2H_5OH$

Ethyl Acetate Ammonia Ethanamide Ethanol

b. An organic compound [A] having molecular formula C_2H_7N on treatment with nitrous acid gives a compound [B] having molecular formula C_2H_6O. [B] on treatment with an organic compound [C] gives a carboxylic acid [D] and a sweet smelling compound [E]. Oxidation of [B] with acidified potassium dichromate also gives [D]. [4]

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

Answer:

$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + (CH_3COO)_2O \longrightarrow CH_3COOH + CH_3COOC_2H_5$

(A) (B) (C) (D) (E)

[O] Acidified $K_2Cr_2O_7$

CH_3COOH

(D)

A → Ethanamine

B → Ethanol

C → Acetic Anhydride

D → Ethanoic Acid

E → Ethyl Ethanoate

ii. Write balanced chemical equation of [D] with chlorine in the presence of red phosphorus and name the reaction.

Answer:

$CH_3COOH + Cl_2 \xrightarrow{Red\ P} ClCH_2COOH$

(D)

Acetic Acid

This reaction is known as Hell Volhard – Zelinsky reaction.

c. Acetamide is amphoteric in nature. Give two equations to support this statement. [2]

Answer:

Acetamide is amphoteric in nature because it behave both as weak bases as well as weak acids.for ex.

Basic Nature:

$CH_3CONH_2 + HCl \rightarrow CH_3C\overset{+}{O}NH_3Cl^-$

Acetamide Ethanamide Hydrochloride

Acidic Nature:

$2CH_3CONH_2 + HgO \rightarrow (CH_3CONH_2)_2Hg + H_2O$

Acetamide Mercuric oxide Mercuric Acetamide