
2010

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2010

Part I (Answer all questions)

Question: 1

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

(benzoic acid, negative, positive, vapour pressure, benzal chloride, more, less, electropositivity, electronegativity, reducing, oxidizing, basic, acidic, PCl_5 , SOCl_2 , phenol, water, ice.) [5]

i. When water freezes to _____ the free energy of the system is _____.

Answer: ice, reducing

ii. The _____ pressure of an aqueous solution of 0.1 M cane sugar is _____ than that of pure water.

Answer: vapour, less

iii. When benzaldehyde reacts with _____ it forms _____ and POI_3 .

Answer: PCl_5 , benzal chloride

iv. An aqueous solution of a mixture of ammonium chloride and ammonium hydroxide is a _____ buffer solution with pH _____ than seven.

Answer: basic, more

v. Halogens are strong _____ agents because of their high _____.

Answer: oxidizing, electronegativity

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

1. The hybridization of the iron atom in $[\text{Fe}(\text{CN})_6]^{-3}$ complex is:

- sp^3
- d^2sp^3
- sp^3d^2
- dsp^2

Answer: 2

2. The product formed when aniline is warmed with chloroform and caustic potash is:

- Phenyl chloride
- Methyl isocyanide

Phenyl isocyanide

Nitro phenol

Answer: 3

3. The molecular weight of sodium chloride determined by measuring the osmotic pressure of its aqueous solution is:

For a dissociated solute in solution the value of van't Hoff factor is:

Zero

One

Greater than one

less than one

Answer: 3

4. The unit of equivalent conductance is:

$\text{ohm}^{-1}\text{cm}^2\text{equiv}^{-1}$

$\text{ohm}^{-1}\text{cm}^2\text{gm}^{-1}$

$\text{ohm cm}^2\text{equiv}^{-1}$

$\text{ohm}^{-1}\text{mole}^{-1}$

Answer: 1

5. An example of an electrophil is:

An example of intensive property is:

Number of moles

Mass

Volume

Density

Answer: 4

- c. Answer the following questions:

[5]

- i. The reduction potential of a metal X is -0.76 volts while that of Y is -2.38 volts. Which of the two metal is a stronger reducing agent? Give a reason for your answer.

Answer: Reduction potential of metal Y is lesser than that of metal X. So metal Y is a stronger reducing agent out of the two.

- ii. The osmotic pressure of a 0.25 M urea solution is 2.67 atm. What will be the osmotic pressure of a 0.25 M solution of potassium sulphate?

Answer: For urea, $\pi_{\text{urea}} = iCRT$

$$C_{\text{urea}} = \frac{\pi_{\text{urea}}}{iRT}$$

For Potassium sulphate solution,

$$\pi_{\text{K}_2\text{SO}_4} = iCRT$$

$$C_{K_2SO_4} \frac{\pi K_2SO_4}{iRT}$$

Because molar concentration of both the solution are same

$$\therefore \frac{\pi_{urea}}{iRT} = \frac{\pi K_2SO_4}{iRT}$$

$$\frac{\pi_{urea}}{i_{urea}} = \frac{\pi K_2SO_4}{i K_2SO_4}$$

For urea $i = 1$, For K_2SO_4 $i = 3$

$$\pi K_2SO_4 = 2.67 \times 3 = 8.01 \text{ atm.}$$

iii. Name the type of isomerism exhibited by lactic acid, $CH_3CH(OH)COOH$ giving reason for your answer.

Answer: lactic acid, $CH_3CH(OH)COOH$ exhibits optical isomerism because it has one asymmetric carbon atom and its spatial arrangements are non superimposable mirror of each other.

iv. Write the relationship between Gibb's free energy, enthalpy, entropy and the temperature of a system. What is this equation known as?

Answer: The relationship between Gibb's free energy (G), enthalpy (H), entropy (S) and the temperature (T) of a system is given by the equation

$$G = H - TS$$

It is called Gibb's free energy equation. The change in Gibb's free energy is expressed by the equation,

$$\Delta G = \Delta H - T\Delta S.$$

This is known as Gibb's Helmholtz equation.

v. The elevation of boiling point produced by dilute equimolala solutions of three substances are in the order $A > \text{glucose} > B$. suggest a reason for this observation.

