Chemistry Delhi (Set 2)

General Instructions:

Read the following instructions very carefully and strictly follow them :
(i) Question paper comprises four sections - A, B, C and D.
(ii) There are **37** questions in the questions paper. **All** questions are compulsory.
(iii) Section - A: Q. No. **1** to **20** are very short answer type questions carrying **one** mark each. Answer these questions in one word or one sentence.
(iv) Section - B: Q. No. **21** to **27** are short answer type questions carrying **two** marks each.
(v) Section - C: Q. No. **28** to **34** are long answer type-**I** questions carrying **three** marks each.
(vi) Section - D: Q. No. **35** to **37** are long answer type**-II** questions carrying **five** marks each.
(vii) There is NO overall choice in the question paper. However an internal choice has been provided in **2** questions of **two** marks, **2** questions of **three** marks and all the **3** questions of five marks. You have to **attempt only one of the choices** in such questions.
(viii) However, separate instructions are given with each section and question, wherever necessary.
(ix) Use of calculators and log tables is NOT permitted.

Read the given passage and answer the question follow:

The halogens have the smallest atomic radii in their respective periods. The atomic radius of fluorine is extremely small. All halogens exhibit – 1 oxidation state. They are strong oxidising agents and have maximum negative electron gain enthalpy. Among halogens, fluroine shows anomalous behaviour in many properties.

For example electro negativity and ionisation enthalpy are higher for fluorine than expected whereas bond dissociation enthalpy, m.p and b.p and electron gain enthalpy are quite lower than expected. Halogens react with hydrogen to give hydrogen halides (HX) and combine amongst themselves to form a number of compounds of the type XX’, XX'_3, XX'_5 and XX'_7 called inter-halogens.

Question 1

Why halogens have maximum negative electron gain enthalpy?

Solution:

Due to the smallest size of halogens in their respective periods, the value of Z_{eff} is maximum hence the negative value of electron gain enthalpy is maximum.

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Question 2

Why fluorine shows anomalous behaviour as compared to other halogens?

Solution:

Fluorine shows abnormal behavior due to its very small size.

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Question 3

Arrange the hydrogen halides (HF to HI) in the decreasing order of their reducing character.

Solution:

Halogen halide in the decreasing order of their reducing character are:

H-I > H-Br > H-Cl > H-F

On moving down the group, bond dissociation enthalpy of H-X decreases hence their reducing character increases.

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Question 4

Why fluorine is a stronger oxidizing agent than chlorine?

Solution:

The tendency to act as an oxidizing agent depends on 3 parameters :

1- Bond dissociation enthalpy of halogens (Endothermic process): Bond dissociation enthalpy of Cl_2 is more than that of F_2.

2- Electron gain enthalpy (Exothermic process): Electron gain enthalpy of Cl is marginally more than F.

3- Hydration enthalpy (Exothermic process): Hydration enthalpy of F^- is more more than Cl^-.

On considering all these 3 factors it is concluded that fluorine is a better oxidizing agent than chlorine.

Read the given passage and answer the question follow:

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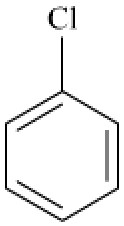
Question 5

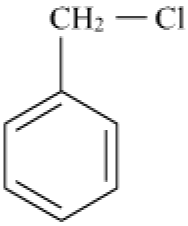
What are the sizes of X and X' in the interhalogen compounds?

Solution:

In interhalogen compounds, X is of larger size and X' is of smaller size.

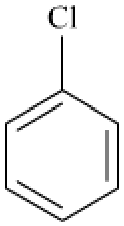
Question 6

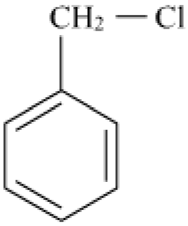
Out of 

and 

, which will undergo S_N1 reaction faster with OH^-?

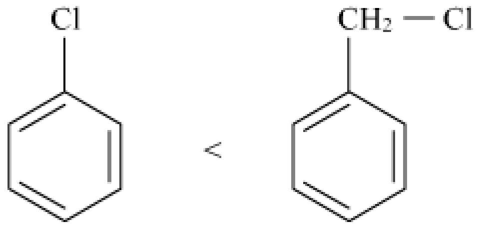
Solution:

Out of 

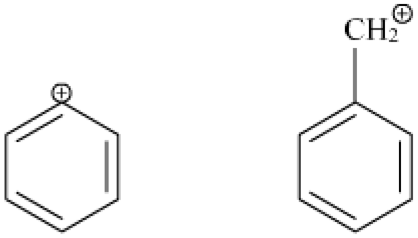
and 

the rate of S_N1 reaction with OH^- would be in the following order :

Rate of S_N1:



Carbocation stability :



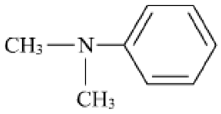
Not possible
(Highly unstable)

Benzylic
Carbocatin
(Highly stable)

Rate of S_N1 reaction depends on the stability of carbocation. More the stability of carbocation, the faster is the rate of S_N1 reaction.

Benzylic carbocation is more stable due to resonance and hence undergoes S_N1 reaction at a faster rate.

Question 7

Write the IUPAC name of  .

Solution:

IUPAC name of the compound is N,N-dimethylaniline.

Question 8

What type of linkage is present in polysaccharides?

Solution:

Glycosidic linkage joins two monosaccharides units in polysaccharides.

Question 9

Name an artificial sweetener whose use is limited to cold drinks.

Solution:

The use of **aspartame** is limited to cold foods and soft drinks because it's unstable at cooking temperature.

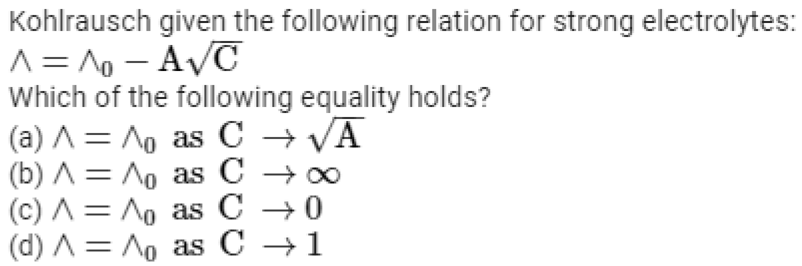
Question 10

Name the polymer which is used for making non-stick utensils.

Solution:

Polytetrafluoroethene (Teflon) is used for making non-stick utensils.

Question 11



Kohlrausch given the following relation for strong electrolytes:

$\wedge = \wedge_0 - A\sqrt{C}$

Which of the following equality holds?

(a) $\wedge = \wedge_0$ as $C \rightarrow \sqrt{A}$

(b) $\wedge = \wedge_0$ as $C \rightarrow \infty$

(c) $\wedge = \wedge_0$ as $C \rightarrow 0$

(d) $\wedge = \wedge_0$ as $C \rightarrow 1$

Solution:

At infinite dilution (C→0) molar conductivity of the strong electrolyte is highest and represented as Λ=Λ0.

Hence, the correct answer is option (c).

