Chemistry Delhi (Set 1)

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.

Read the given passage and answer the question follow:

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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:

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.

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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

Name the cell used in hearing aids and watches.

Solution:

Mercury cell is used in hearing aids and watches.

Question 7

How much charge in terms of Faraday is required to reduce one mol of MnO_4^- to Mn^{2+}?

Solution:

When MnO_4^- in which Mn is in +7 oxidation state, changes to Mn^{2+}, the change in oxidation state of Mn is +5. Therefore, the charge required to reduce MnO_4^- to Mn^{2+} is **5F**.

Question 8

Write the slope value obtained in the plot of log $[R_o]/[R]$. Vs. time for a first order reaction.

Solution:

We know that for a first-order reaction,

$$K = \frac{2.303}{t} \log \frac{[R_o]}{[R]}$$

$$\log \frac{[R_o]}{R} = \frac{K}{2.303} \times t$$

On comparing the above expression with the equation of straight line, we have:

$$y = mx + c$$

Therefore, the slope is $\frac{K}{2.303}$.

Question 9

Name the sweetening agent used in the cooking of sweets for a diabetic patient.

Solution:

Saccharin is used in the cooking of sweets for a diabetic patient.

Question 10

Name the polymer which is used for making electrical switches and combs.

Solution:

Bakelite is used for making electrical switches and combs.

Question 11

In the Mond's process the gas used for the refining of a metal is
(a) H_2
(b) CO_2
(c) CO
(d) N_2

Solution:

In the Mond's process the gas used for the refining of a metal is CO.

Hence the correct answer is option (c).

Question 12

The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as
(a) a dehydrohalogenation reaction
(b) a substitution reaction
(c) an addition reaction
(d) a dehydration reaction

Solution:

The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as substitution reaction.

Hence, the correct answer is option (b).

Question 13

CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives
(a) $CH_3CH_2NH_2$
(b) CH_3CH_2Br
(c) CH_3NH_2
(d) CH_3COONa

Solution:

CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives CH_3NH_2. The reaction is represented as :

$CH_3CONH_2 + Br_2 + KOH \rightarrow CH_3NH_2 + KBr$

Hence, the correct answer is option (c).

Question 14

The oxidation state of Ni in $[Ni(CO)_4]$ is
(a) 0
(b) 2
(c) 3
(d) 4

Solution:

The oxidation state of Ni in $[Ni(CO)_4]$ is zero.

Hence, the correct answer is option (a).

Question 15

Amino acids are
(a) acidic
(b) basic
(c) amphoteric
(d) neutral

Solution:

Amino acids can act as an acid as well as a base, due to the presence of COOH and NH_2 group, so they are amphoteric in nature.

Hence, the correct answer is option (c).

Question 16

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 17

Assertion (A): The C-O-C bond angle in ethers is slightly less than tetrahedral angle.
Reason (R) : Due to the repulsive interaction between the two alkyl groups in ethers.

(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:

According to the VSEPR theory, repulsions are considered for defining the bond angle for a particular molecule. In ether, the bond pair repulsions between the two alkyl groups are higher than the lone pair repulsions on the oxygen atoms. Therefore, the bond angle is greater than the tetrahedral value i.e. 109°.

Hence, the correct answer is option D.

Question 18

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 19

Assertion (A) : Elevation in boiling point is a colligative property.
Reason (R) : Elevation in boiling point is directly proportional to molarity.

(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 expression for elevation in boiling point may be written as follows:

$$\Delta T_b = K_b \times m$$

Where, ΔT_b = elevation in boiling point.
m = molality.

Since, ΔT_b depends upon number of moles (or molality), therefore, it's a colligative property and also, is directly proportional to the molality and not molarity.

Hence, the correct answer is option C.

Question 20

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 21

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 22

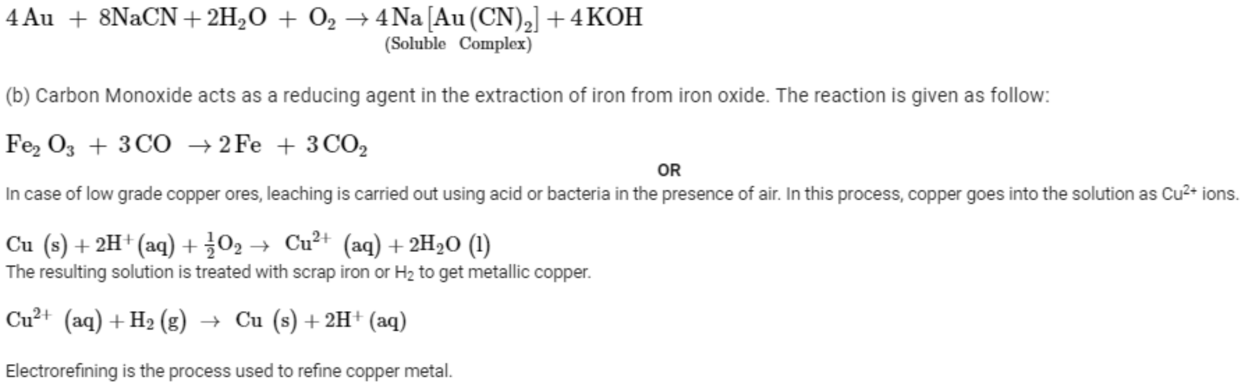
Write the role of
(a) Dilute NaCN in the extraction of Gold.
(b) CO in the extraction of Iron.