Answer: This observation suggests that substance A dissociates while substance B associates in the solution because elevation in boiling point depends upon number of particles of the solute present in the solution and not on the molal concentration.

d. Match the following:

i. Nernst equation	a. Chiral carbon law
ii. Phenol	b. Hexadentate
iii. Entropy	c. Electrochemical cells
iv. EDTA	d. Reimer Tiemann reaction
v. Polarised light	e. Second law of Thermodynamics

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

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. What is the mass of anon-volatile solute (molar mass of 60) that needs to be dissolved in 100g of water in order to decrease the vapour pressure of water by 25%. What will be the molality of the solution? [3 $\frac{1}{2}$]

Answer: Given $\Delta P = 25(\text{atm})$ $P = 100(\text{atm})$

$m = 60$, $W = 100\text{g}$, $M = 18$ (H_2O)

according to Raoult's Law,

$$\frac{\Delta P}{P} = X_{\text{solute}} = \frac{n}{n+N}$$

$$\frac{25}{100} = \frac{w/60}{w/60 + 100/18}$$

$$4 = 1 + \frac{60 \times 100}{w \times 18}$$

$$3 = \frac{6000}{18w}$$

$$w = 111.11\text{g}$$

$$\text{Molality of the solution} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in Kg.}} = \frac{w/60}{100/1000} = \frac{111.11/60}{100/1000} = 18.518$$

\therefore Mass of solute required is 111.11g and molality of the solution is 18.518.

- ii. Show that the time required for the completion of 75% of a reaction of first order is twice the time required for the completion of 50% of the reaction. [2 $\frac{1}{2}$]

Answer: for a first order reaction, rate constant

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$\text{For 75\% completion, } k = \frac{2.303}{t(75\%)} \log \frac{a}{(a-x)}$$

$$= \frac{1.403}{t(75\%)}$$

$$\text{For 50\% completion, } k = \frac{0.693}{t(50\%)}$$

Because k is constant for a given reaction, so

$$\frac{1.403}{t(75\%)} = \frac{0.693}{t(50\%)}, \quad 2.02 \, t_{50\%} = t(75\%)$$

$$2t_{(50\%)} = t_{(75\%)}$$

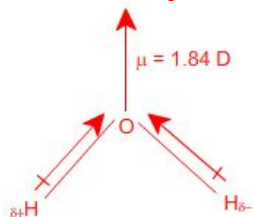
This shows that the time required for 75% completion of a reaction is nearly twice the time required for 50% completion.

b. Give reasons for the following:

i. The density of ice is less than that of water.

[2]

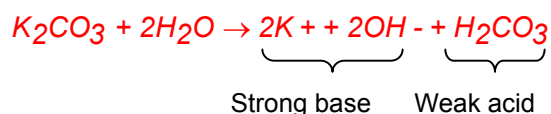
Answer: In ice lattice each water molecule is tetrahedrally bonded to four other molecules through H-bonds. The arrangement is extended to three dimensional open cage like structure with large empty spaces. These empty spaces increase the volume. Hence density of ice decreases.



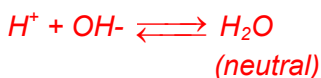
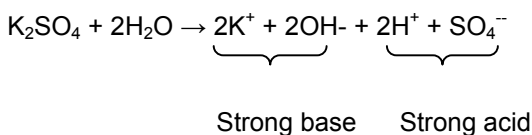
ii. A solution of potassium carbonate turns red litmus paper blue while that of potassium sulphate has no effect on litmus.

[2]

Answer: potassium carbonate is salt of strong base and weak acid. When it is dissolved in water it undergoes anionic hydrolysis making the solution alkaline so it turns red litmus blue.



On the other hand, potassium sulphate is a salt of strong base and strong acid. Therefore, its aqueous solution remains neutral and has no effect on litmus.

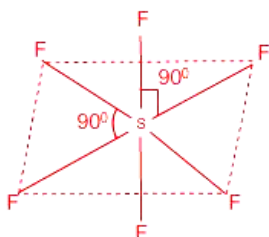


Question: 3

a.

i. Draw the structure of sulphur hexafluoride molecule. State the hybridization of the central atom and the geometry of the molecule. How many sigma bonds are present in the molecule?

[2]

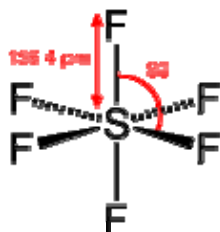


Answer:

Structure of sulphur hexafluoride, SF_6 .

Hybridization of central atom S is sp^3d^2 .