Question 12

In an electrochemical process, a salt bridge is used
(a) as a reducing agent.
(b) as an oxidizing agent.
(c) to complete the circuit so that current can flow.
(d) None of these

Solution:

Salt bridge is used to complete the circuit so that the current can flow.

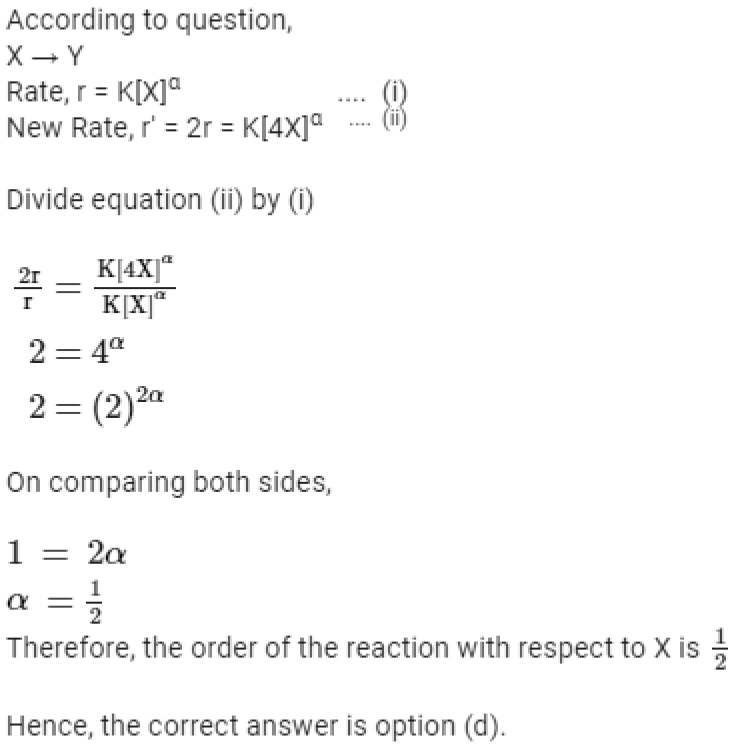
Hence, the correct answer is option (c).

Question 13

In a chemical reaction X → Y. it is found that the rate of reaction doubles when the concentration of X is increased four times. The order of the reaction with respect to X is
(a) 1
(b) 0

(c) 2
(d) 1/2

Solution:



According to question,
$X \rightarrow Y$
Rate, $r = K[X]^{\alpha}$ .... (i)
New Rate, $r' = 2r = K[4X]^{\alpha}$ .... (ii)

Divide equation (ii) by (i)

$$\frac{2r}{r} = \frac{K[4X]^{\alpha}}{K[X]^{\alpha}}$$
$$2 = 4^{\alpha}$$
$$2 = (2)^{2\alpha}$$

On comparing both sides,

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

Therefore, the order of the reaction with respect to X is $\frac{1}{2}$

Hence, the correct answer is option (d).

Question 14

Which of the following will give a white precipitate upon reacting with $AgNO_3$?
(a) $K_2[Pt(en)_2Cl_2]$
(b) $[CO(NH_3)_3Cl_3]$
(c) $[Cr(H_2O)_6]Cl_3$
(d) $[Fe(H_2O)_3 Cl_3]$

Solution:

Coordination entity can not undergo dissociation but the species present outside the coordination sphere can undergo dissociation very easily. Upon treatment with $AgNO_3$, the complex **$[Cr(H_2O)_6]Cl_3$** will form white precipitate of AgCl because it will give three chloride ions upon dissociation as follows:

$[Cr(H_2O)_6]Cl_3 \rightleftharpoons [Cr(H_2O)_6]^{3+} + 3Cl^-$

Hence, the correct answer is option (c).

Question 15

Copper matte contains
(a) Cu_2S, Cu_2O and silica
(b) Cu_2S, CuO and silica
(c) Cu_2S, FeO and silica
(d) Cu_2S, FeS and silica

Solution:

Copper matte contains copper(I) sulphide (Cu_2S), iron (II) sulphide (FeS) and silica (SiO_2).

Hence, the correct answer is option (d).

Question 16

Assertion (A) : 0.1 M solution of KCl has greater osmotic pressure than 0.1 M solution of glucose at same temperature.
Reason (R) : In solution, KCl dissociates to produce more number of particles.

(A) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(B) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(C) Assertion (A) is correct, but Reason (R) is wrong statement.
(D) Assertion (A) is wrong, but Reason (R) is correct statement.

Solution:

Osmotic pressure is a colligative property that depends upon the number of solute particles. KCl is a strong electrolyte which completely dissociates in the solution and number of particle increases, while in case of glucose which is a weak electrolyte and does not dissociate in the solution so, there is no change in the number of particles in the solution.

Therefore, KCl has more osmotic pressure than glucose, as in case of KCl more number of particles are there than glucose and hence, both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

Hence, the correct answer is option (A).

Question 17

Assertion (A): Conductivity of an electrolyte increases with decrease in concentration.
Reason (R) : Number of ions per unit volume decreases on dilution.

(A) Both Assertion (A) and Reason. (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(B) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(C) Assertion (A) is correct, but Reason (R) is wrong statement.
(D) Assertion (A) is wrong, but Reason (R) is correct statement.

Solution:

Conductivity is directly proportional to the number of ions present in the solution. Therefore, Assertion is incorrect, while the number of ions per unit volume decreases on dilution hence, the reason is correct statement.

Hence, the correct answer is option D.

Question 18

Assertion (A) : Ortho and para-nitrophenols can be separated by steam distillation.
Reason (R) : Ortho isomer associates through intermolecular hydrogen bonding while Para isomer associates through intramolecular hydrogen bonding.
(A) Both Assertion (A) and Reason. (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(B) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(C) Assertion (A) is correct, but Reason (R) is wrong statement.
(D) Assertion (A) is wrong, but Reason (R) is correct statement.

Solution:

Due to intermolecular bonding in para nitrophenol, para nitrophenol has a more boiling point than ortho nitrophenol. Therefore, they can be separated by steam distillation.

The assertion is the correct statement whereas reason is the wrong statement.

Hence, the correct answer is option (C).

Question 19

Assertion (A) : Oxidation of ketones is easier than aldehydes.
Reason (R) : C-C bond of ketones is stronger than C-H bond of aldehydes.
(A) Both Assertion (A) and Reason. (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(B) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is correct, but Reason (R) is wrong statement.
(D) Assertion (A) is wrong, but Reason (R) is correct statement.

Solution:

The difference between an aldehyde and a ketone is the presence of a hydrogen atom attached to the carbon-oxygen double bond in the aldehyde (R-CHO). Ketones don't have that hydrogen (R-CO-R) and contain a (C-C) bond which is stronger than (C-H) bond in aldehydes. The presence of that hydrogen atom makes aldehydes to provide their hydrogen easily i.e. they can reduce others and self oxidized.

Hence, the correct answer is option D.

Question 20

Assertion (A): Low spin tetrahedral complexes are rarely observed.
Reason (R): Crystal field splitting energy is less than pairing energy for tetrahedral complexes.
(A) Both Assertion (A) and Reason. (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(B) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(C) Assertion (A) is correct, but Reason (R) is wrong statement.
(D) Assertion (A) is wrong, but Reason (R) is correct statement.