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 23

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 24

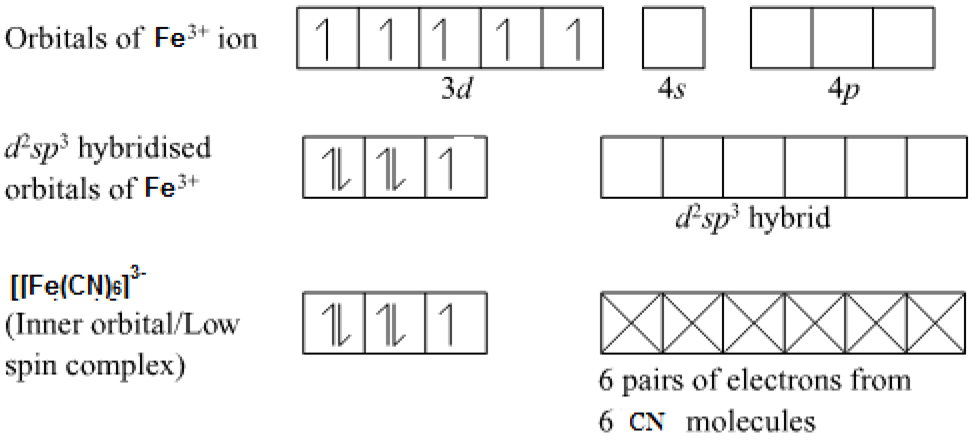
(a) Write the IUPAC name and hybridization of the complex $[Fe(CN)_6]^{3-}$.
(Given: Atomic number of Fe = 26)
(b) What is the difference between an ambidentate ligand and a chelating ligand?

Solution:

(a) The IUPAC name of the complex $[Fe(CN)_6]^{3-}$ is **hexacyanoferrate(III) ion**.

since, CN^- is a strong field ligand, therefore, it will pair up the d-orbital electrons of Fe and result in the formation of low spin (inner orbital) complex with the hybridization **d^2sp^3.**

Hybridisation Scheme



(b) Ambidentate ligands can attach to the central metal atom/ion in two places but only one at a time. Good examples are SCN^-, NO_2^- etc. which can attach to the central metal ion from either side.

If the ligands with two or more donor groups positioned in such a way that they form a five or six membered ring with the central metal ion, then the ligands are called **chelating ligands** and the ring formed is called **chelate ring.**

Question 25

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

Solution:

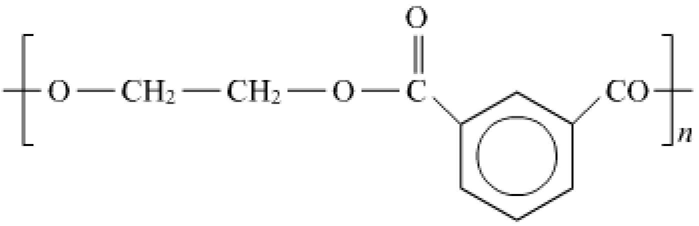
Antiseptics and disinfectants are effective against micro-organisms. Antiseptics are applied to the living tissues such as wounds, cuts, ulcers, and diseased skin surfaces, while disinfectants are applied to inanimate objects such as floors, drainage systems, instruments, etc. Disinfectants are harmful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

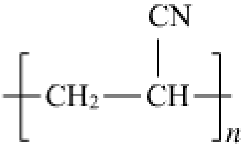
Question 26

Identify the monomers in the following polymers:

(i)

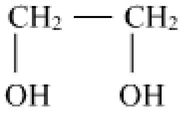


(ii)

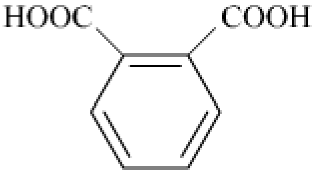


Solution:

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

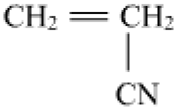


(Ethylene glycol)



(Phthalic acid)

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



$CH_2 = CH_2 - CN$

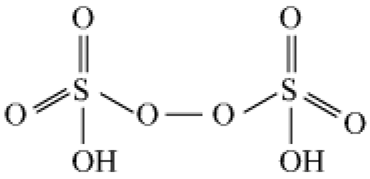
(Acrylonitrile)

Question 27

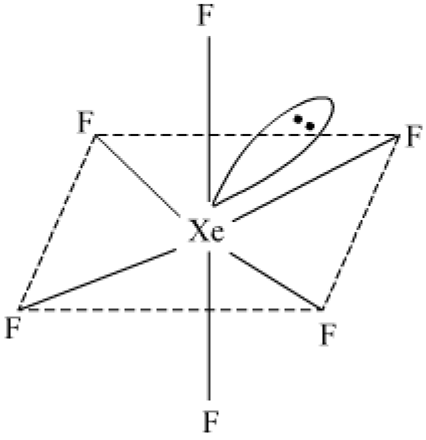
Draw the structures of the following:
(i) $H_2S_2O_8$
(ii) XeF_6