Geometry of the molecule is octahedral. There are six sigma bonds present. Four σ -bonds in the same plane, one above and one below the plane.



- ii. Lead(II) sulphide has FCC crystal structure. The edge length of the unit cell of PbS crystal is 500 pm. What is its density ? [Pb = 207.2, S = 32]

Answer: For a cubic crystal, density ρ is given by

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

Given: $Z = 4$ formula units for FCC arrangement.

$M = (207.2 + 32)$ for Pbs.

$A = 500\text{pm} = 500 \times 10^{-10} \text{ cm}$.

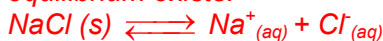
$N_A = 6.02 \times 10^{23}$

$$\therefore \text{Density of Pbs, } \rho = \frac{4 \times 239.2}{(500 \times 10^{-10})^3 \times 6.02 \times 10^{23}} = 12.715 \text{ g cm}^{-3}$$

b.

- i. Explain the purification of common salt by bubbling hydrogen chloride through the aqueous solution.

Answer: Purification of common salt by bubbling HCl through the aqueous solution is based on the concept of solubility product. In a saturated solution of NaCl following equilibrium exists.



For this $K_{sp} = [\text{Na}^+][\text{Cl}^-]$

When hydrogen chloride gas is bubbled through the saturated aqueous solution of impure NaCl, concentration of Cl^- ions increases and the product $[\text{Na}^+][\text{Cl}^-]$ exceeds K_{sp} for NaCl. Therefore pure NaCl starts precipitating leaving the impurities in the solution.

- ii. Calculate the pH of a buffer solution containing 0.45 moles of NH_4OH and 0.75 moles of NH_4Cl . K_b for NH_4OH is 1.8×10^{-5} [3]

Answer: For basic buffer, Henderson's equation is

$$\text{pOH} = \text{p}K_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

Given $K_b = 1.8 \times 10^{-5}$ $[\text{Salt}] = 0.75$, $[\text{Base}] = 0.45$

$$\therefore \text{pOH} = -\log_{10}(1.8 \times 10^{-5}) + \log_{10} \frac{0.75}{0.45}$$

$$= 4.745 + 0.2218$$

$$= 4.9668$$

$$\text{Now pH} = 14 - \text{pOH}$$

$$= 14 - 4.9668$$

$$= 9.033$$

So, pH of given basic buffer of NH_4Cl and NH_4OH is 9.033.

- c. Will nickel displace copper from a 1M solution of copper sulphate? Justify your answer.

$$[E_{\text{Ni}^{2+}/\text{Ni}}^0 = 0.25\text{V}, E_{\text{Cu}^{2+}/\text{Cu}}^0 = +0.34\text{V}] \quad [1]$$

Answer: Nickel will displace Cu^{++} ions from 1 M Copper solution because E_{red} for Nickel is less than that of Copper.



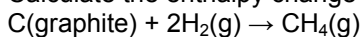
Question: 4

- a. State Kohlrausch's Law and give its mathematical expression mentioning the terms involved in it. [2]

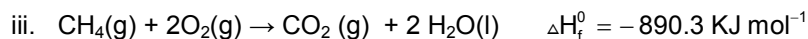
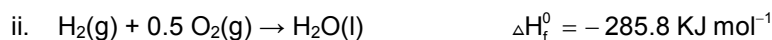
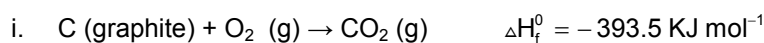
Answer: Kohlrausch's law of independent migration of ions

- b. Name the type of isomerism shown by the following pairs of co-ordination compounds: [2]

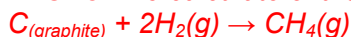
Calculate the enthalpy change for the reaction:



Given that:



Answer: To calculate enthalpy for the following reaction,



We multiply equation (ii) by 2 and add it to equation (i), We get



Now we subtract equation (iii) from equation (iv)

We get:



c. For the following cell, calculate the emf:

- i. A solution of 0.1 (N) KCl offers a resistance of 245 ohms. Calculate the specific conductance and the equivalent conductance of the solution if the cell constant is 0.571 cm⁻¹. [2]

Answer: Given $R = 245 \text{ ohm}$, cell constant = 0.571 cm⁻¹
Normality = 0.1

Now, specific conductance, $k = \frac{1}{R} \times \text{cell constant}$

$$\frac{1}{245} \times 0.571$$

$$\Lambda_{eq} = \frac{1000 \times k}{\text{Normality}}$$

$$= \frac{1000 \times 2.33 \times 10^{-4}}{0.1}$$

$$= 2.33 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

For the given solution, specific conductance is $2.33 \times 10^{-4} \text{ ohm}^{-1}$ and Λ_{eq} is $2.33 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$.