Solution:

In tetrahedral complexes, the splitting of orbitals is less as compared to octahedral complexes. In this case, $\Delta_\circ$ (crystal field splitting energy) is always less than pairing energy, i.e. $\Delta_\circ < P$, therefore, the electrons prefer to go to higher orbital and once all orbitals are singly occupied, then only pairing began.

Hence, high spin tetrahedral complexes are formed.

Both assertion and reason are correct statements, and the reason is the correct explanation of the assertion.

Hence, the correct answer is option A.

Question 21

Write the role of
(a) Dilute NaCN in the extraction of Gold.
(b) CO in the extraction of Iron.

OR

How is leaching carried out in the case of low grade copper ores? Name the method used for refining of copper metal.

Solution:

(a) The finely powdered native gold is treated with a dilute solution of sodium cyanide while a current of air is continuously passed. Gold gets oxidised which then combines with CN^- ions forming their soluble complex cyanides while the impurities remain unaffected which are filtered off.

$$4\,Au + 8NaCN + 2H_2O + O_2 \rightarrow \underset{\text{(Soluble Complex)}}{4\,Na[Au(CN)_2]} + 4\,KOH$$

(b) Carbon Monoxide acts as a reducing agent in the extraction of iron from iron oxide. The reaction is given as follow:

$$Fe_2O_3 + 3\,CO \rightarrow 2\,Fe + 3\,CO_2$$

OR

In case of low grade copper ores, leaching is carried out using acid or bacteria in the presence of air. In this process, copper goes into the solution as Cu^{2+} ions.

$$Cu\ (s) + 2H^+(aq) + \tfrac{1}{2}O_2 \rightarrow Cu^{2+}\ (aq) + 2H_2O\ (l)$$

The resulting solution is treated with scrap iron or H_2 to get metallic copper.

$$Cu^{2+}\ (aq) + H_2\ (g) \rightarrow Cu\ (s) + 2H^+\ (aq)$$

Electrorefining is the process used to refine copper metal.

Question 22

State Raoult's law for a solution containing volatile components. What is the similarity between Raoult's law and Henry's law?

Solution:

Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

Thus if there is a solution of two liquid components 1 and 2,
Then for component 1, $p_1 \propto x_1$
And, For component 2, $p_2 \propto x_2$
where p_1, p_2 = Partial vapour pressure of two volatile components 1 and 2 of the solution

x_1, x_2 are mole fractions of the components 1 and 2, respectively

Henry's law states that
$p = K_H x$

In both the laws, the partial pressure is directly proportional to the mole fraction of the components. therefore, on comparing both laws it has been observed that Raoult's law becomes a special case of Henry's law in which K_H becomes equal to pi°.

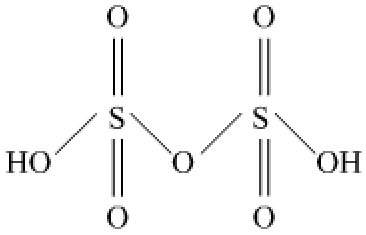
Question 23

Draw the structures of the following:
(i) $H_2S_2O_7$
(ii) BrF_5

Solution:

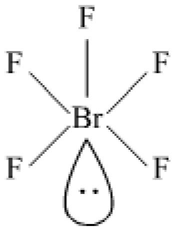
(i)

$H_2S_2O_7$



(ii)

BrF_5



Question 24

Define adsorption with an example. What is the role of adsorption in heterogeneous catalysis?

OR

Define Brownian movement. What is the cause of Brownian movement in colloidal particles? How is it responsible for the stability of Colloidal Sol?

Solution:

Adsorption may be defined as the phenomenon of higher concentration of the molecular species (gases or liquids) on the surface of the solid than in the bulk.
Example - In humid weather, silica gel helps in adsorbing water vapours from the air.
The heterogeneous catalysis carried out on the surface of metal catalysts is explained with the help of adsorption theory. The reactant molecules are adsorbed on the surface of the catalyst and mutually combine to form activated complex which finally releases the product from the surface.

OR

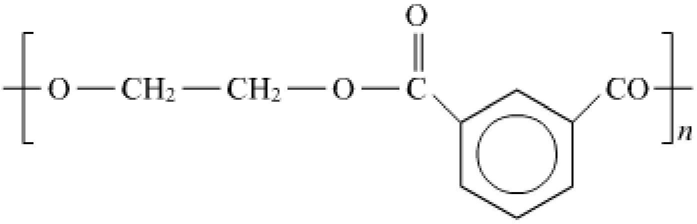
The Brownian movement was coined by Brown (botanist) may be defined as the continuous zig-zag motion of the colloidal particles.

This zig-zag motion was observed due to the constant collisions of dispersed phase particles of the colloidal solution, by the molecules of the dispersion medium. This movement opposes the force of gravity on the colloidal particles. As a result, these particles always remain in a state of motion and don't settle down and thus, are stable.

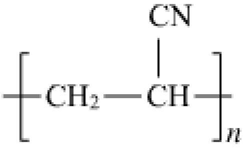
Question 25

Identify the monomers in the following polymers:

(i)



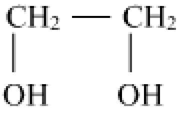
(ii)



$$\left[CH_2-\underset{}{\overset{CN}{\overset{|}{CH}}} \right]_n$$

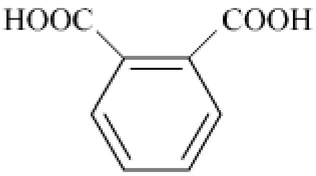
Solution:

(i) The polymer given is **glyptal** whose monomeric units are **ethylene glycol** and phthalic acid.



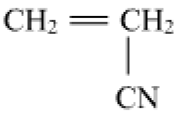
$$\underset{OH}{\underset{|}{CH_2}} - \underset{OH}{\underset{|}{CH_2}}$$

(Ethylene glycol)



(Phthalic acid)

(ii) The polymer given is **polyacrylonitrile** whose monomeric unit is **acrylonitrile** or **vinyl cyanide.**



$$CH_2 = \underset{CN}{\underset{|}{CH_2}}$$

(Acrylonitrile)

Question 26

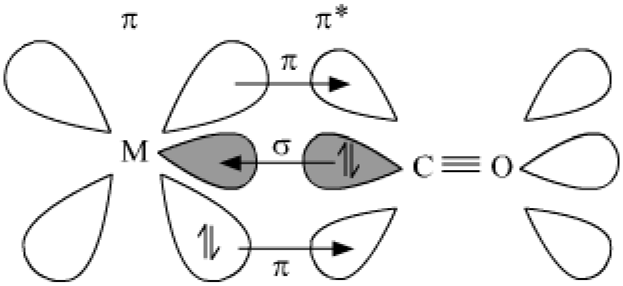
Discuss the nature of bonding in metal carbonyls.

Solution:

The metal-carbon bonds in metal carbonyls have both σ and π characters. A σ bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant d orbital of the metal.