Solution

(i) The structure of $H_2S_2O_8$ may be drawn as follows:



(ii) The structure of XeF_6 may be drawn as follows:

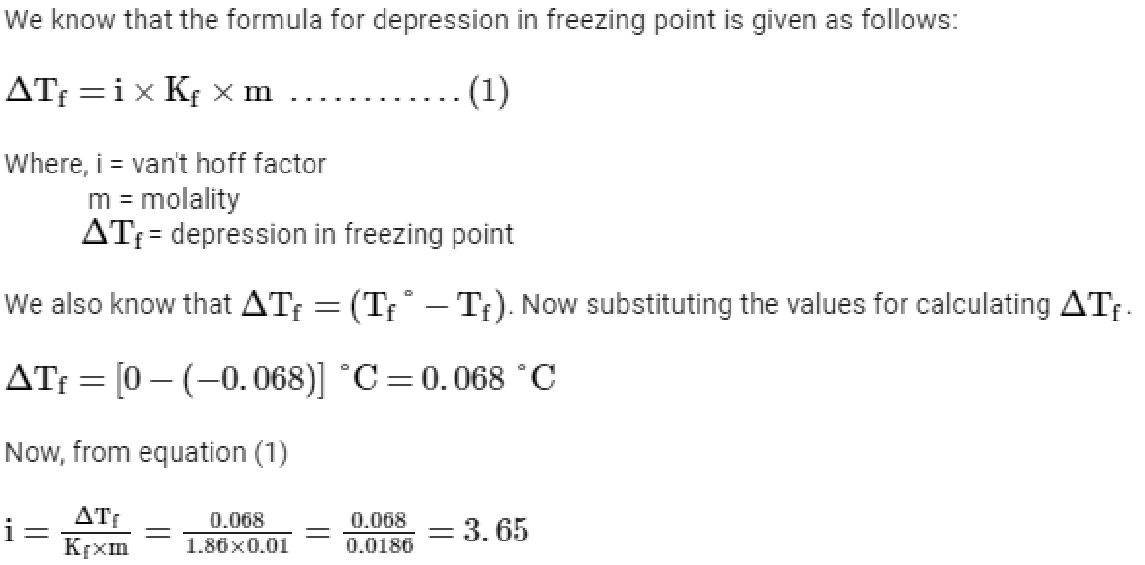


distorted - octahedral

Question 28

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 29

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 30

Differentiate between following:
(i) Amylose and Amylopectin
(ii) Globular protein and Fibrous protein
(ii) Nucleotide and Nucleoside

Solution:

Amylose and Amylopectin:

Amylose molecules are formed from several glucose units arranged in a linear manner. Amylopectin is formed from several glucose units arranged in a branched manner.

Fibrous Protein and Globular Protein:

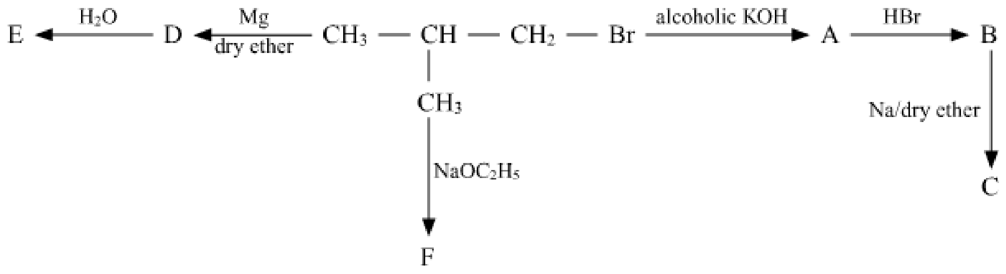
When the polypeptide chains run parallel and are held together with the help of hydrogen and disulphide bonds it is called fibrous protein.
In case of a globular protein, the chains of polypeptides coil around and give a spherical shape.

Nucleotide and Nucleoside:

