2014

Part I (Answer all questions)

Question: 1

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

(hydrolysis, reduction, oxidation, vacant, osmotic, above, benzoic acid, phenol, aniline, below, can, decreases, increases, cannot, crystal, ionization, rate, rate constant.) [5]

i. A catalyst _____ start a reaction but it can increase the _____ of the reaction.

Answer:

ii. Electrons trapped in the _____ sites of the _____ lattice are called F-centres.

Answer:

iii. An aqueous solution of sugar boils _____ 100oC and freezes _____ 0oC.

Answer:

iv. Toluene on _____ with alkaline potassium permanganate gives_____.

Answer:

v. The degree of _____ of ammonium hydroxide _____ on addition of ammonium chloride.

Answer:

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

1. For reaction $2N_2O_5 \rightarrow 2\ NO_2 + O_2$, the rate and rate constants are 1.02×10^{-4} mole litre^{-1} sec^{-1} and 3.4×10^{-5} sec^{-1} respectively. The concentration of N_2O_5 at that time will be:

   1.732 mol lit^{-1}

   3 mol lit^{-1}

   1.02×10-4 mol lit^{-1}

   3.2×105 mol lit^{-1}

2. Ethanoic acid dimerises in solution. Its molecular mass determined from its depression of freezing point of the solution will be:

   Same as the theoretical value

   Half its theoretical value

Double its theoretical value

One third of its theoretical value

3. Magnesium displaces hydrogen from dilute acid solution because:

   The oxidation potential of magnesium is less than that of hydrogen

   The reduction potential of magnesium is less than that of hydrogen

   Both magnesium and hydrogen have same oxidation potential

   Both magnesium and hydrogen have same reduction potential

4. In the series of reactions $CH_3COOH \xrightarrow{NH_3} A \xrightarrow{heat} B \xrightarrow{P_2O_5} C$, the product C is:

   Acetyl chloride

   Ammonium acetate

   Acetic anhydride

   Methyl cyanide

5. In the reaction $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$, the equilibrium will shift in the opposite direction, if:

   Rickets

   Gout

   Scurvy

   Night blindness

c. Answer the following questions: [5]

i. Among equimolal aqueous solutions of $MgCl_2$, $NaCl$, $FeCl_3$ and $C_{12}H_{22}O_{11}$, which will show minimum osmotic pressure? Why?

Answer:
$C_{12}H_{22}O_{11}$. Osmotic pressure is a colligative property which depends on the number of particles. $C_{12}H_{22}O_{11}$ is a nonelectrolyte and so it does not ionize in water. $MgCl_2$, $NaCl$ and $FeCl_3$ are electrolytes and so ionize in water to give more particles. Hence osmotic pressure is higher than $C_{12}H_{22}O_{11}$.

ii. If Kc for the reaction $N_2 + 3H_2 \rightarrow 2NH_3$ is 1.5×10^{-5} (mol/lit)$^{-2}$, write the value of K_{c1} for the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$

Answer:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]} = 1.5 \times 10^{-5}$$

$$K_c = \frac{[NH_3]}{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}} = \sqrt{1.5 \times 10^{-5}}$$

= 3.8729 x 10^{-3} (mol/litre)$^{-2}$

iii. The pH of acetic acid decreases on dilution. State the Law governing this statement.

Answer:
Ostwald's dilution law. "The degree of dissociation of a weak electrolyte is directly proportional to the square root of its dilution or inversely proportional to the square root of its concentration.

$$\alpha = \sqrt{KV}$$

$$\alpha = \sqrt{\frac{K}{C}}$$

K = the dissociation constant or ionization constant

iv. Xenon gives a series of flourides, but Helium and Neon do not. Why? (At. No: Xe = 54, Ne = 10, He = 2

Answer:
Xenon has large size and less ionization energy. Helium and Neon do not contain d-orbitals in their respective valence shells and hence their electrons cannot be promoted to higher energy levels like that in Xenon to form compounds with fluorine.

v. Calculate the number of coulombs required to deposite 20.25 g of aluminium (at. mass = 27) from a solution containing Al^{+3}.

Answer:
$$\frac{96500 \times 20.25}{9} = 217125 \text{ coulombs}$$

96500 coulombs is the quantity of electricity required to deposit 1 gram equivalent of any substance and 9 is the equivalent weight of aluminium.

d. Match the following:

i. $CHCl_3$ + NaOH	a. Fluorine
ii. Proteins	b. Starch
iii. Carbohydrate	c. Ammonia
iv. Lewis base	d. Peptide linkage
v. KHF_2	e. Isocyanide test

Answer:

$CHCl_3$ + NaOH	Isocyanide test
Proteins	Peptide linkage
Carbohydrate	Starch
Lewis base	Ammonia
KHF_2	fluorine

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 certain aqueous solution boils at 100.303°C. What is its freezing point? K_b for water = 0.5 K mol^{-1} and K_f = 1.87 K mol^{-1} [3]

Answer:

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f}$$

$$\frac{0.303}{\Delta T_f} = \frac{0.5}{1.87}$$

$$\Delta T_f = \frac{0.303 \times 1.87}{0.5}$$

= 1.133

ΔT_f = 273 – 1.133

= 271.867K

   ii. A solution containing 1g of sodium chloride in 100g of water freezes at 0.604°C. Calculate the degree of dissociation of sodium chloride. (Na = 23, Cl = 35.5, K_f for water = 1.87 k mol^{-1} [2]

Answer:

$$\Delta T_f = \frac{1000 \, K_f \, w}{m \, W}$$

$$m = \frac{1000 \times 1.87}{0.604 \times 100} = 30.96$$

$$i = \frac{58.5}{30.96}$$

= 1.889

(56.5 is the molecular mass of NaCl ie. 23 + 35.5 = 58.5)

$$\alpha = \frac{i - 1}{x - 1} \text{ (x = 2 for NaCl i.e NaCl} \rightleftharpoons Na^+ + Cl^-$$

$$\alpha = \frac{1.889 - 1}{2 - 1}$$

= 0.889

The degree of dissociation of NaCl = 88.9%

b.

   i. Explain graphically how the rate of a reaction changes with every 10°C rise in temperature. [2]

Answer:
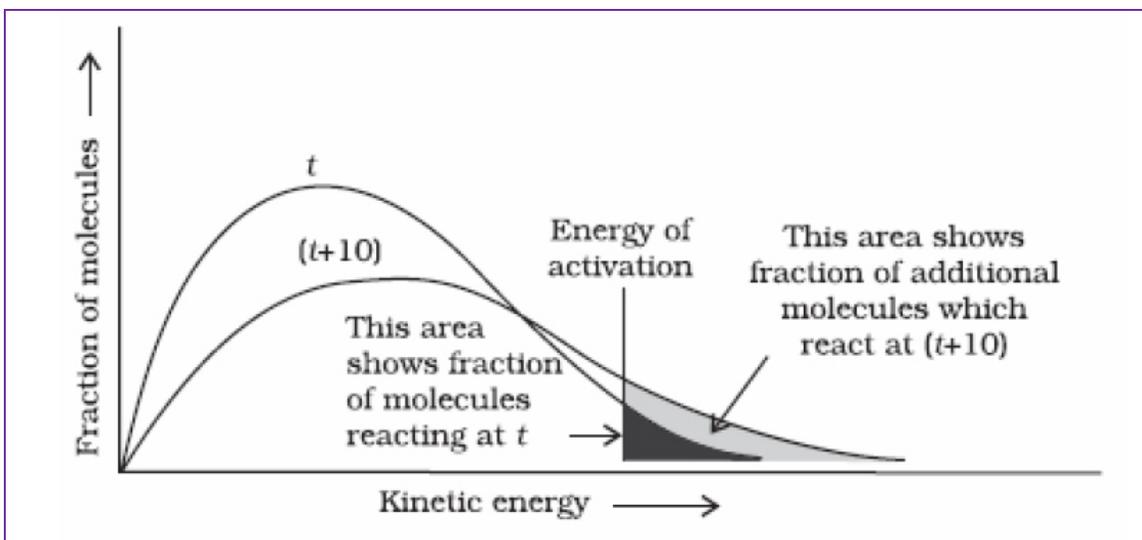
Energy distribution curve of a gaseous reacting system at a temperature t and and t + 10. With rise in temperature the kinetic energy of the molecules increases. The energy distribution curve flattens out and shifts towards higher enrgy regions. At (t + 10) collisions of a much larger fraction of molecules become effective to form products. This is why the rate of reaction becomes nearly two times for every 10oC rise in temperature.

ii. How is the activation energy of a reaction related to its rate constant. [1]

Answer:
Arrhenius equation

$$k = Ae^{\frac{-Ea}{RT}}$$

Or

$$\ln k = \ln A - \frac{-Ea}{RT}$$

Or

$$\log k = \log A \frac{-Ea}{2.303RT}$$

A is a constant called frequency factor
k = rate constant
Ea = Activation energy of a reaction
R = gas constant
T = temperature of the reaction on absolute scale.

iii. The half life period for the decomposition of a substance is 2.5 hours. If the initial weight of the substance is 160 g, how much of the substance will be left after 10 hours? [1]

Answer:

Quantity left after n half life period = $\left(\frac{1}{2}\right)^n$ x initial quantity

Number of half life for 10 hours = 4

So the quantity left after 4 half life = $\left(\frac{1}{2}\right)^4$ x 160 = 10 g

_____

Question: 3

a.

i. Define Frenkel defects of an ionic crystal. [1]

Answer:
Frenkel defect is due to shifting of an ion from its normal position to an interstitial in the crystal lattice thus causing vacancy in the original position. The overall density is not affected by this change. These defects are found in silver halides.

ii. Iron has an edge length 288pm. Its density is 7.86 gm cm-1. Find the type of cubic lattice to which the crystal belongs(atomic mass of iron is 56) [3]

Answer:

$$7.86 = \frac{z \times 56}{6.023 \times 10^{23} \times (288 \times 10^{-10})^3}$$

$$z = \frac{7.86 \times 6.023 \times 10^{23} \times (288 \times 10^{-10})^3}{56}$$

$$= 2.0194 \approx 2$$

(1 pm = 10^{-10} cm)

Number of particles in a body centred cubic unit cell = No of corners $x\dfrac{1}{8}$ + centre particle =

$8x\dfrac{1}{8}+1=2$. So the crystal belongs to body centred unit cell.

b. Explain giving reasons why:

i. $Mg(OH)_2$ is sparingly soluble in water but highly soluble in ammonium chloride solution. [1]

Answer:
$Mg(OH)_2$ is a weak base. NH_4Cl is acidic due to hydrolysis. So neutralization takes place and dissolves.

ii. When hydrogen sulphide is passed through acidified zinc sulphate solution, white ppt of zinc sulphide is not formed. [2]

Answer:
The solubility product of zinc sulphide is high and is not exceeded by ionic product in acid solution and so remains insolution. In acid solution dissociation of H2S is suppressed due to common ion effect of H^+. It gives less S^{2-} ions.

c. The equilibrium constant for the reaction $H_2(g)+I_2(g) \rightarrow 2HI(g)$ is 49.5 at 440°C. If 0.2 mole of H_2 and 0.2 mole of I_2 are allowed to react in a 10 litre flask at thistemperature, calculate the concentration of each at equilibrium.

Answer:

$$49.5 = \frac{4x^2}{(0.2 - x)^2}$$

$$49.5 = \frac{(2x)^2}{(0.2 - x)^2}$$

_____

_____

$$\sqrt{49.5} = \frac{2x}{(0.2 - x)}$$

$$7.03 = \frac{2x}{(0.2 - x)}$$

2x = 7.03 x 0.2 = 7.03x
2x = 1.406 – 7.03x

$$x = \frac{1.406}{9.03} = 0.1557$$

$[H_2]$ = 0.2 -1.557 = 0.0443
$[I_2]$ = 0.0443
[HI] = 2x = 2 x 0.443 = 0.0886

Question: 4

a.
i. What is specific conductance of a solution and what is its unit? How is it related to the equivalent conductance of the solution? [2]

Answer:
The reciprocal of specific resistance is called specific conductance of a solution.

$$\text{specific conductance} = \frac{1}{\rho}$$

It is defined as the conductance of a solution taken in a cell when electrodes are at unit distance from each other and each has area equal to 1 cm^2
Unit: $ohm^{-1}\ m^{-1}$ (S I Unit)
$Ohm^{-1}cm^{-1}$ (CGS Unit)

ii. 2.5 amperes of current is passed through copper sulphate solution for 30 minutes. Calculate the number of copper atoms deposited at the cathode (Cu = 63.54). [2]

Answer:

$$w = \frac{Eiz}{96500} = \frac{63.54 \times 2.5 \times 30 \times 60}{63.54 \times 2 \times 96500}$$

= 0.1404 x 10^{23}
= 1.404 x 10^{22} atoms

iii. Four metals W, X, Y and Z have the following values of Eo red.:
Eo
red
W = -0.140 V
X = - 2.93 V
Y = +0.80 V
Z = +1.50 V
Arrange them in the increasing order of reducing power.

Answer:
Reduction potential more negative is the most reducing. So the increasing order of reducing power is Z,Y,W and X.

b.
i. On adding sodium acetate to aqueous solution of acetic acid, what happens to the pH of the solution? Give a reason for your answer. [2]

_____

_____

Answer:

$CH_3COOH \rightleftharpoons CH_3COO^- + Na^+$

Due to common ion effect of CH_3COO^- Hydrogen ion concentration $[H^+]$ decreases. So the pH value increases.

ii. Calculate the pH of an aqueous solution of ammonium formate assuming complete dissociation. pka for formic acid = 3.8 and pkb of ammonia = 4.8   [1]

Answer:

Ammonium formate is a salt of weak acid and weak base.

$$pH = \frac{(pKw + pKa - pKb)}{2}$$

$$pH = 7 + \frac{3.8}{2} - \frac{4.8}{2} = 6.5$$

c.   Explain auto catalysis with one example.   [1]

Answer:

A substance formed in the course of a reaction, sometimes acts as a catalyst. This phenomenon is known as autocatalysis. For example, when acidified potassium permanganate is added to warm oxalic acid the decolourisation of the permanganate does not take place readily in the beginning. But after the first portion of the permanganate is decolourised, the reaction becomes quite fast. The manganese sulphate formed in the reaction acts as an autocatalyst.

Section B *(Answer any two questions)*

Question: 5

a.

i.   State the geometry and magnetic property of tetracarbonyl nickel according to the valence bond theory. [2]

Answer:

Nickel atom: $3d^8$, $4s^2$
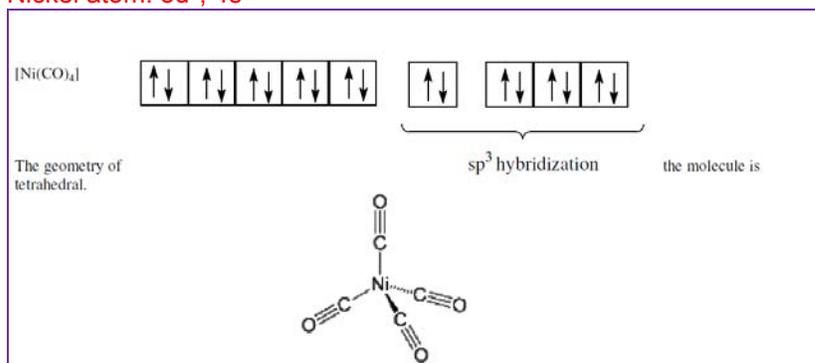
The number of unpaired electrons is 0 It is diamagnetic.

ii. $[Co(NH_3)_5 (CO_3)Cl]$ What type of structural isomers are $[Pt(OH)_2(NH_3)_4]SO_4$ and $[PtSO4(NH3)4] (OH)_2$?

Answer:

Ionization isomers.

_____

_____

$[Pt(OH)_2(NH_3)_4]SO_4$ gives test for $SO4^{2-}$ ion. With $BaCl_2$ solution a thick white ppt is formed. [Pt $SO_4(NH_3)_4$] $(OH)_2$ will not give a thick white ppt with $BaCl_2$.

b. Name the co-ordination compound used for the following: [3]
i. Treatment of cancer

Answer:
Cis $[PtCl_2(NH_3)_2]$ known as cisplatin is useful in the treatment of cancer.

ii. Treatment of lead poisoning.

Answer:
Ethylenediaminetetraacetic acid [EDTA]

Question: 6

a.   Draw the resonating structures of ozone molecule.   [1]

Answer:
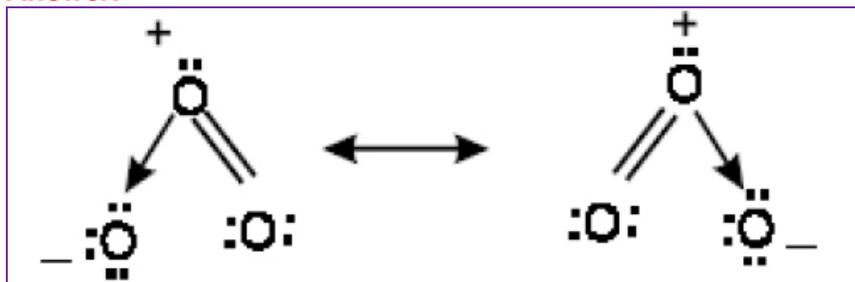
b. Explain giving reasons why: [2]

i. The halogens are coloured and the colour deepens from fluorine to iodine.

Answer:

Halogen	Fluorine	Chlorine	Bromine	Iodine
Colour	Pale yellow	Greenish yellow	Reddish brown	Violet

The colour of halogens is due to the fact that their molecules absorb radiations from visible light and the outer electrons are easily excited to higher energy levels. The amount of energy required for excitation depends upon the size of the atom. Fluorine atom is the smallest and the force of attraction between the nucleus and the outer electrons is very large. As a result it requires large excitation energy and absorbs violet light (high energy) and therefore appears pale yellow. The size of halogen atom increases from fluorine to iodine. Iodine needs less excitation energy and absorbs yellow light of low energy. Thus it appears dark violet. So the colour deepens from fluorine to iodine.

ii. In a given transition series, the atomic radius does not change very much with increasing atomic number.   [2]

Answer:
The screening effect caused by 3d electrons decreases the magnitude of nuclear charge and consequently the atomic radii do not change very much.

Question 7

a. .

i. Give an equation to show how the use of aqua region in dissolving platinum. [1]

Answer:
$Pt + 2HNO_3 + 8HCl \rightarrow H_2[PtCl_6] + 2NOCl + 4H_2O$

ii. Draw the structure of Xenon hexafluoride molecule and state the hybridisation of the central atom and the structure of the molecule. [2]

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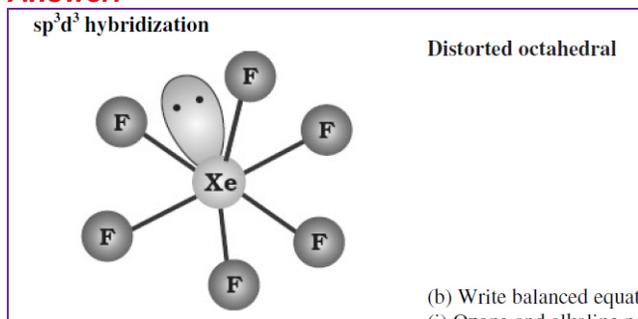
b. Write balanced equations for the following reactions: [2]

i. Ozone and alkaline potassium iodide.

Answer:
Ozone is oxidized to KIO3 and KIO4
$KI + 3O_3 \rightarrow KIO_3 + 3O_2$
$KI + 4O_3 \rightarrow KIO_4 + 4O_2$

ii. Sodium sulphite and acidified potassium permanganate.

Answer:
Acidified KMnO₄ oxidizes sodium sulphite to sodium sulphate

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$[Na_2SO_3 + [O] \longrightarrow Na_2SO_4] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5 Na_2SO_3 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5 Na_2SO_4$$
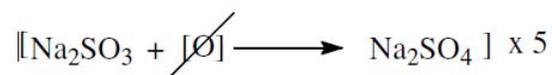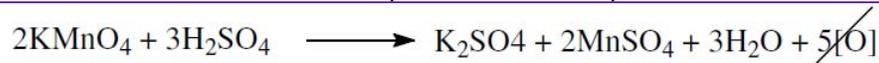
Answer:

Section C *(Answer any two questions)*

Question: 8

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

i. Benzene diazonium chloride is treated with copper and hydrochloric acid. [3]

Answer:

This reaction is called Gatterman reaction
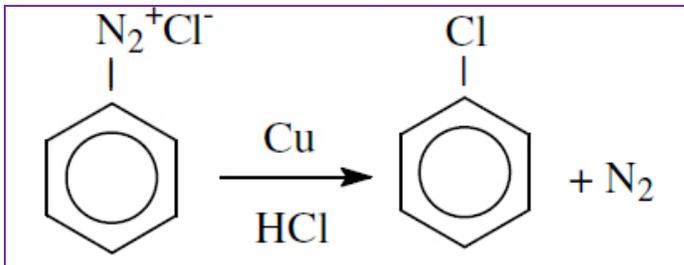
ii. Formaldehyde is treated with 50% caustic soda solution. [1]
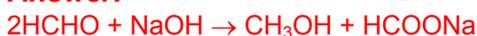
Answer:
$2HCHO + NaOH \rightarrow CH_3OH + HCOONa$
Methanal   Methanol   sodium formate
This reaction is called Cannizzaro reactions.

b.

i. How can chloroform be obtained from ethanol? [1]

Answer:
Chloroform can be readily separated from methanol, ethanol or isopropanol by extractive distillation. Typical effective agents are: for methanol, isopropanol or 4-methyl-2-pentanone; for ethanol, n-butanol or isobutyl acetate; for isopropanol, butyl acetate or ethylene glycol ethyl ether.

ii. Give reactions to show how aniline and nitrobenzene are separately treated with chlorine in the presence of iron. [1]

Answer:
On an industrial scale , aniline is prepared by the reduction of nitrobenzene by catalytic hydrogenation (H_2/Pt or V or CuO) or by chemical means using Fe/HCl or Sn/HCl.

c. Give one good chemical test to distinguish between the following pairs of compounds: **[3]**
i. Urea and acetamide

Answer:
On heating gently urea form biuret which gives violet colour with copper sulphate solution. Acetamide will not give this reaction.

ii. 1-propanol and 2-propanol.

**Answer:**
Lucas test: With Lucas reagent (HCl and ZnCl2) cloudiness appears immediately for 2-methyl-2-propanol while 1-
propanol does not react with Lucas reagent and no cloudiness is produced.

d. Name the monomeric units of Nylon 66.

_____

Answer:

COOH

$\left(\text{CH}_2\right)$

COOH

Adipic acid

and H_2N ——— $\left(\text{CH}_2\right)_6$ ——— NH_2

Hexamethylene diamine
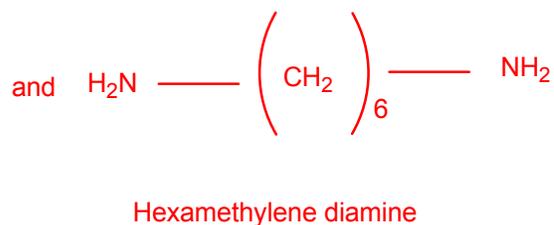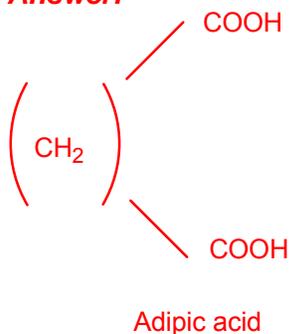
Question: 9

a.   Identify the compounds A, B, C, D, E and F.   [3]

C_6H_6 ⟶ $C_6H_5CH_3$ ⟶ C_6H_5CHO ⟶ $C_6H_5CH_2OH$ + D

alc. | KCN

E

F
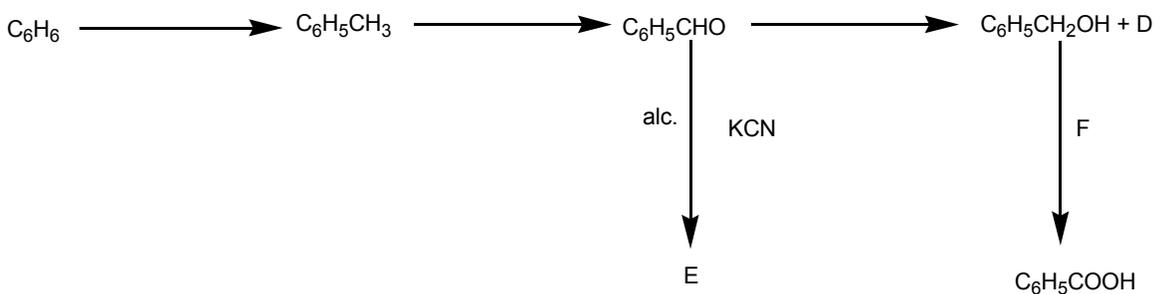
C_6H_5COOH

Answer:
A = CH_3Cl (Friedel Craft's alkylation
B = Chromyl chloride (CrO_2Cl_2): Etard's reaction
C = NaOH
D = Benzoic acid (C_6H_5COOH)
E = Benzoin

OH   O

C_6H_5-CH-C-C_6H_5

F = $K_2Cr_2O_7/H_2SO_4$
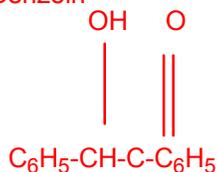
b.   How can the following conversions be brought about? :   [3]

i.   Ethanoic acid to ethylamine.

Answer:
CH_3COOH ⟶ NH_3 ⟶ CH_3COONH_4 ⟶ CH_3CO-NH_2 + H_2O

P_2O_5

$CH_3CH_2NH_2$ ⟵ $\xleftarrow{LiA1H_4}$ CH_3CN ⟵
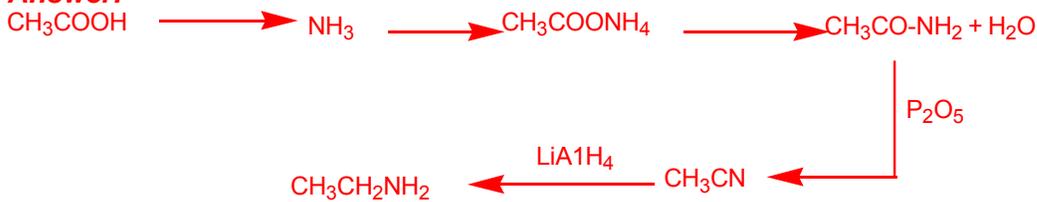
ii.   Aniline to benzoic acid

_____

_____

Answer:

NH$_2$ → (NaNO$_2$ / dil. HCl, Below 5^{0}C) → N = NCl → (Cu$_2$(CN)$_2$, KCN alcoholic) → CN → (H$_2$O, (H$^+$)) → COOH (Benzoic acid)
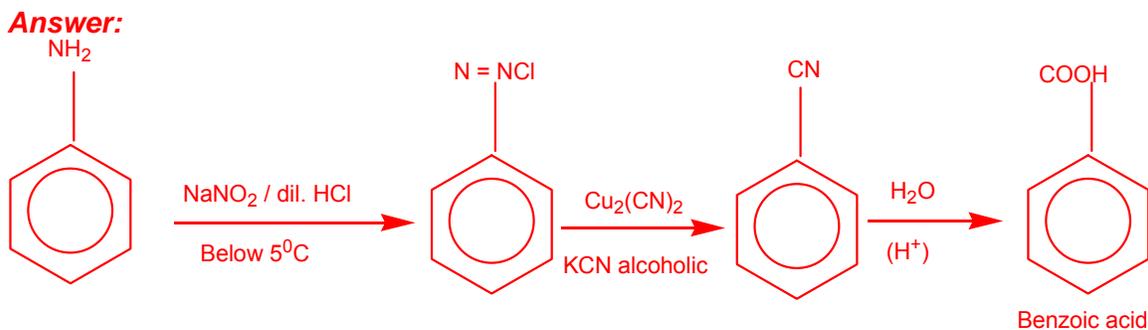
c. What is a zwitter ion? Represent the zwitter of glycine. [1]

Answer:
Amino acids contain both acidic and an amino group in the same molecule.In aqueous solution the –COOH group loses a proton while the –NH$_2$ group gains a prton to form a dipolar ion having the terminals as –COO$^-$ and -NH$_3^+$. It is called zwitter ion.

$$H_3N^+ \text{---} \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \text{---} COO^-$$
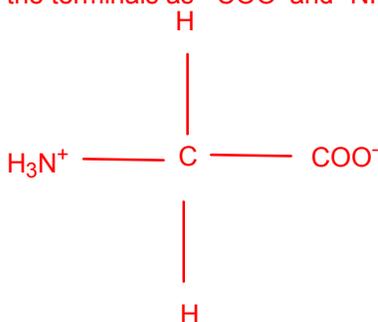
Question: 10   (**)

a. Write balanced equation for the following reactions:
An organic compound A on treatment with ethanol gives a carboxylic acid B and a compound C. Hydrolysis of C under acidic condition gives B and D. Oxidation of D with acidified potassium permanganate also gives B. B on heating with calcium hydroxide gives E with molecular formula C$_3$H$_6$O. E does not give Tollen's test but reacts with iodine and caustic potash to give a yellow precipitate. [4]
i. Identify A,B,C,D and E.

Answer:

ii. Write balanced equation of E with iodine and caustic potash and name the reaction.

Answer:
$CH_3 - CO - CH_3 + 3I_2 + 4KOH \rightarrow CHI_3 + CH_3COOK + 3KI + 3H_2O$
  Acetone   Iodoform
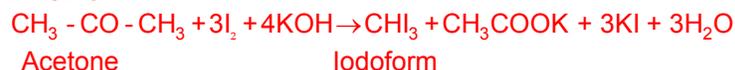
   E
Iodoform reaction

b.

_____

i. Name the functional groups that distinguish glucose and fructose. How will you distinguish between the two compounds? [2]

Answer:
Glucose functional group is aldehydes group –CHO
Fructose functional group is keto group

$$\backslash \!\!\! / \text{C}O$$

Glucose forms a brown resinous mass with warm sodium hydroxide solution. Fructose does not form a resin with sodium hydroxide solution.

ii. What are polyesters? Give one example of polyester and the monomers. [2]

Answer:
Polyesters are condensation polymers of diols with aromatic dicarboxylic acids and contain ester linkage eg. Terylene or Dacron. The monomers are Ethylene glycol.

$$CH_2OH$$
$$|$$
$$CH_2OH$$

and Terephthalic acid

HOOC ⬡ COOH
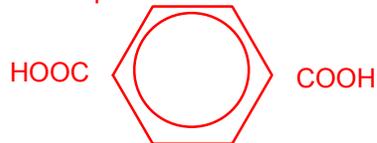
1,4-   1,4-benzene dicarboxylic acid

c. Give balanced equations for the following: [2]

i. Aniline and benzoyl chloride.

Answer:

NH_2 ⬡ $+ C_6H_5COCl \longrightarrow$ $NHCOC_6H_5$ ⬡ $+ HCl$
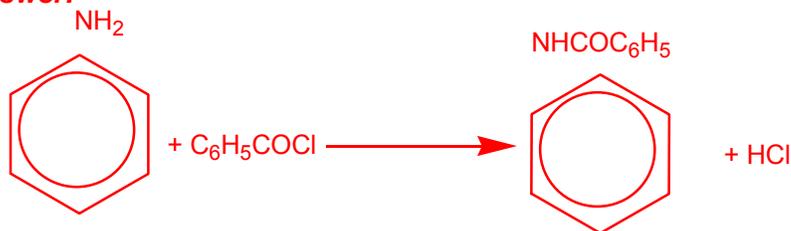
ii. Diethyl ether and hydroiodic acid (cold).

Answer:
$$C_2H_5\text{-}O\text{-}C_2H_5 + HI \xrightarrow{\text{cold}} C_2H_5OH + C_2H_5I$$

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