A π bond is formed by the donation of a pair of electrons from the filled metal d orbital into the vacant anti-bonding π orbital (also known as back bonding of the carbonyl group). The σ bond strengthens the π bond and vice-versa.

Thus, a synergic effect is created due to this metal-ligand bonding. This synergic effect strengthens the bond between CO and the metal.



Question 27

How do antiseptics differ from disinfectants? Name a substance which can be used as a disinfectant as well as an antiseptic.

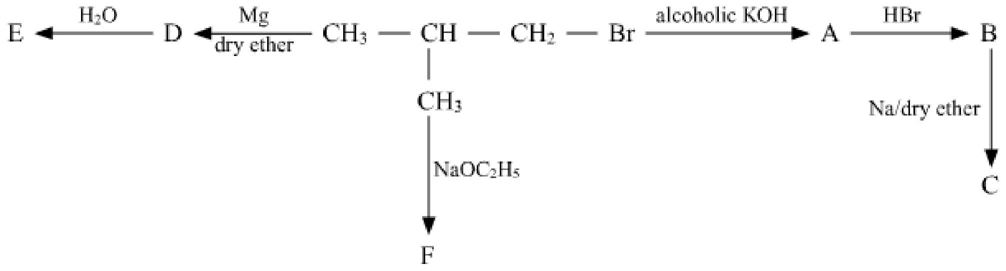
Solution:

Antiseptics and disinfectants are effective against micro-organisms. Antiseptics are applied to the living tissues such as wounds, cuts, ulcers, and diseased skin surfaces, while disinfectants are applied to inanimate objects such as floors, drainage systems, instruments, etc. Disinfectants are harmful to living tissues.

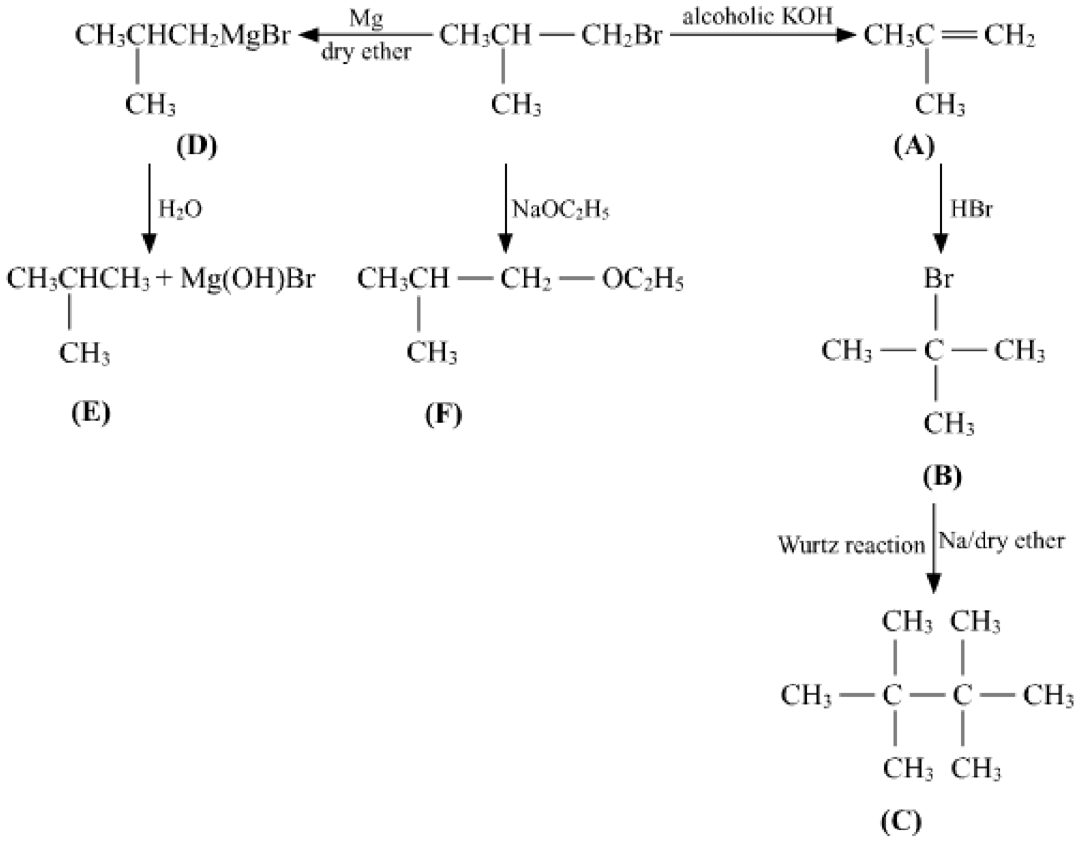
Phenol can be used as an antiseptic as well as a disinfectant. 0.2 percent solution of phenol is used as an antiseptic, while 1 percent of its solution is used as a disinfectant.

Question 28

Identify A, B, C, D, E and F in the following:



Solution:



Question 29

A 0.01 m aqueous solution of $AlCl_3$ freezes at – 0.068 °C. Calculate the percentage of dissociation. [Given: K_f for Water = 1.86 K kg mol^{-1}]

Solution:

We know that the formula for depression in freezing point is given as follows:

$$\Delta T_f = i \times K_f \times m \; \ldots\ldots\ldots\ldots (1)$$

Where, i = van't hoff factor
m = molality
ΔT_f = depression in freezing point

We also know that $\Delta T_f = (T_f^\circ - T_f)$. Now substituting the values for calculating ΔT_f.

$$\Delta T_f = [0 - (-0.068)]\ ^\circ C = 0.068\ ^\circ C$$

Now, from equation (1)

$$i = \frac{\Delta T_f}{K_f \times m} = \frac{0.068}{1.86 \times 0.01} = \frac{0.068}{0.0186} = 3.65$$

for dissociation, the relation between van't hoff factor and degree of dissociation may be written as:

$$\alpha = \frac{i-1}{n-1} \; \ldots\ldots\ldots\ldots\ldots\ldots \left(2\right)$$

$AlCl_3$ will undergo dissociation as follows:

$$AlCl_3 \rightarrow Al^{3+} + 3\,Cl^-$$

Therefore, n = 4.

From equation (2)

$$\alpha = \frac{i-1}{n-1} = \frac{3.65-1}{4-1} = \frac{2.65}{3} = 0.883$$

Therefore, the percent dissociation = $0.883 \times 100 = 88.3\,\%$

Question 30

Define the following terms with a suitable example in each:
(a) Polysaccharides
(b) Denatured protein
(c) Fibrous protein

Solution:

Polysaccharides: The carbohydrates which yield a large number of monosaccharide unit upon hydrolysis are called polysaccharides.
for example - Starch.

Denatured protein: When the native protein (biological system with a unique 3-D structure and biological activity) is subjected to either some physical change (e.g. change in temperature) or chemical change by taking part in certain chemical reactions which bring about a change in pH, this leads to denaturation.
for example - Coagulation of milk.

Fibrous protein: In this type, the proteins consist of linear molecules which are placed side by side to form fibers. The different polypeptide chains are held by intermolecular hydrogen bonding. They have a long thread-like structure. These are water-insoluble proteins.
for example - keratin.