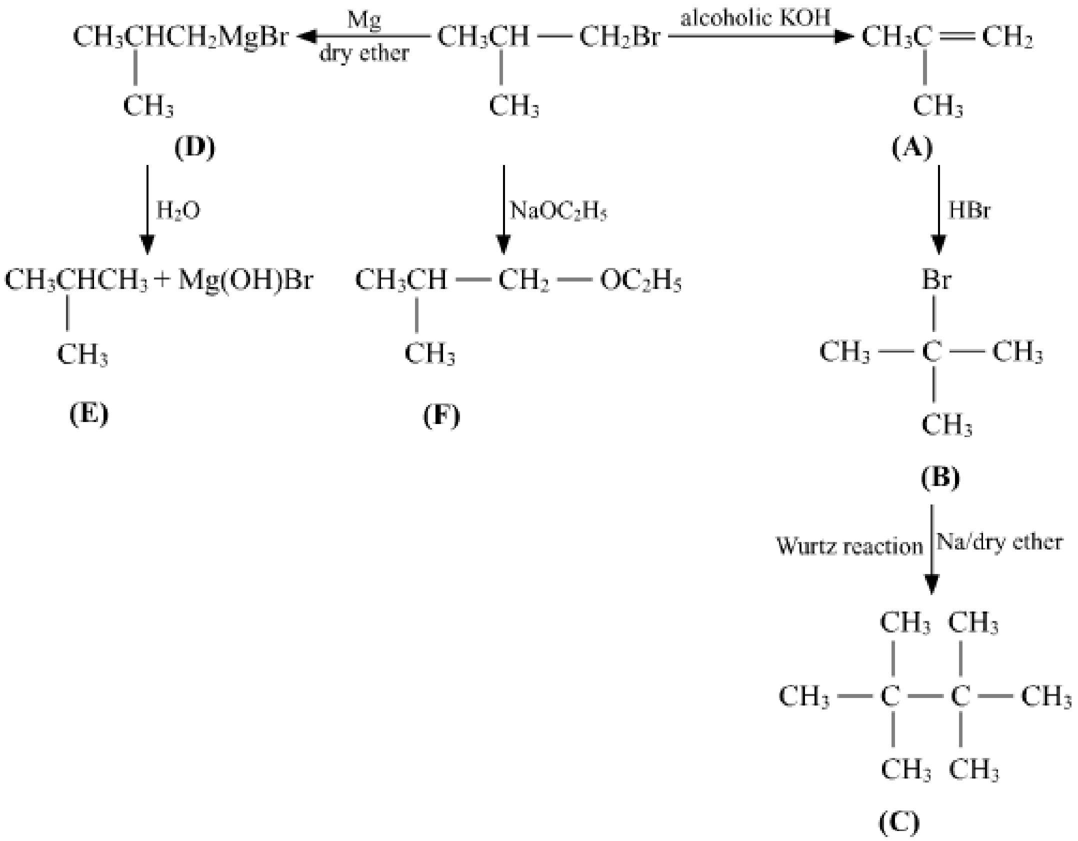
A nucleoside consists of a nitrogenous base covalently attached to a sugar (ribose or deoxyribose) but without the phosphate group. A nucleotide consists of a nitrogenous base, a sugar (ribose or deoxyribose) and one to three phosphate groups.

Question 31

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



Solution:



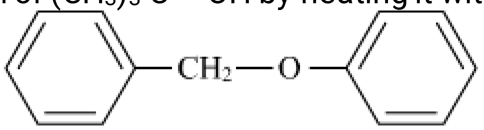
Question 32

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?

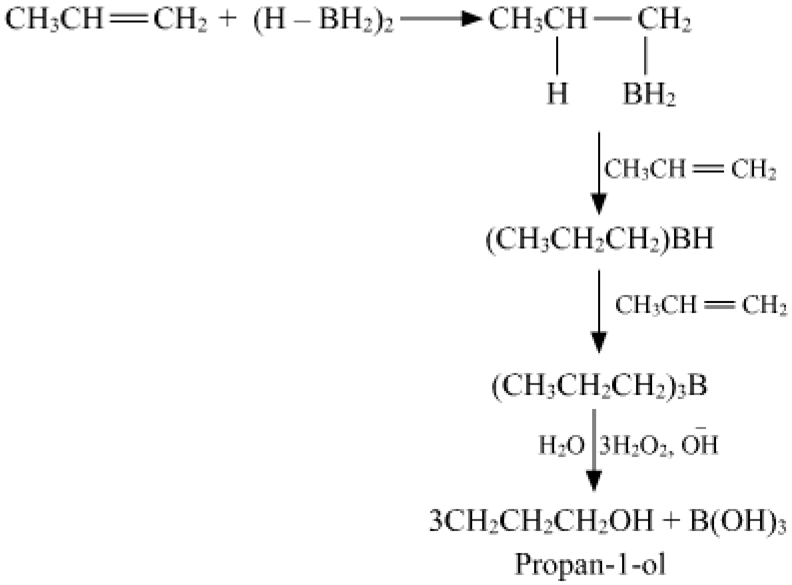
(i) Phenol to o-hydroxy benzaldehyde.

(ii) Methanal to ethanol

(iii) Phenol to phenyl ethanoate.