- ii. Compare the crystals of copper and diamond giving one similarity and one difference. [2]

Answer: Similarity: Crystals of both, copper and diamond show FCC arrangement of constituent particles.

Difference: In copper coordination number is 12 and lattice sites are occupied by Cu⁺⁺ ions.

In diamond coordination number is 4 and lattice sites are occupied by C atoms.

- iii. If the standard free energy change for a reaction is found to be zero, what is the value of the equilibrium constant for the reaction? [1]

Answer: Standard free energy change,

$$\Delta G^\circ = 2.303 RT \log_{10} K_C$$

$$\Delta G^\circ = 0, \text{ then}$$

$$0 = 2.303 RT \log_{10} K_C$$

$$\log_{10} K_C = 0$$

$$K_C = 1$$

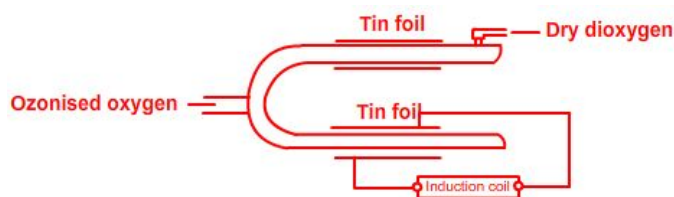
The value of equilibrium constant is one.

Section B (Answer any two questions)

Question: 5

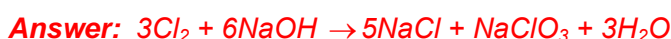
- a. How can ozone be manufactured by siemen's ozonizer? How is pure ozone recovered from the products? [3]

Answer: Figure 2: Ozonation and artificial ozonizers



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

i. Chlorine and hot concentrated caustic soda.



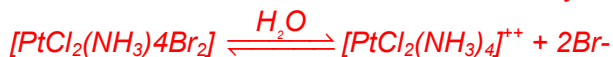
ii. Sulphur dioxide and acidified potassium permanganate.



Question: 6

a.
i. Name the type of isomerism shown by the following pair of compounds: [2]
 $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$
 Give a chemical test to distinguish between the given pair of isomers.

Answer: Ionisation isomerism is exhibited by the given pair of coordination compound.

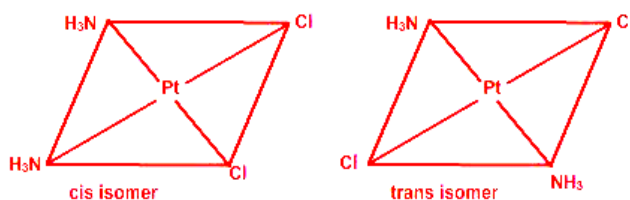


Test to distinguish the two :

Aqueous solution of $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ when treated with AgNO_3 solution gives a pale yellow ppt of AgBr which dissolves in excess of NH_4OH with difficulty.

On the other hand, aqueous solution of $[\text{PtCl}_2(\text{NH}_3)_4]\text{Cl}_2$ when treated with AgNO_3 solution gives a white ppt of AgCl which readily dissolves in NH_4OH .

ii. Draw the geometrical isomers exhibited by the compound $[\text{PtCl}_2(\text{NH}_3)_2]$ [1]



Answer:

b. Write the formulae of the following co-ordination compounds: [2]

i. Tetracarbonyl nickel (0)



ii. Potassium dicyanoargentate (I)

Answer: $K[Ag(CN)_2]$ – potassium dicyanoargentate (I).

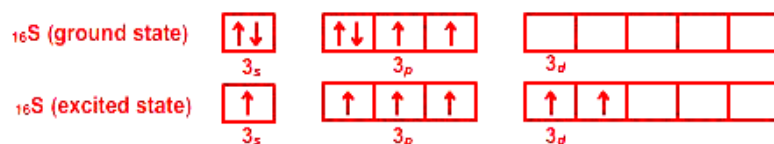
Question 7

a. Account for the following:

[3]

- i. SF_6 exists but OF_6 does not, though both oxygen and sulphur belong to the same group in the Periodic table.

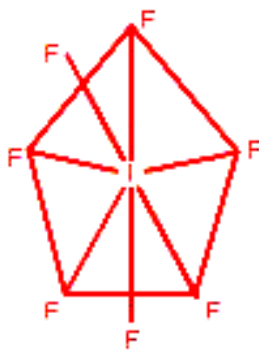
Answer: $16S^{32}$ lies in third period of the periodic table. It has $6e^-$ in its valence shell and 3d sub-shell is lying vacant. Therefore it can show a maximum covalency of 6. And form molecules like SF_6 .



$8O^{16}$ lies in 2nd period of the periodic table. It also has $6e^-$ in its valence shell but there is no d-sub shell present. So its maximum covalency remains 2 and it does not form OF_6 .



- ii. Zn^{+2} compounds are white in colour but Cu^{+2} compounds are coloured, though both zinc and copper are d-block elements.



Answer:

Both zinc and copper are d-block elements but zinc has no unpaired e^- in its $(n-1)$ d sub shell. So its ion Zn^{++} is colourless.

Copper, on the other hand has one unpaired e^- in its $(n-1)$ d subshell when it forms Cu^{++} compounds. This unpaired electron can absorb a definite quantum of energy from its visible spectrum and jump on to the higher sub-shell wavelength transmitted showing a complementary colour.

b.

- i. To which class of compounds does IF_7 belong? What is the structure of the molecule?

Answer: IF_7 belongs to class of inter halogen compounds.

It has pentagonal bipyramidal structure.

- ii. Give the balanced equation for the preparation of silver nitrate in the laboratory. [1]

Answer: Equation for the laboratory preparation of AgNO_3 :
 $3\text{Ag} + \text{HNO}_3 \rightarrow 3\text{AgNO}_3 + 2\text{H}_2\text{O} + \text{NO}$

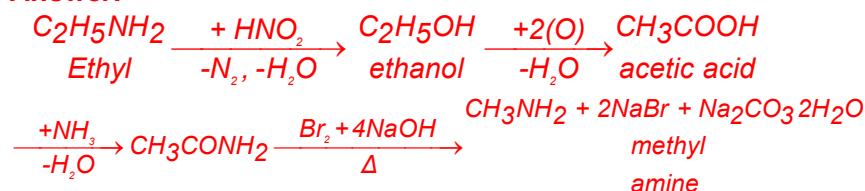
Section C (Answer any two questions)

Question: 8

- a. How can the following conversions be brought about:

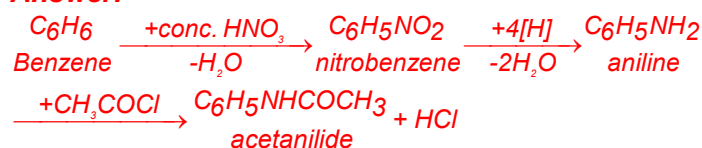
- i. Ethylamine to methylamine [3]

Answer:

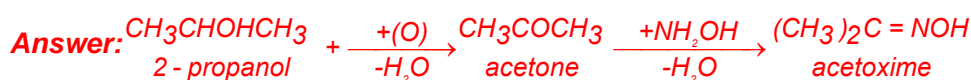


- ii. Benzene to acetanilide. [3]

Answer:



- iii. 2 propanol to acetoxime. [2]



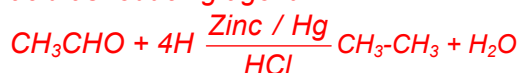
- b. Give one example for each of the following name reactions:

- i. Hell Volhard Zelinsky (HVZ) reaction [1]

Answer: When chlorine reacts with acetic acid in presence of traces of phosphorus, α -H atoms of the acid get substituted by chlorine.

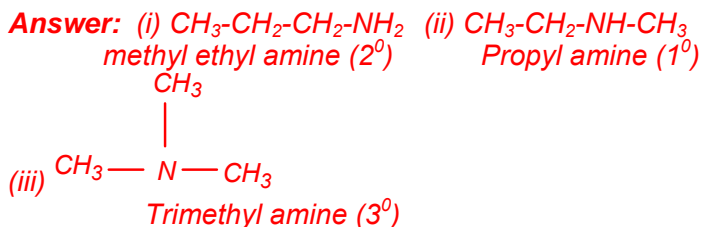
- ii. Clemmensen's reduction. [1]

Answer: Reduction of acetaldehyde to ethane using Zinc amalgam and hydrochloric acid as reducing agent.



Question: 9

- a. Draw three isomers of a compound with the molecular formula C_3H_9N . Name the isomers. [3]



- b. Give one good chemical test to distinguish between the following pairs of compounds:

- i. 1 propanol and 2 propanol

Answer: To distinguish between 1-propanol and 2-propanol Lucas test can be used. When Lucas reagent (solution of HCl and $ZnCl_2$) is added to 2-propanol, cloudiness appears within 5 minutes. When Lucas reagent is added to 1-propanol, solution remains clear.

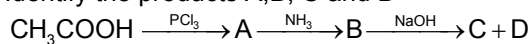
- ii. Oxalic acid and benzoic acid

Answer: Oxalic acid decolourises hot solution of acidified $KMnO_4$. Benzoic acid does not give this test.

c.

- i. Identify the products A, B, C and D

[2]



Answer: $A \rightarrow CH_3COCl$ (Acetyl Chloride)

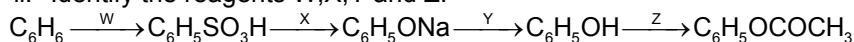
$B \rightarrow CH_3CONH_2$ (Acetamide)

$C \rightarrow CH_3COONa$ (sodium acetate)

$D \rightarrow NH_3$ (Ammonia)

- ii. Identify the reagents W, X, Y and Z.

[2]



Answer: $W \rightarrow \text{Conc. } H_2SO_4$

$X \rightarrow NaOH$

$Y \rightarrow HCl$

$Z \rightarrow CH_3COCl$

Question: 10

a.

- i. What are thermoplastics and thermosetting plastics. Give one example of each kind. [3]

Answer: Thermoplastics: These are linear polymer. They soften on heating and harden on cooling. Intermolecular forces in them are intermediate between those of elastomers and fibrous polymers. Example: Polypropylene.

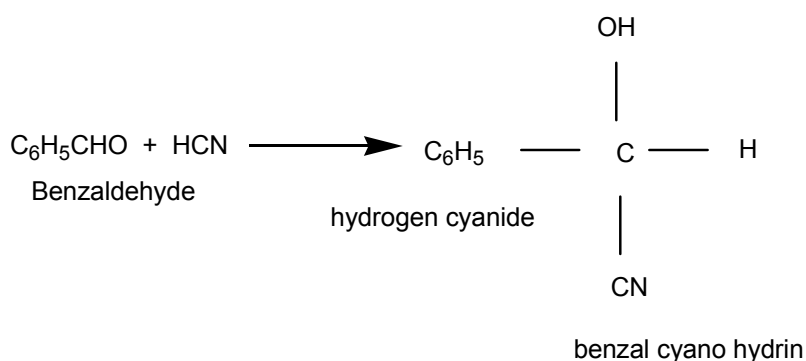
Thermosetting plastics: These plastics are made by heating relatively low molecular mass semi-fluid polymers. These polymers become infusible and form a hard mass on heating in a mould due to cross linking. Once molded, thermosetting plastics cannot be remelad or reshaped by heating. Example: Bakelite made from urea – formaldehyde resins.

- ii. Give one example of a fibrous protein. Name the final product of hydrolysis of proteins. What is denaturation of proteins? [2]

Answer: *Classification of proteins*
Denaturation

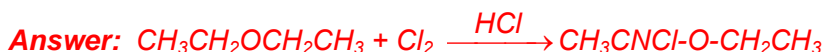
- b. Give balanced equations for the following reactions:

- i. Benzaldehyde treated with hydrogen cyanide.

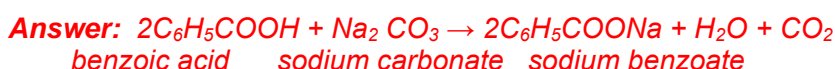


Answer:

- ii. Chlorine is passed through diethyl ether.



- iii. Benzoic acid solution is treated with sodium carbonate.



- c. An organic compound A with molecular formula $\text{C}_3\text{H}_8\text{O}_3$ reacts with oxalic acid at 110°C to give a monocarboxylic acid B. B gives a silver mirror with Tollen's reagent and reduces acidified potassium permanganate solution. Identify A and B and give the reaction B with acidified KMnO_4 solution.

Answer: *A is glycerol ($\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH}$)*

B is formic acid (HCOOH).

When B reacts with acidified KMnO_4 solution, the later gets decolourised.