Question 31

When a steady current of 2A was passed through two electrolytic cells A and B containing electrolytes $ZnSO_4$ and $CuSO_4$ connected in series, 2g of Cu were deposited at the cathode of cell B. How long did the current flow?
What mass of Zn was deposited at cathode of cell A?
[Atomic mass: Cu = 63.5 g mol^{-1}, Zn = 65 g mol^{-1}; 1F = 96500 C mol^{-1}]

Solution:

According to Faraday's first law :

$$W = \frac{EW \times I \times t}{96500}$$

Where W is the weight of metal deposited, EW is the equivalent weight of metal deposited, I is the amount of current passes and t is the time in seconds.

As 2 g of Cu is deposited hence, W = 2 g, EW of Cu is $\frac{63.5}{2}$, I is 2 A

Hence, the time for which current is flowing is calculated as :

$$\frac{2\times 96500}{\frac{63.5}{2}\times 2} = t = 3039 \text{ sec} = 50.65 \text{ min}$$

According to 2nd faraday law :

$$\frac{Weight\ of\ Zn\ deposited}{Equivalent\ weight\ of\ Zn} = \frac{Weight\ of\ Cu\ deposited}{Equivalent\ weight\ of\ Cu}$$

$$\frac{?}{32.5} = \frac{2}{31.75}$$

Wight of Zn deposited would be 2.047 g.

Question 32

Write three differences between lyophobic sol and lyophilic sol.

OR

Define the following terms:
(i) Protective colloid
(ii) Zeta potential
(iii) Emulsifying agent

Solution:

Lyophilic colloids (solvent attracting)
These are formed by simply mixing substances like gelatine, starch, rubber, etc with a suitable liquid (dispersion medium). These are quite stable and cannot be easily coagulated. These are also called as reversible sols.

Lyophobic colloids (solvent repelling)
These colloids are formed by substances like metals, metal sulphides. These cannot be prepared by simply mixing the substances with dispersion medium and require special methods. They are also called as irreversible sols. They are unstable and can be easily coagulated. These sols require stabilising agents for their preservation.

OR

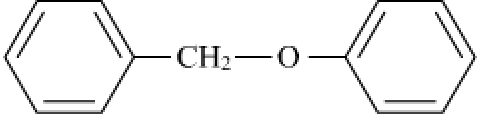
(i) The protective colloid is a type of lyophilic (water-loving) colloid which is used to protect the lyophobic colloids from precipitation in an electrolytic solution. The common examples of protective colloids are gelatin, casein, hemoglobin, egg albumin, etc.

(ii) The potential difference between the stationary layer of compensating charges and the diffuse layer (present in the body of the solution) is called electro kinetic or zeta potential.

(iii) The substances which are added to stabilize the emulsions are called emulsifier or emulsifying agents. The function of emulsifier is to reduce the interfacial tension between the two liquids forming the emulsion.
Ex: gum, soap, gelatin, albumin etc.

Question 33

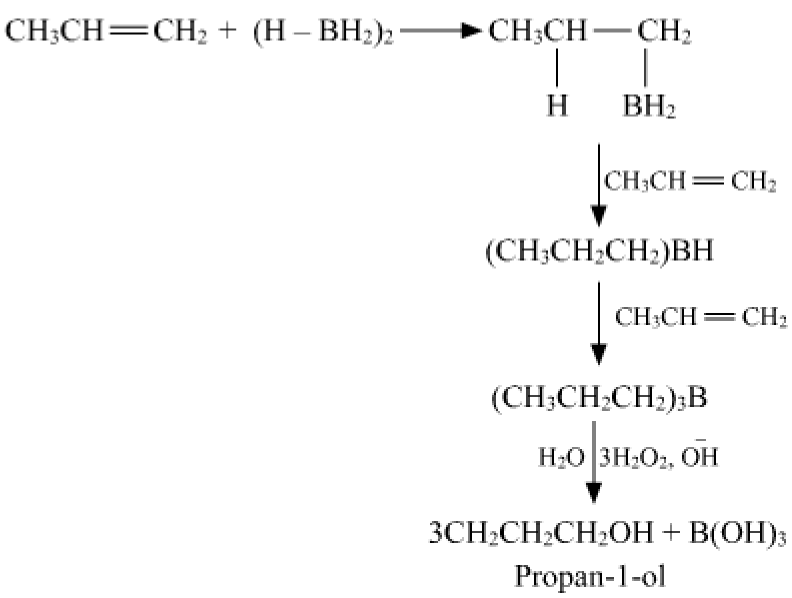
Give the structures of final products expected from the following reactions:
(i) Hydroboration of propene followed by oxidation with H_2O_2 in alkaline medium.
(ii) Dehydration of $(CH_3)_3$ C – OH by heating it with 20% H_3PO_4 at 358 K.

(iii) Heating of  with HI.

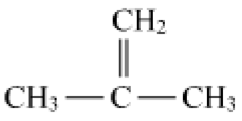
OR

How can you convert the following?
(i) Phenol to o-hydroxy benzaldehyde.
(ii) Methanal to ethanol
(iii) Phenol to phenyl ethanoate.

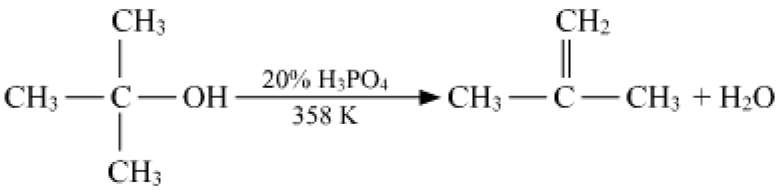
Solution:
(i)



(b)

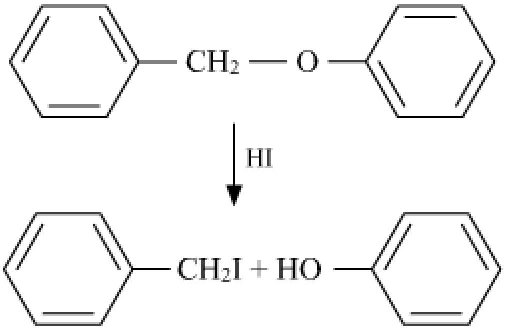


$$CH_3-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_3$$



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow[358\text{ K}]{20\%\ H_3PO_4} CH_3-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_3 + H_2O$$

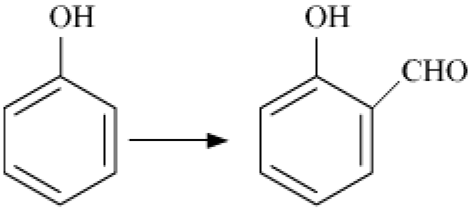
(c)