Solution:

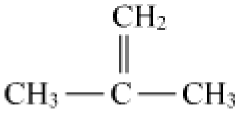
(i)



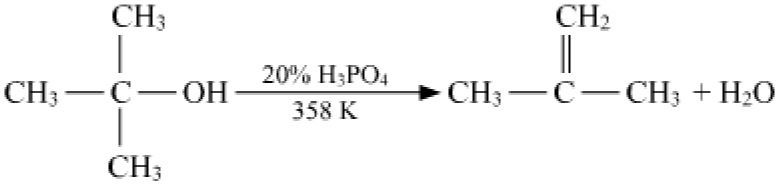
$$CH_3CH{=}CH_2 + (H-BH_2)_2 \longrightarrow \underset{H}{CH_3CH}-\underset{BH_2}{CH_2} \xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)BH \xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_3B \xrightarrow{H_2O\ |\ 3H_2O_2,\ \bar{O}H} 3CH_2CH_2CH_2OH + B(OH)_3$$

Propan-1-ol

(b)

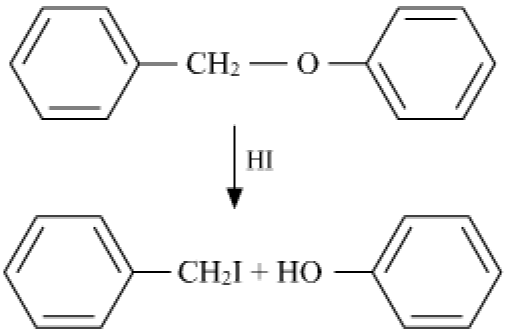


$$CH_3-\overset{\overset{CH_2}{\|}}{C}-CH_3$$



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

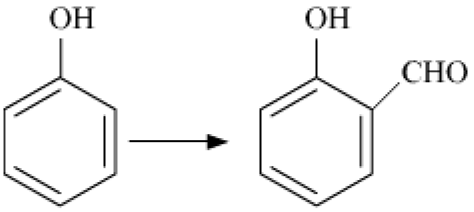
(c)



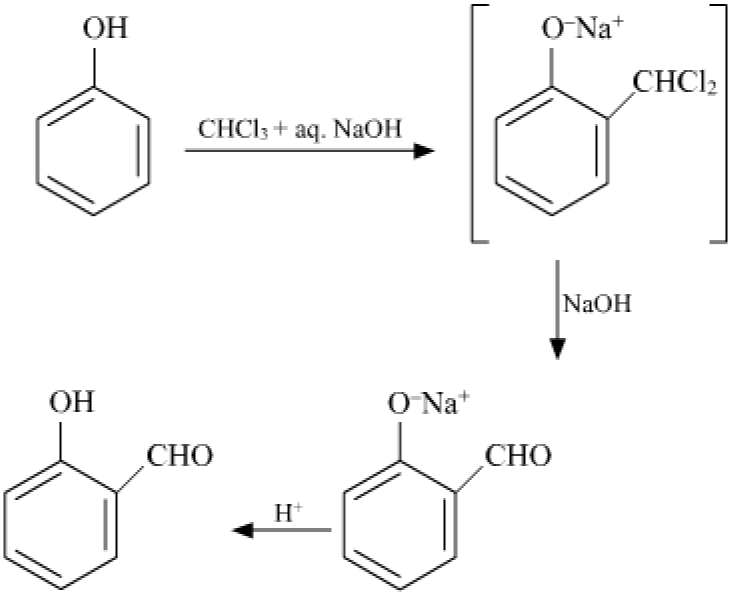
OR

(i)

Phenol to *o*-hydroxybenzaldehyde

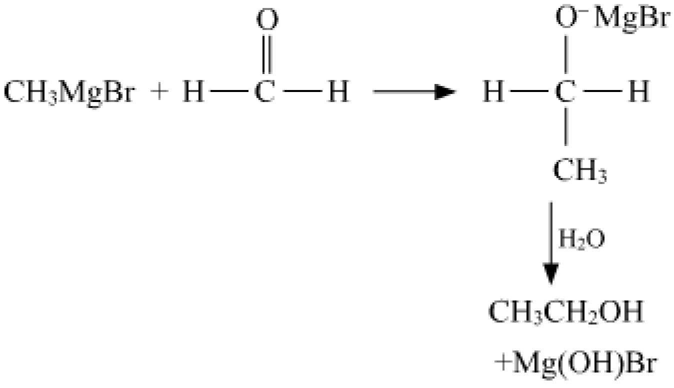


Reimer-Tiemann Reaction

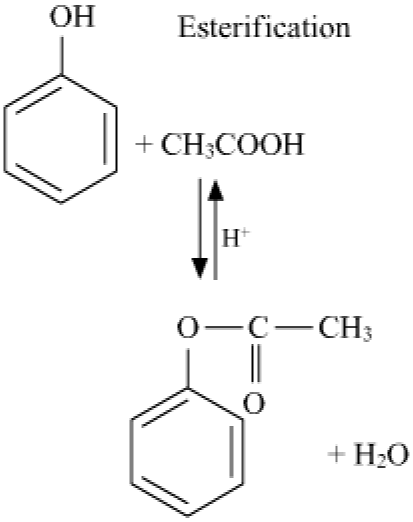


Salicylaldehyde

(ii)



(iii)

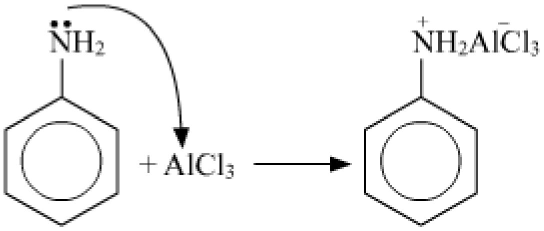


Question 33

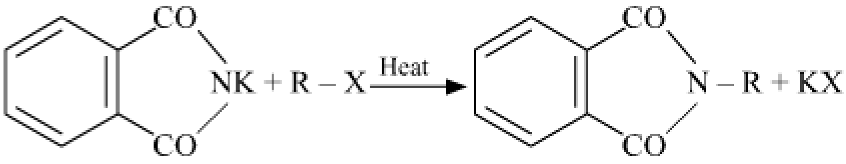
Give reasons:
(i) Aniline does not undergo Friedal-Crafts reaction.
(ii) Aromatic primary amines cannot be prepared by Gabriel's phthalimide synthesis.
(iii) Aliphatic amines are stronger bases than ammonia.

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.



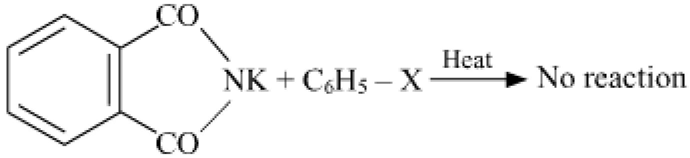
(ii) In Gabriel phthalimide reaction, the potassium salt of phthalimide is formed. It readily reacts with an alkyl halide to form the corresponding alkyl derivative.



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 34

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 35

(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) $2\,\mathrm{Na_2\,CrO_4} + \mathrm{H_2\,SO_4} \rightarrow \mathrm{Na_2\,Cr_2}\,O_7 + \mathrm{Na_2\,SO_4} + \mathrm{H_2O}$

ii)

$$2\,\mathrm{MnO_2} + 4\,\mathrm{KOH} + \mathrm{O_2} \overset{\text{heat}}{\rightarrow} 2\mathrm{K_2\,MnO_4} + 2\mathrm{H_2O}$$

OR

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

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)

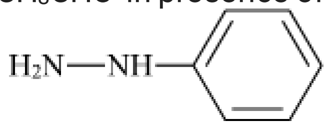
$$3\,\mathrm{MnO_4^{2-}} + 4\mathrm{H^+} \rightarrow 2\,\mathrm{MnO_4^-} + \mathrm{MnO_2} + 2\mathrm{H_2O}$$

Question 36

(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:

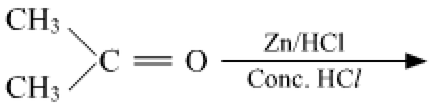
(i) $CH_3-CH=CH-CO-CH_3$ and $CH_3-CH_2-CO-CH=CH_2$

(ii) Benzaldehyde and Benzoic acid.

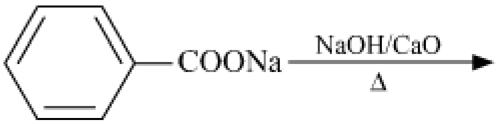
OR

(a) Write the final products in the following:

(i)



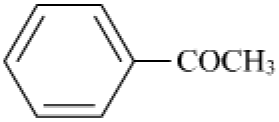
(ii)



(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,

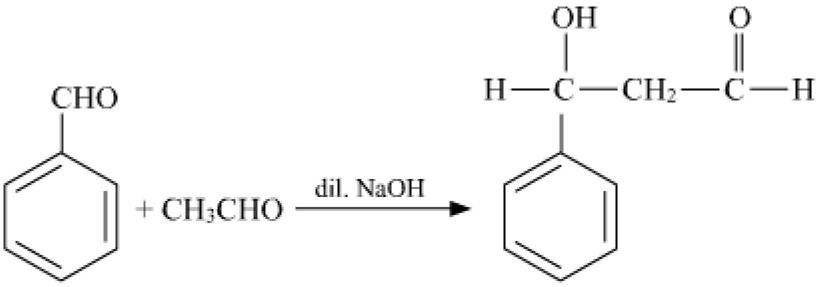


(c) Draw the structure of 2, 4 DNP derivative of acetaldehyde.

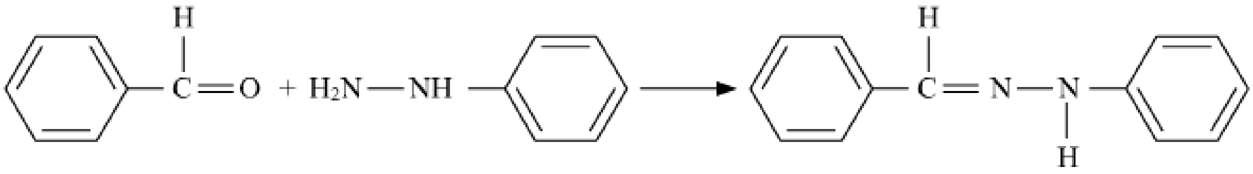
Solution:

(a)

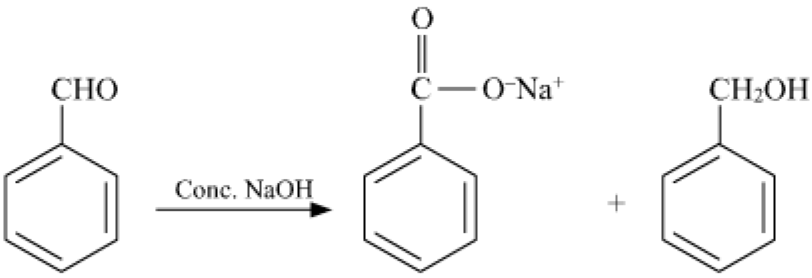
(i) It is aldol condensation reaction and the product will be:



(ii)

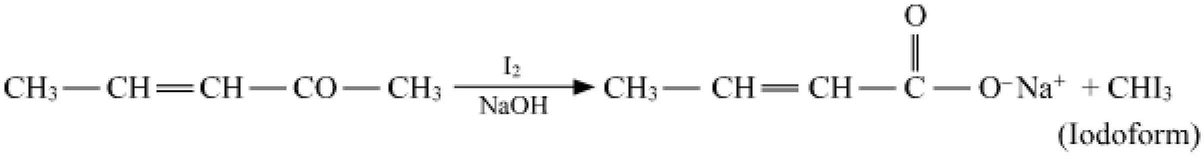


(iii) It is Cannizzaro reaction and the product will be:



(b)

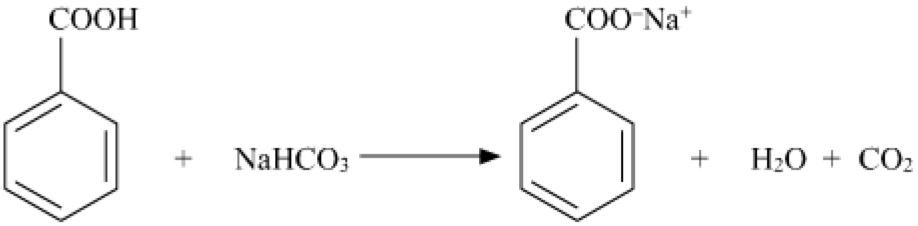
(i) They can be differentiated by the iodoform test. One of them contains a methyl ketonic group (-$COCH_3$) and thus undergo iodoform reaction whereas, the other won't undergo this reaction. The reaction may be shown as follows:

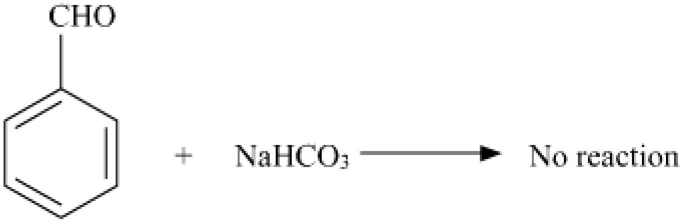


$$CH_3-CH=CH-CO-CH_3 \xrightarrow[NaOH]{I_2} CH_3-CH=CH-\overset{\overset{O}{\|}}{C}-O^-Na^+ + \underset{\text{(Iodoform)}}{CHI_3}$$

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

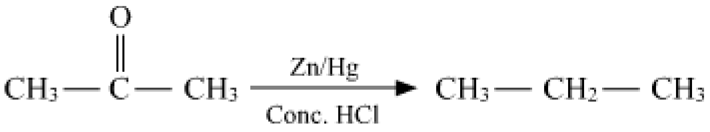
(ii) Carboxylic acids evolve carbon dioxide upon reaction with sodium bicarbonate whereas aromatic aldehydes don't react with it. The reaction may be shown as:



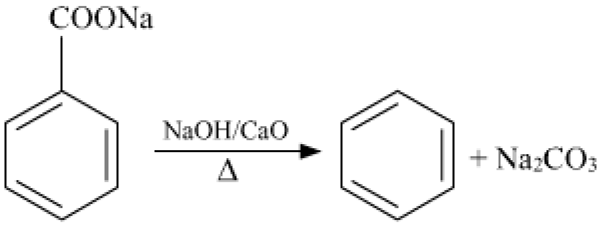


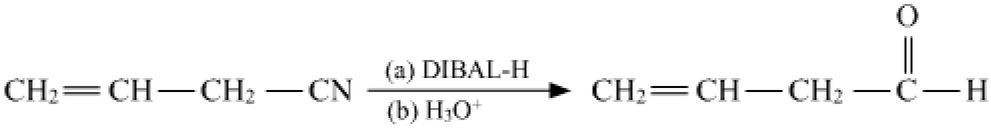
OR

(a)



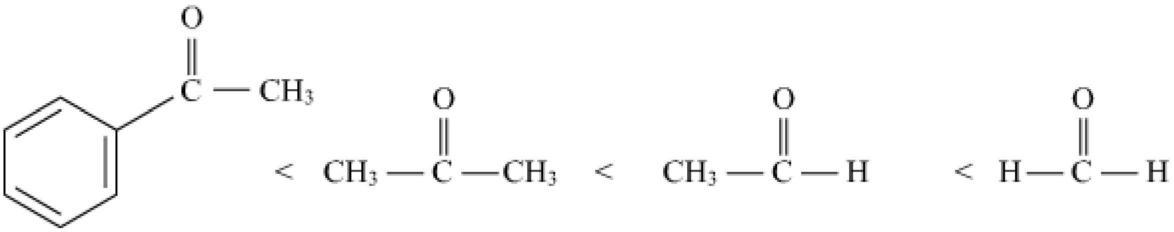
$$CH_3-\overset{\overset{\Large O}{\|}}{C}-CH_3 \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} CH_3-CH_2-CH_3$$





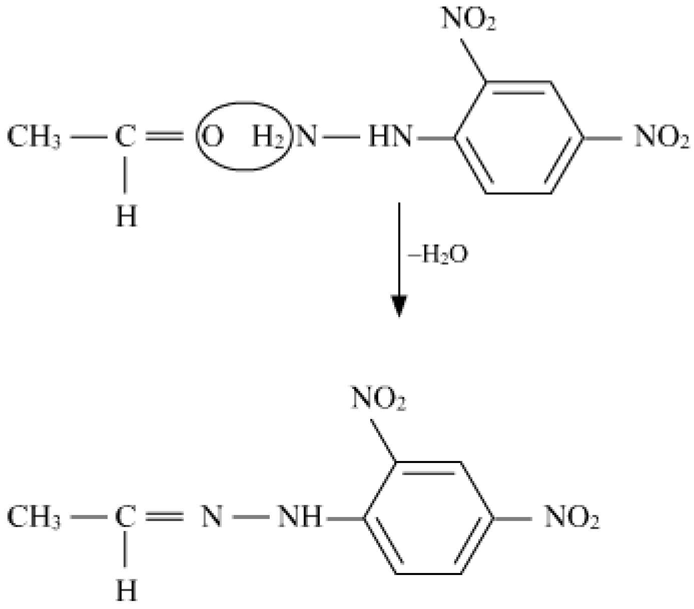
$$CH_2{=}CH-CH_2-CN \xrightarrow[\text{(b) } H_3O^+]{\text{(a) DIBAL-H}} CH_2{=}CH-CH_2-\overset{\overset{\Large O}{\|}}{C}-H$$

(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:



Question 37

(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, $k = \frac{2.303}{t}\log\frac{a}{a-x}$ ..... (1)
Given, 25% of the reaction completes so $x = \frac{25}{100}a = 0.25 \times a$,
and $t = 40$ minutes

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

$$\Rightarrow k = \frac{2.303}{40}\log\left(\frac{1}{0.75}\right)$$
$$\Rightarrow k = \frac{2.303}{40}\log\left(\frac{4}{3}\right)$$
$$\Rightarrow k = \frac{2.303}{40}\left(\log\ 4 - \ \log\ 3\right)$$
$$\Rightarrow k = \frac{2.303}{40}\left(0.6024 - \ 0.4771\right)$$
$$\Rightarrow k = \frac{2.303}{40}\left(0.123\right)$$
$$\Rightarrow k = 7.081 \times 10^{-3}\ \mathrm{min}^{-1}$$

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

$$t = \frac{2.303}{7.096 \times 10^{-3}}\ \log\frac{\mathrm{a}}{\mathrm{a} - x}$$
$$t = \frac{2.303}{7.096 \times 10^{-3}}\ \log\frac{\mathrm{a}}{\mathrm{a} - 0.8\mathrm{a}}$$
$$t = \frac{2.303}{7.096 \times 10^{-3}}\ \log\frac{1}{0.2}$$
$$t = \frac{2.303}{7.096 \times 10^{-3}}\ \log\ 5$$
$$t = \frac{2.303}{7.096 \times 10^{-3}}\ \times 0.6991$$
$$t = 226.89\ \mathrm{min}$$

(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.

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

OR

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

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

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

$$\frac{2.303}{30}\ \log\frac{a}{a-0.5a}=\mathrm{k}_1$$

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

$$\frac{2.303}{10}\ \log\frac{a}{a-0.5a}=\mathrm{k}_2$$

Therefore, $\frac{\mathrm{k}_2}{\mathrm{k}_1}=\frac{\frac{2.303}{10}\ \log\frac{\mathrm{a}}{\mathrm{a}-0.5\mathrm{a}}}{\frac{2.303}{30}\ \log\frac{\mathrm{a}}{\mathrm{a}-0.5\mathrm{a}}}=\frac{30}{10}=3$

Arrhenius Equation is given as follows:

$$\log\frac{\mathrm{k}_2}{\mathrm{k}_1}=\frac{\mathrm{E_a}}{2.303\ \mathrm{R}}\left(\frac{1}{\mathrm{T}_1}-\frac{1}{\mathrm{T}_2}\right)$$

$$\log\ 3=\frac{\mathrm{E_a}}{2.303\times8.314}\left(\frac{1}{300}-\frac{1}{320}\right)$$

$$0.4771=\frac{\mathrm{E_a}}{19.14}\left(\frac{320-300}{300\times320}\right)$$

$$E_a=\frac{0.4771\times19.14}{0.0002083}$$

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

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

(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.