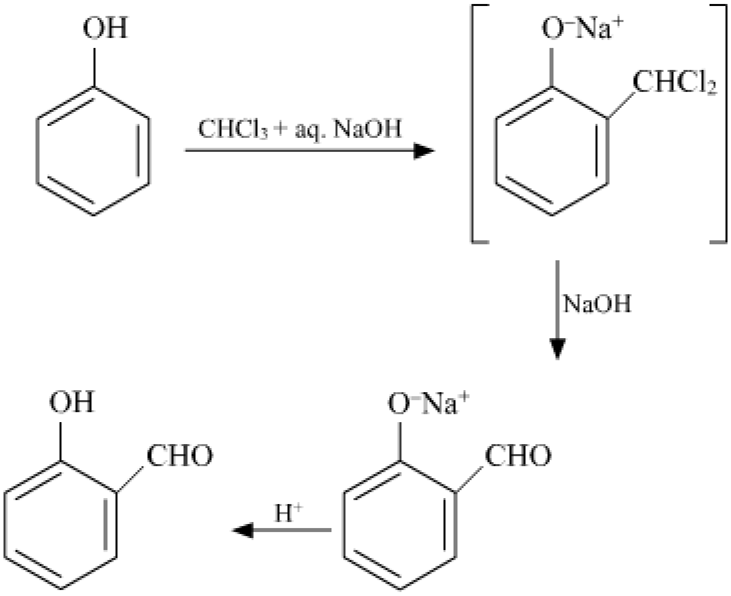
OR

(i)

Phenol to *o*-hydroxybenzaldehyde

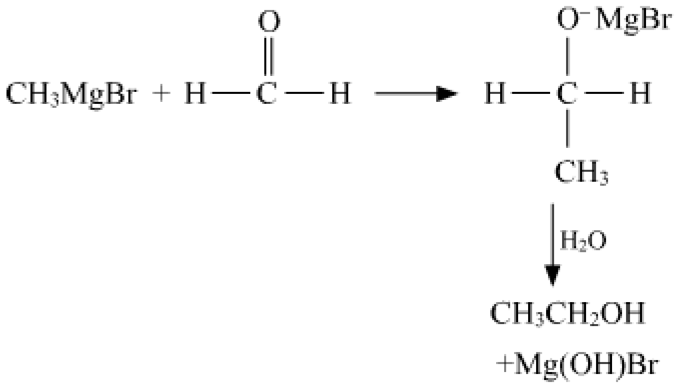


Reimer-Tiemann Reaction

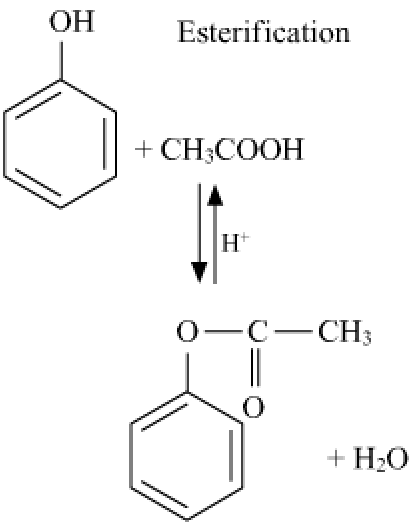


Salicylaldehyde

(ii)



(iii)

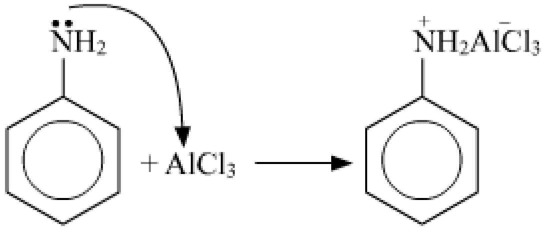


Question 34

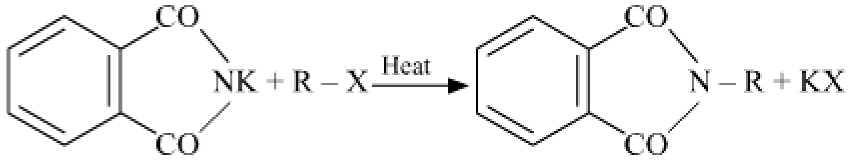
Give reasons:
(i) Aniline does not undergo Friedal-Crafts reaction.
(ii) Aromatic primary amines cannot be prepared by Gabriel's phthalimide synthesis.
(iii) Aliphatic amines are stronger bases than ammonia.

Solution:

(i) Aniline being a lewis base forms a complex with $AlCl_3$ which is a lewis acid. The amino group ($-NH_2$) is not able to activate the benzene ring towards electrophilic substitution. Therefore, the reaction is not possible.

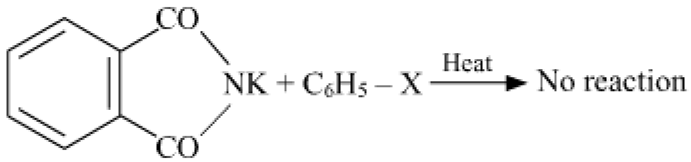


(ii) In Gabriel phthalimide reaction, the potassium salt of phthalimide is formed. It readily reacts with an alkyl halide to form the corresponding alkyl derivative.



Pot. phthalimide N-alkyl phthalimide

But it is not in a position to react with the aryl halide in case primary aromatic amine is to be prepared. Actually, the cleavage of the C-X bond in haloarene or aryl halide is quite difficult due to the partial double bond character. Therefore, aromatic primary amines can not be prepared by this method.



Pot. phthalimide Haloarene

(iii) Aliphatic amines are stronger bases than ammonia due +I (electron releasing) effect of alkyl groups and in aromatic amines, lone pair of electrons are not available due to the resonance. Therefore, electron density on nitrogen atom increases in the case of aliphatic amines and lone pair of electrons can be easily donated.

$R - \ddot{N}H_2, NH_3$

amine ammonia

Question 35

(a) A first order reaction is 25% complete in 40 minutes. Calculate the value of rate constant. In what time will the reaction be 80% completed?
(b) Define order of reaction. Write the condition under which a bimolecular reaction follows first order kinetics.

OR

(a) A first order reaction is 50% complete in 30 minutes at 300 K and in 10 minutes at 320 K. Calculate activation energy (E_a) for the reaction. ($R = 8.314\ J\ K^{-1}\ mol^{-1}$)
(b) Write the two conditions for collisions to be effective collisions.
(c) How order of reaction and molecularity differ towards a complex reaction?
[Given: log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021, log 5 = 0.6991]

Solution:

(a) For the first order reaction, $k = \frac{2.303}{t}\ \log \frac{a}{a-x} \quad \ldots\ldots (1)$

Given, 25% of the reaction completes so $x = \frac{25}{100}a = 0.25 \times a$, and $t = 40$ minutes

$$\therefore\ k = \frac{2.303}{40}\log\left(\frac{a}{a - 0.25\ a}\right)$$

$$\Rightarrow k = \frac{2.303}{40}\log\left(\frac{1}{0.75}\right)$$

$$\Rightarrow k = \frac{2.303}{40}\log\left(\frac{4}{3}\right)$$

$$\Rightarrow k = \frac{2.303}{40}\left(\log\ 4 - \ \log\ 3\right)$$

$$\Rightarrow k = \frac{2.303}{40}\left(0.6024 - \ 0.4771\right)$$

$$\Rightarrow k = \frac{2.303}{40}\left(0.123\right)$$

$$\Rightarrow k = 7.081 \times 10^{-3}\ \ \min^{-1}$$

Using equation (1), to find t, using the calculated value of k, we have

$$t = \frac{2.303}{7.096 \times 10^{-3}}\ \ \log \frac{a}{a-x}$$

$$t = \frac{2.303}{7.096 \times 10^{-3}}\ \ \log \frac{a}{a - 0.8a}$$

$$t = \frac{2.303}{7.096 \times 10^{-3}}\ \ \log \frac{1}{0.2}$$

$$t = \frac{2.303}{7.096 \times 10^{-3}}\ \ \log\ 5$$

$$t = \frac{2.303}{7.096 \times 10^{-3}}\ \ \times 0.6991$$

$$t = 226.89\ \ \min$$

(b)
Order of a reaction is the sum of the powers of the concentration of the reactants in the rate law expression of a chemical reaction.

When a bimolecular follows first-order kinetics it is known as pseudo first-order reaction, this happens when one of the reacting species is present in excess. For example, inversion of cane sugar.

$$C_{12}H_{22}O_{11} + \underset{\text{EXCESS}}{H_2O} \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

OR

(a) The rate equation for a first order is given as follows:

$$2.303\ \log \frac{a}{a-x} = kt$$

Given, at 300 K, 50% of the reaction completes so $x = \frac{50}{100}a = 0.5 \times a$, and $t = 30$ minutes

$$\frac{2.303}{30} \log \frac{a}{a-0.5a} = k_1$$

And at 320K, 50% of the reaction completes so $x = \frac{50}{100}a = 0.5 \times a$, and $t = 10$ minutes

$$\frac{2.303}{10} \log \frac{a}{a-0.5a} = k_2$$

$$\text{Therefore, } \frac{k_2}{k_1} = \frac{\frac{2.303}{10} \log \frac{a}{a-0.5a}}{\frac{2.303}{30} \log \frac{a}{a-0.5a}} = \frac{30}{10} = 3$$

Arrhenius Equation is given as follows:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\ 3 = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{300} - \frac{1}{320}\right)$$

$$0.4771 = \frac{E_a}{19.14}\left(\frac{320-300}{300 \times 320}\right)$$

$$E_a = \frac{0.4771 \times 19.14}{0.0002083}$$

$$= 43832.1312\ \text{J/mol}$$

$$= 43.832\ \text{kJ/mol}$$

(b) For an effective collision, the molecules must possess sufficient kinetic energy (also called threshold energy) and proper orientation.

(c) For complex reactions, molecularity is given for elementary steps. Molecularity of slowest step is same as the order of reaction whereas for complex reaction the order of reaction is given by slowest step.

Question 36

(a) Give reasons:
(i) Transition metals and their compounds show catalytic activities.
(i) Separation of a mixture of Lanthanoid elements is difficult.
(iii) Zn, Cd and Hg are soft and have low melting point.
(b) Write the preparation of the following:
(i) $Na_2Cr_2O_7$ from Na_2CrO_4
(ii) K_2MnO_4 from MnO_2

OR

(a) Account for the following:
(i) Ti^{3+} is coloured whereas Sc^{3+} is colourless in aqueous solution.
(ii) Cr^{2+} is a strong reducing agent.
(b) Write two similarities between chemistry of lanthanoids and actinoids.
(c) Complete the following ionic equation:

$$3\,MnO_4^{2-} + 4\,H^+ \rightarrow$$

Solution:

(a)
i. Transition elements show catalytic properties because they provide suitable large surface area on which reactants may be adsorbed and therefore come closer to one another for the reaction, they have vacant orbitals as well and show variable oxidation states.

ii) Separation of lanthanides mixture is difficult because they show almost similar atomic size due to lanthanoid contraction.

iii) Zn, Cd and Hg are soft and have low melting point because they have no unpaired electrons in their neutral and most stable oxidation states due to which metallic bonding is weaker and considered as transition elements.

(b)
i) $2\,Na_2\,CrO_4 + H_2\,SO_4 \rightarrow Na_2\,Cr_2\,O_7 + Na_2\,SO_4 + H_2O$

ii)

$$2\,MnO_2 + 4\,KOH + O_2 \xrightarrow{heat} 2K_2\,MnO_4 + 2H_2O$$

OR

$$MnO_2 + 2\,KOH + KNO_3 \rightarrow K_2\,MnO_4 + KNO_2 + H_2O$$

OR

(a)

(i) Ti^{3+} has one unpaired electron whereas Sc^{3+} has zero unpaired electron. Hence, Sc^{3+} is colourless.

(ii) Cr^{2+} is a stronger reducing agent, as on oxidation it becomes Cr^{3+}. In Cr^{3+}, three electrons are present in the t_{2g} level. Hence, the t_{2g} level is half-filled which makes Cr^{3+} extremely stable.

(b)

(i)They both show + 3 as the most common oxidation state.

(ii) They both show a contraction of radii: The progressive decrease in the radii of atoms of the lanthanide and actinide elements as the atomic number increases.

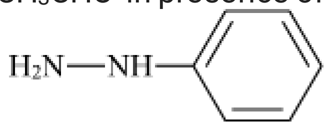
(c)

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Question 37

(a) Write the products formed when benzaldehyde reacts with the following reagents:

(i) CH_3CHO in presence of dilute NaOH



(ii)
(iii) Conc. NaOH

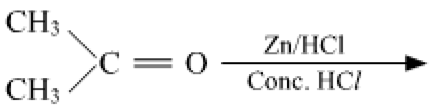
(b) Distinguish between following:

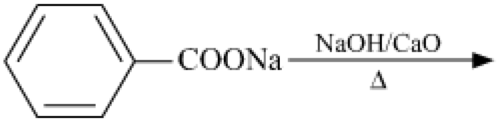
(i) $CH_3 - CH = CH - CO - CH_3$ and $CH_3 - CH_2 - CO - CH = CH_2$

(ii) Benzaldehyde and Benzoic acid.

OR

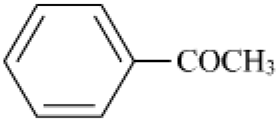
(a) Write the final products in the following:

(i) 

(ii) 

(iii) $CH_2{=}CH-CH_2-CN \xrightarrow[\text{(b) } H_3O^+]{\text{(a) DIBAL-H}}$

(b) Arrange the following in the increasing order of their reactivity towards nuclephilic addition reaction:

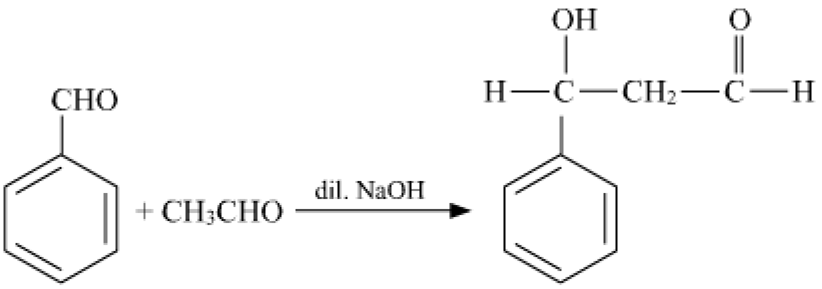
CH_3COCH_3, HCHO, CH_3CHO, 

(c) Draw the structure of 2, 4 DNP derivative of acetaldehyde.

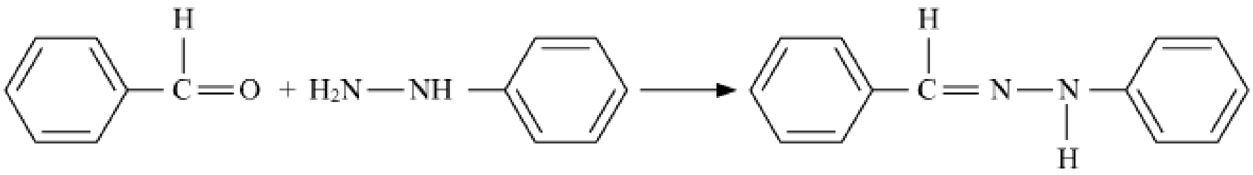
Solution:

(a)

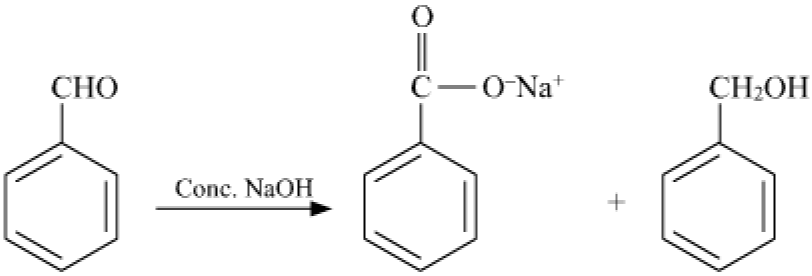
(i) It is aldol condensation reaction and the product will be:



(ii)

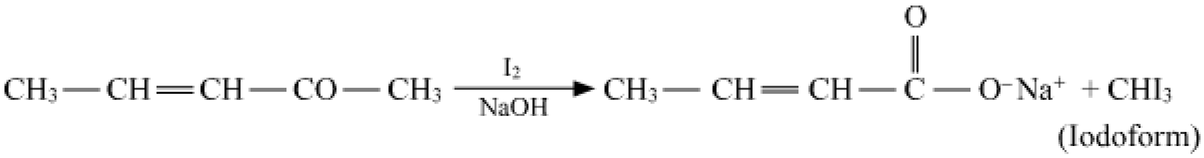


(iii) It is Cannizzaro reaction and the product will be:



(b)

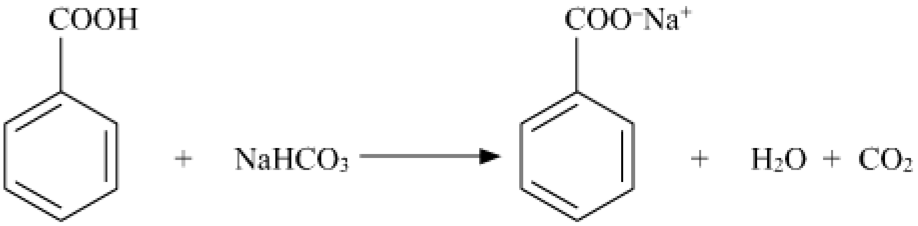
(i) They can be differentiated by the iodoform test. One of them contains a methyl ketonic group (-$COCH_3$) and thus undergo iodoform reaction whereas, the other won't undergo this reaction. The reaction may be shown as follows:

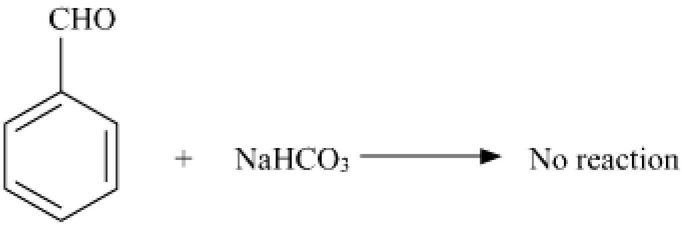


$$CH_3-CH=CH-CO-CH_3 \xrightarrow[NaOH]{I_2} CH_3-CH=CH-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ + \underset{\text{(Iodoform)}}{CHI_3}$$

$$CH_3-CH_2-CO-CH=CH_3 \xrightarrow[NaOH]{I_2} \text{No reaction}$$

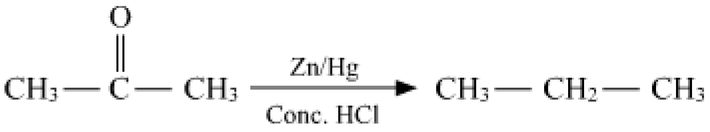
(ii) Carboxylic acids evolve carbon dioxide upon reaction with sodium bicarbonate whereas aromatic aldehydes don't react with it. The reaction may be shown as:



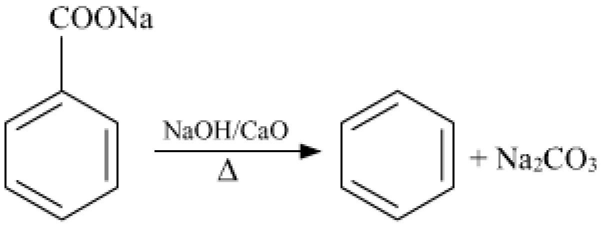


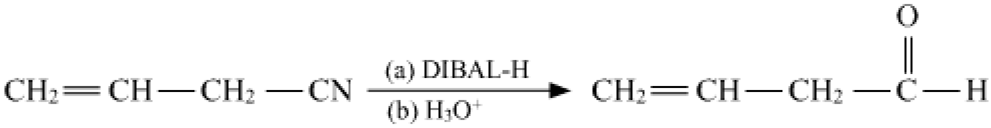
OR

(a)



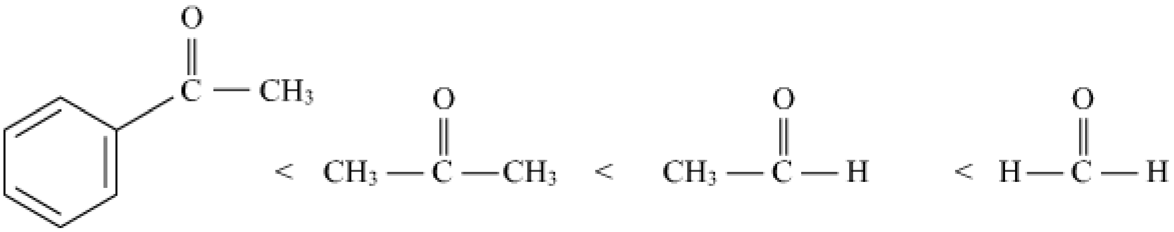
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} CH_3-CH_2-CH_3$$





$$CH_2{=}CH-CH_2-CN \xrightarrow[\text{(b) } H_3O^+]{\text{(a) DIBAL-H}} CH_2{=}CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

(b) The increasing order of reactivity towards nucleophilic addition reaction is as follows:



As steric hinderence decreases the rate of nucleophilic addition increases.

(c) The structure of 2,4 DNP derivative of acetaldehyde: