Maharashtra State Board
Class XII Chemistry
Board Paper – 2016 Solution

SECTION-I

1.

(i) The substances which can be permanently magnetised even in the absence of a magnetic field are called ferromagnetic substances, and the mechanism is called ferromagnetism.
Iron (z = 26), with electronic configuration [Ar] $3d^6 4s^2$, contains four unpaired electrons. Hence, iron is strongly ferromagnetic.

(ii) The boiling point is the temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure.

Depression of freezing point and molar mass of the solute:
When W_2 gram of solute with molar mass M_2 is dissolved in W_1 gram of solvent, the molality m is given by

$$m = \frac{\text{Mass of solute in kg}}{\text{Molar mass of solue in kg} \times \text{Mass of solvent in kg}}$$

$$m = \frac{W_2}{M_2 \times W_1}$$

∴ The molar mass of a solute using freezing depression method is givenby,

$$\Delta\ T_f = \frac{K_f\, W_2}{M_2\, W_1}$$

(iii) The first law of thermodynamics can be applied to processes carried out under different conditions.

(a) Adiabatic process:

In an adiabatic process, there is no exchange of heat between the system and its surroundings, i.e. $q = 0$.
Therefore, the equation $\Delta U = q + W$ becomes

$$\Delta U = W \text{ or } -\Delta U = -W$$

The above equation indicates that the increase in internal energy of the system is due to the work done on it by the surroundings or that the work done by the system on the surroundings is at the expense of the system's internal energy which decreases in the process.

(b) Isochoric process:

By substituting equation $W = -p_{ex}.\Delta V$ in the equation $\Delta U = q + W$, we get

$$\Delta U = q - p_{ex}.\Delta V \quad ... (1)$$

If the reaction is carried out in a closed container so that the volume of the system is constant, then $\Delta V = 0$. In such a case, no work is involved. The equation (1) becomes $\Delta U = q_v$.

Equation (1) suggests that the change in internal energy of the system is due to heat transfer. The subscript v indicates a constant volume process. As U is a state function, q_v is also a state function. We see that an increase in the internal energy of a system is numerically equal to the heat absorbed by the system in a constant volume (isochoric) process.

(iv) The Arrhenius equation is given by

$$k = Ae^{-E_a/RT}$$

On taking logarithms of both sides, we get

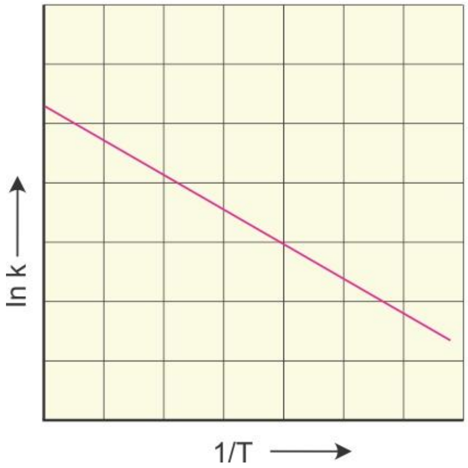
$$\ln k = \ln A - \frac{E_a}{RT}$$

Or

$$\log_{10} K = -\frac{E_a}{3.303RT} + \log_{10} A$$

The rate constant of a reaction is determined at various temperatures.

$\log_{10}$ k is plotted against the reciprocal of temperature. The graphical representation is



The slope of the straight line graph is $-E_a/2.303R$ from which the activation energy can be calculated.

(v) The important ores of iron are Haematite Fe_2O_3, Limonite $2Fe_2O_3.3H_2O$, Magnetite Fe_3O_4, Siderite $FeCO_3$ and Pyrite FeS_2.

The important ores of zinc are zinc blende ZnS, Calamine $ZnCO_3$, Zincite ZnO and Willemite Zn_2SiO_4.
(Note: Write any one ore in the examination)

(vi)

(a) Action of sodium on arsenic
Heating arsenic powder with excess sodium forms sodium arsenide Na_3As_2.

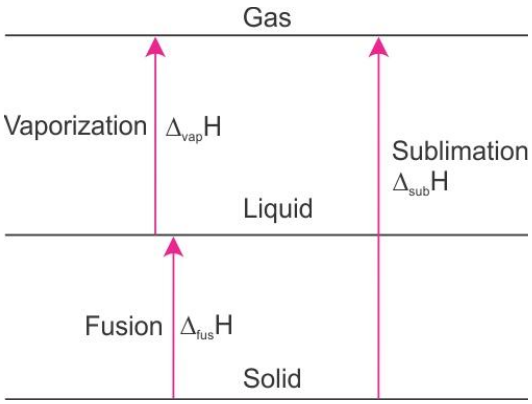
$$\underset{\text{Arsenic}}{2As} + \underset{\text{Sodium}}{3Na} \rightarrow \underset{\text{Sodium arsenide}}{Na_3As_2}$$

(b) Action of magnesium on bismuth
Bismuth forms magnesium bismuthide Mg_3Bi_2 with magnesium.

$$\underset{\text{Bismuth}}{2\ Bi} + \underset{\text{Magnesium}}{3\ Mg} \rightarrow \underset{\text{Magnesium bismuthide}}{Mg_3Bi_2}$$

(vii) The enthalpy change which accompanies the conversion of one mole of solid directly into its vapour at constant temperature and pressure is called its enthalpy of sublimation. It is denoted by $\Delta_{Sub} H$.

Relation of enthalpy of sublimation with enthalpy of fusion and enthalpy of vaporisation:



The enthalpy of sublimation of ice at 0°C and 1 atm pressure is 51.08 kJ mol^{-1}. $H_2O(s) \rightarrow H_2O(g)$, $\Delta H = 51.08$ kJ mol^{-1} at 0°C.
When solid is converted to vapour, either in one step or two steps, the solid first gets converted to the liquid state and then to the vapour state. The enthalpy change remains the same. This is because enthalpy is a state function.
For example,
$H_2O(s) \rightarrow H_2O(l)$, $\Delta_{fus} H = +6.01$ kJ mol^{-1} at 0°C
$H_2O(l) \rightarrow H_2O(g)$, $\Delta_{vap} H = +45.07$ kJ mol^{-1} at 0°C

$H_2O(s) \rightarrow H_2O(g)$, $\Delta H = 51.08$ kJ mol^{-1} at 0°C
Therefore, it follows that
$\Delta_{sub} H = \Delta_{fus} H + \Delta_{vap} H$

(viii) **Ellingham diagrams:**

The plots between $\Delta_f G^\Theta$ of formation of oxides of elements and temperature are called Ellingham diagrams. It provides a sound idea about selecting a reducing agent in the reduction of oxides. Such diagrams help in predicting the feasibility of a thermal reduction of an ore. ΔG must be negative at a given temperature for a reaction to be feasible.

Features of Ellingham diagram:

(a) The graph for the formation of a metal oxide is a straight line with an upward slope.

(b) There is a sudden change in the slopes for some metal oxides, such as MgO, ZnO and HgO.

(c) For a few metal oxides of silver and mercury (Ag_2O and HgO), the graph is at the upper part in the Ellingham diagram.

2.

(i) Given: Density of silver is 10.51 g cm^{-3}.

Unit cell of FCC has 4 atoms.

$$\text{Mass of unit cell} = \frac{4 \times 108}{6.022 \times 10^{23}} = 71.74 \times 10^{-23}$$

$$\text{Density of silver} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\text{Volume of unit cell} = \frac{\text{Mass of unit cell}}{\text{Density of silver}} = \frac{71.74 \times 10^{-23}}{10.51}$$

$$\text{Volume of unit cell} = 68.27 \times 10^{-24}\ \text{cm}^3$$

(ii) By the Raoult's law,

$$x_1 = \frac{P_1}{P_1^\circ} = \frac{600\ \text{mmHg}}{640\ \text{mmHg}} = 0.9375$$

$$\text{Also, } x_1 = \frac{n_1}{n_1 + n_2} = \frac{(39/78)}{(39/78)} + \frac{2.175}{M}$$

$$0.9375 = \frac{(39/78)}{(39/78)} + \frac{2.175}{M}$$

$$= 65.91\ \text{g/mol}$$

(iii)

$$CH_3Cl_{(g)} + Cl_{2(g)} \rightarrow CH_2Cl_{2(g)} + HCl_{(g)}$$

$$C-H = 414\ kJ/mol$$

$$Cl-Cl = 243\ kJ/mol$$

$$H-Cl = 431\ kJ/mol$$

$$\Delta H^o = -104\ kJ$$

$$\Delta H^o = \sum \Delta H^o\ (reactant\ bond) - \sum \Delta H^o\ (product\ bond)$$

$$= [3 \times \Delta H^o\ (C-H) + \Delta H^o\ (C-Cl) + \Delta H^o\ (Cl-Cl)] - [2 \times \Delta H^o\ (C-H) + 2 \times \Delta H^o\ (C-Cl) + \Delta H^o\ (H-Cl)]$$

$$= [3 \times 414 + \Delta H^o\ (C-Cl) + 243] - [2 \times 414 + 2 \times \Delta H^o\ (C-Cl) + 431]$$

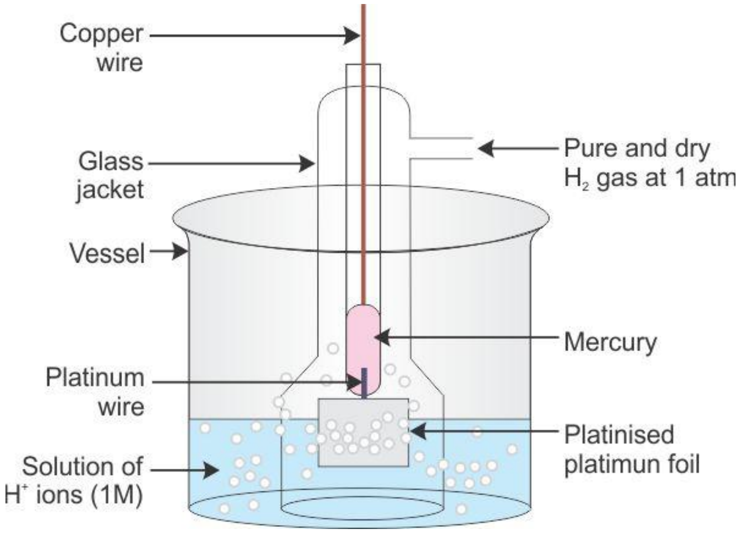
$$-104 = 1242 + \Delta H^o\ (C-Cl) + 243 - 828 - 2 \times \Delta H^o\ (C-Cl) - 431$$

$$\Delta H^o\ (C-Cl) = 330\ kJ$$

(iv) Cell constant is the ratio of the distance between the electrodes divided by the area of cross-section of the electrode. It is denoted by b.

Thus, Cell constant = b = $\frac{\ell}{a}$. It is expressed in unit m^{-1}.

Primary reference electrode:



Standard Hydrogen Electrode
(Primary Reference Electrode)

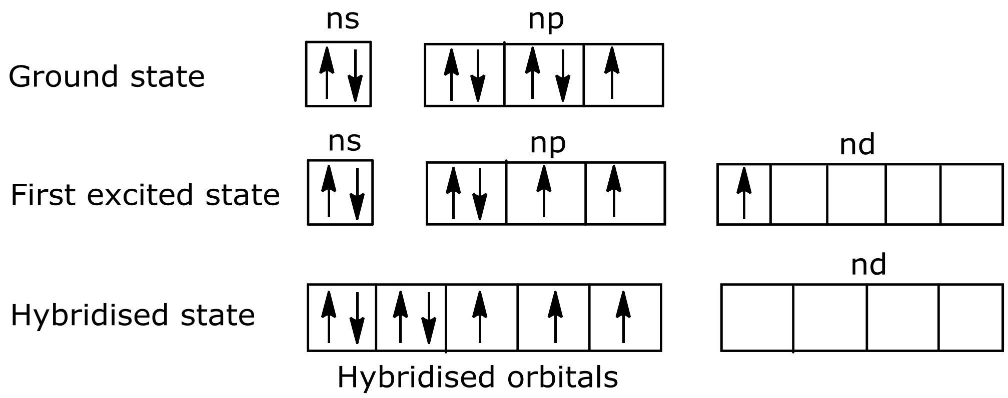
3.

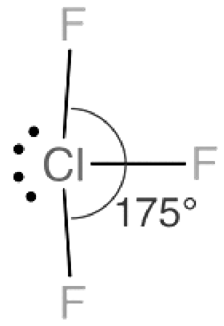
(A) **Differences between properties of nitrogen and other elements of group 15:**

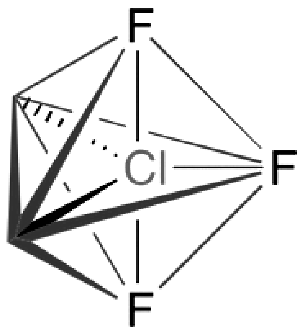
(i) Nitrogen molecule is diatomic, whereas other elements form tetra-atomic molecules.
(ii) Catenation property is more pronouncedly shown by nitrogen than the other elements of group 15.
(iii) Nitrogen is in the gaseous state, while the others are in the solid state at room temperature.
(iv) Hydride of nitrogen is stable, while the hydrides of other elements are not stable.

Structure of ClF_3:

ClF_3 is formed by sp^3d hybridisation. It shows T-shaped or trigonal bipyramidal structure.







Cross-sectional area of electrode:

$$k = \frac{1}{R} \times \frac{\ell}{a}$$

$$a = \frac{1}{R} \times \frac{\ell}{k}$$

$$a = \frac{1}{13710} \times \frac{0.7}{6.23 \times 10^{-5}}$$

$$a = 0.82\ \text{cm}^2$$

Molality:
Molality is amount of solute per mass of solvent. So, the concentration of solvent is expressed in terms of mass, and the mass of a substance is not affected by the change in temperature. Hence, molality is independent of temperature.

(B) **Neutral oxides:**
These are the oxides which show neither basic nor acidic properties, i.e. they are non-metal oxides which do not react with acids or bases.
Zinc oxide is an amphoteric oxide which shows both basic and acidic properties.

$ZnO + 2HCl \rightarrow \underset{\text{Zinc chloride}}{ZnCl_2} + H_2O$ (basic nature)

$ZnO + 2NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2O$ (acidic nature)

Molar conductivity:
Molar conductivity is the conductance of a volume of solution containing 1 mole of dissolved electrolyte when placed between two parallel electrodes 1 cm apart and large enough to contain between them all the solution.

Zero order reaction:
Zero order reaction is the reaction whose rate is independent of the reactant concentration and remains constant throughout the course of the reaction.

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_o}{[A]_t}$$
$$k = \frac{2.303}{t} \log_{10} \frac{100}{40}$$
$$k = \frac{2.303}{45} \log_{10} \frac{100}{40}$$
$$k = \frac{2.303}{45} \log_{10} 2.5$$
$$k = \frac{2.303}{45} \times 0.3979$$
$$k = 0.0204 \text{ min}^{-1}$$

4.

(i) (b) Thiosulphurous acid

Thiosulphurous acid has chemical formula $H_2S_2O_2$.

(ii) (c) Non-polar molecular solid

In case of iodine, the atoms are held together by weak London forces or van der Waal forces, so it exists as a non-polar molecular solid.

(iii) (a) Measuring heat capacity of substance at various temperatures.

By using the formula, we will be able to calculate the increase in the entropy. Absolute entropy (S_T) can be determined by measuring heat capacity of substance at various temperatures.

(iv) (c) ebullioscopy

Determination of molar mass from elevation in boiling point is called ebullioscopy.

(v) (d) Hall's process

In Hall's process, the ore and sodium carbonate are fused to convert aluminium oxide into soluble sodium meta aluminate.

(vi) (b) 2

$Q = I \times t$

$840 = I \times 420$

$I = 2\ A$

(vii) (b) $1.1 \times 10^{-4}\ s^{-1}$

Rate law for the reaction,

$\text{Rate} = k\ [A]$

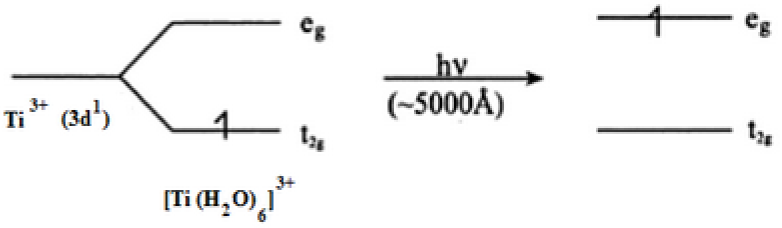
$6.6 \times 10^{-5} = k \times 0.6$

$k = 1.1 \times 10^{-4}$

SECTION-II

5.

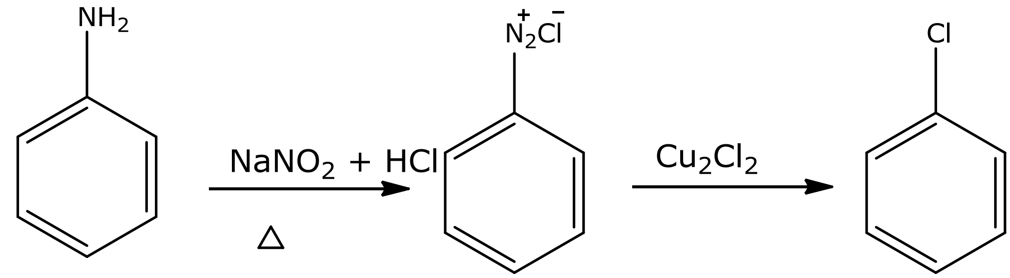
(i)Ti^{3+} is a $3d^1$ system. The colour is due to d–d transition. There is one d electron present in the 3d subshell. When light falls on the Ti^{3+} complex, the t_{2g} electron is excited to the e_g level. This excitation takes place in the greenish yellow region (≈5000 A°) and the rest is transmitted. The complementary colour is transmitted which is violet.



Sc^{3+} is a $3d^0$ system. There are no d electrons; hence, d–d transition is not possible. Hence, Sc^{3+} is colourless.

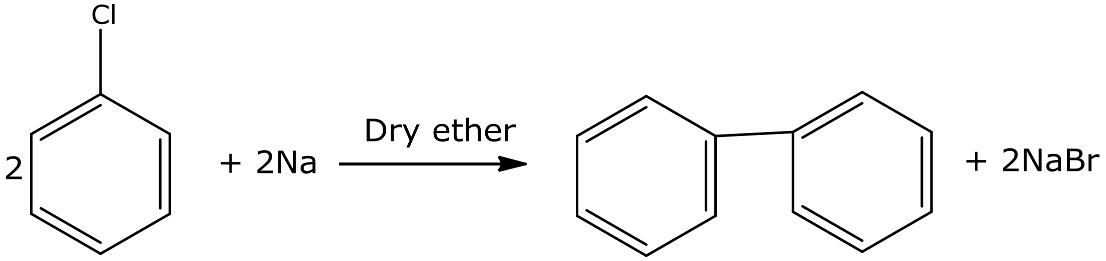
(ii) Double salts are molecular compounds which are formed by the evaporation of solution containing two or more salts in stoichiometric proportions. They dissociate into their constituent ions in solution.
A coordination (complex) compound is a compound formed from a Lewis acid and a Lewis base. They do not dissociate into their constituent ions in solutions.

(iii) Aniline reacts with nitrous acid to give benzene diazonium chloride which on treatment with cuprous chloride gives chlorobenzene.



Aniline

Chlorobenzene

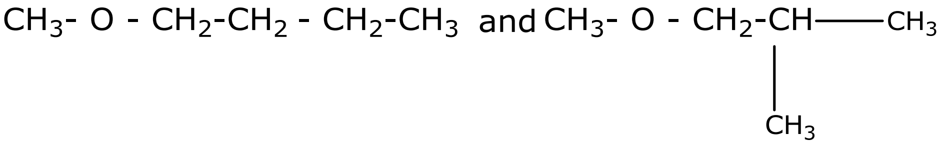


Chlorobenzene

Diphenyl

(iv) The ethers with the same molecular formula but different alkyl groups attached on either side of the oxygen atom are called metamers of each other, and the phenomenon is called metamerism.

Chain isomerism: n-Butyl methyl ether and isobutyl methyl ether are chain isomers of each other.



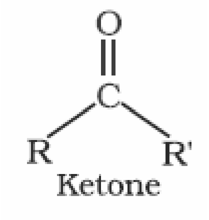
$CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ and $CH_3\text{-}O\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}CH_3$

Functional isomerism: Dimethyl ether and ethyl alcohol are functional isomers.

$CH_3\text{–}O\text{–}CH_3$ and CH_3CH_2OH

(v) Ketones are the organic compounds in which the carbonyl group is attached to two alkyl groups or aryl groups or both alkyl and aryl groups.

General formula:



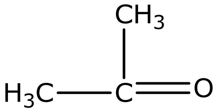
Ketone

R, R′ may be an alkyl or aryl group.

On the basis of types of alkyl groups attached to the carbonyl carbon, ketones are classified as

Simple or symmetrical ketones: The ketones in which both alkyl groups attached to the carbonyl carbon are identical are called simple ketones (R = R′).

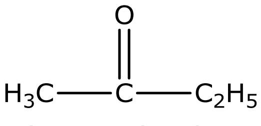
Example:



$H_3C\text{—}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}O$

Acetone

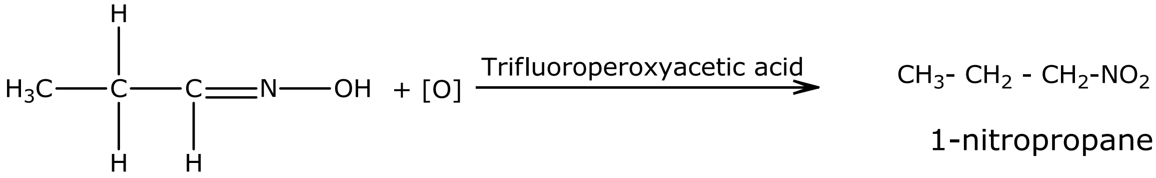
Mixed or unsymmetrical ketones: The ketones in which the two alkyl groups attached to the carbonyl carbon are different are called mixed ketones (R ≠ R′).



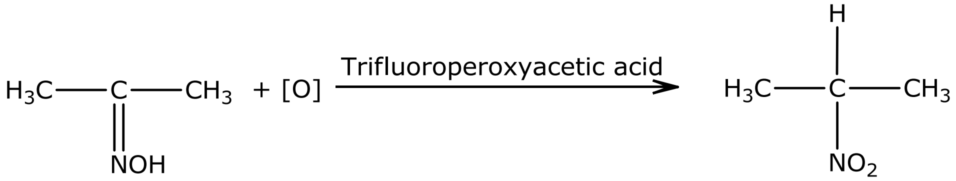
$H_3C\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}C_2H_5$

Ethyl methyl ketone

(vi) 1-nitropropane and 2-nitropropane are prepared by oxidising propionaldehyde oxime and propan-2-one oxime with the help of trifluoroacetic acid.

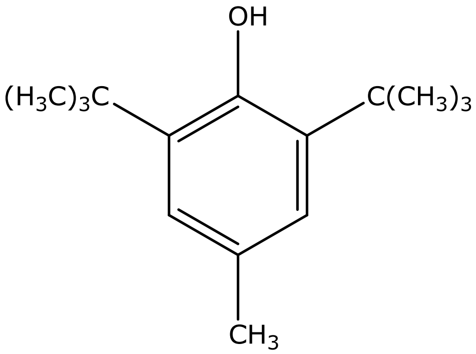


1-nitropropane



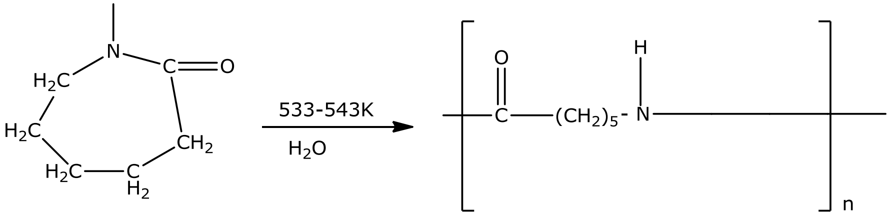
2-nitropropane

(vii) Antioxidant is a substance which when added to food retards or prevents the oxidative deterioration of food.



(viii) Carbohydrates are optically active polyhydroxy aldehydes or polyhydroxy ketones or compounds which can be hydrolysed to polyhydroxy aldehydes or polyhydroxy ketones.

Nylon-6: It is obtained by heating caprolactam with water at a high temperature.



Nylon-6

6.

(i) The elements in which the differentiating electron (last electron) enters (n-2) f orbital are known as f-block elements. The differentiating electron enters the pre-penultimate shell. The f-block elements are the lanthanides and actinides and are also called inner transition elements. All 28 elements from atomic numbers 58 to 71 and from atomic numbers 90 to 103 are collectively called f-block elements.

Differences between lanthanoids and actinoids:

Lanthanoids	**Actinoids**
1. Differentiating electron enters 4f orbitals.	1. Differentiating electron enters 5f orbitals.
2. Belong to the sixth period and form part of the third transition series. They constitute the first inner transition series.	2. Belong to the seventh period and form part of the fourth transition series. They constitute the second inner transition series.
3. Binding energy of 4f orbitals is higher.	3. Binding energy of 5f orbitals is lower.
4. Besides the +3 oxidation state, lanthanoids show +2 and + 4 oxidation states in few cases.	4. Besides the +3 oxidation state, actinoids show higher oxidation states such as +4, +5 and +7.
5. They show lesser tendency to form complexes.	5. They show greater tendency to form complexes.
6. Some of the lanthanoids are fairly coloured.	6. Most of the ions of actinoids are deeply coloured. Examples: U^{3+} (red), U^{4+} (green)
7. Only promethium is radioactive.	7. All the members of this series are radioactive.

(ii)

(a) Optical activity:

Optical activity is the property of certain organic substances to rotate the plane of plane polarised light towards the right (clockwise) or towards the left (anticlockwise).

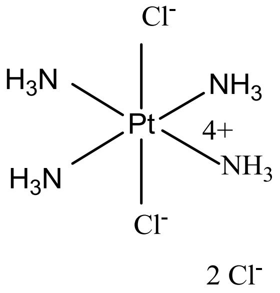
(b) Ligands:

Ligands are ions or neutral molecules which bind to a central metal atom or ion. They act as Lewis bases (electron pair donors). They have at least one donor atom with an electron pair used to form covalent bonds with the central atom.

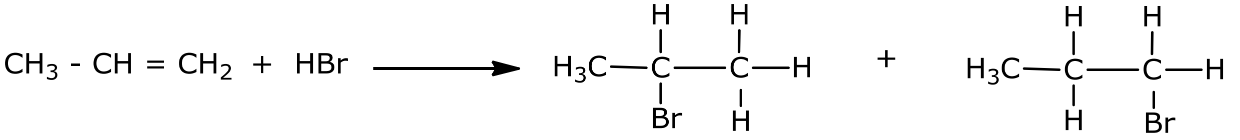
(c) Interstitial compounds:

Interstitial compounds are formed when small atoms such as H, C or N are trapped inside the crystal lattices of metals. They are usually non-stoichiometric and are neither typically ionic nor covalent.

(iii) The formula of tetraminodichloroplatinum(IV)chloride is $(NH_3)_4\ PtCl_4$.



The addition of hydrogen halide to an unsymmetrical alkene gives two products.
Propene on reaction with hydrogen bromide forms 80% 2-bromopropane (isopropyl bromide) and 20% 1-bromopropane (n-propyl bromide).



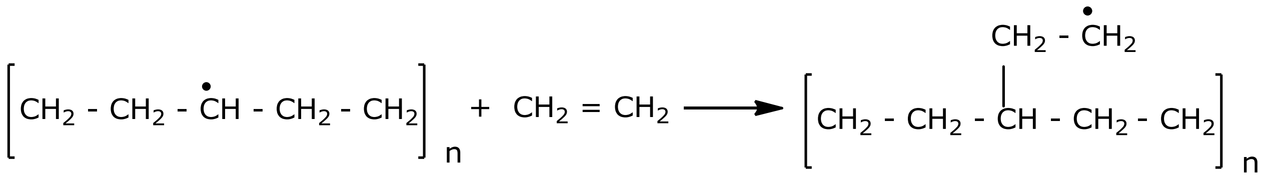
2-bromopropane
(isopropyl bromide)
80%

1-bromopropane
(n-propyl bromide)
20%

(iv) The antibiotics which are effective against a wide range of gram-positive and gram-negative bacteria are known as broad spectrum antibiotics.
Examples: Chloramphenicol, ampicillin, amoxicillin

Preparation of polythene:
The monomer used is ethane. It is an addition polymer. There are two ways of preparation of ethane.

Low-density polymer (LDPE): It is formed by heating ethene at 200° to 300°C and at 1000 atm pressure using a small amount of oxygen as a catalyst. Oxygen forms peroxide and the reaction is initiated.

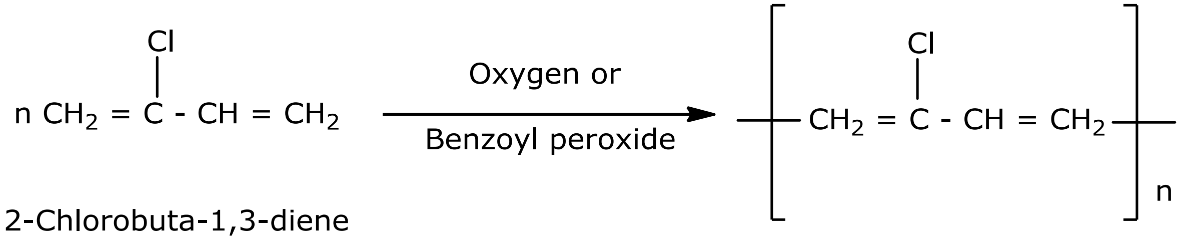


Ethene

High-density polymers (HDPE): The catalyst used is called Ziegler–Natta catalyst. It is titanium chloride and triethyl aluminium $[TiCI_4 + (C_2H_5)_3\ Al]$. The polymerisation takes place at 373 K, 6–7 atm pressure in the presence of the Ziegler–Natta catalyst.

Preparation of neoprene:

2-Chlorobuta-1,3-diene in the presence of benzoyl peroxide forms neoprene. Here, 2-chlorobuta-1,3-diene (chloroprene) acts as a monomer.



$$n\,CH_2=\overset{\overset{Cl}{|}}{C}-CH=CH_2 \xrightarrow[\text{Benzoyl peroxide}]{\text{Oxygen or}} \left[-CH_2=\overset{\overset{Cl}{|}}{C}-CH=CH_2-\right]_n$$

2-Chlorobuta-1,3-diene
(chloroprene)

Neoprene

7.

(i) Carboxylic acid reacts with alcohols in the presence of mineral acid as a catalyst and forms esters. This reaction is called esterification.

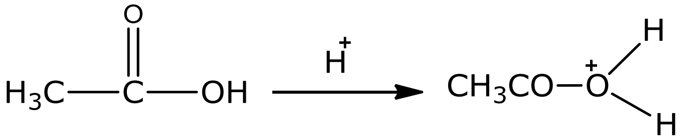
Consider the following reaction for the preparation of ethyl acetate from ethanoic acid.

$$CH_3COOH + C_2H_5OH \xrightarrow{H^+} \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

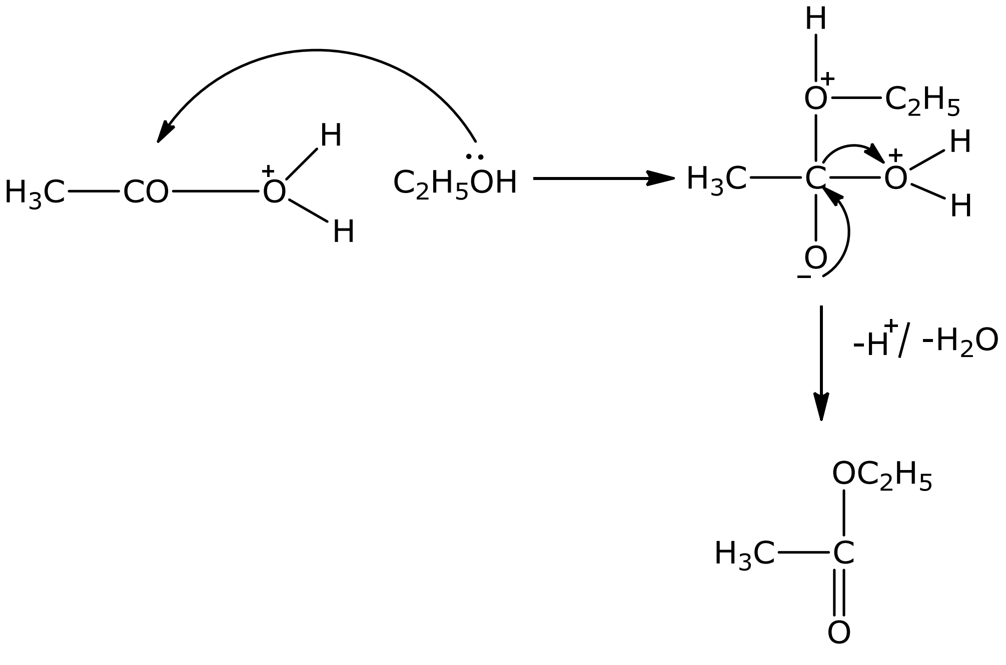
The mechanism involved in the above esterification reaction can be explained as follows:

Protonation of the –OH group of the acid enhances the nucleophilic attack by alcohol to give the ester.

Step 1: Protonation of carboxylic acid



Step 2: Attack by nucleophile

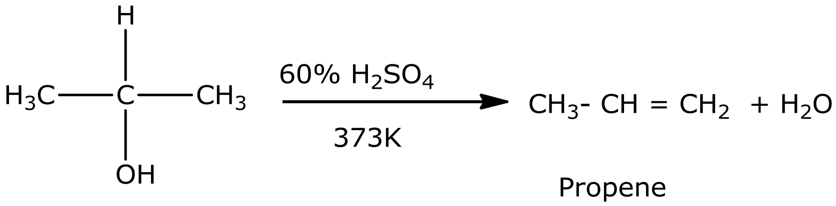


Primary alcohol on dehydration:

$$CH_3CH_3OH \xrightarrow[443K]{95\%\ H_2SO_4} CH_2{=}CH_2$$

Ethanol Ethene

Secondary alcohol on dehydration:

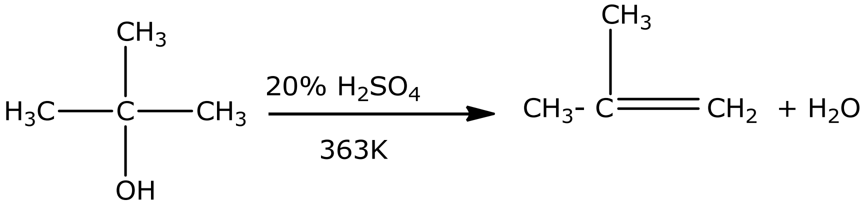


$$H_3C-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CH_3 \xrightarrow[373K]{60\%\ H_2SO_4} CH_3-CH=CH_2 + H_2O$$

2-propanol

Propene

Tertiary alcohol on dehydration:



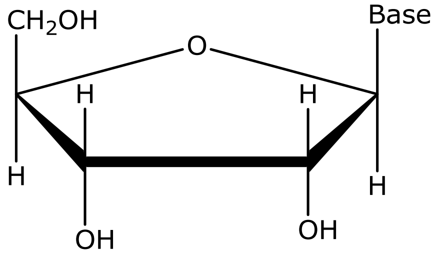
$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_3 \xrightarrow[363K]{20\%\ H_2SO_4} CH_3-\overset{\displaystyle CH_3}{C}{=}CH_2 + H_2O$$

2-methylpropan-2-ol

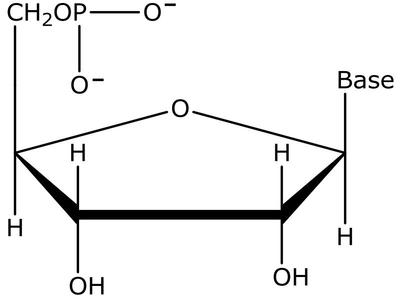
2-methylpropene

(ii) Vitamins are organic substances which must be supplied to permit growth in living beings or for the maintenance of structure.
Diseases caused by deficiency of Vitamin A are night blindness and dryness of skin and hair.

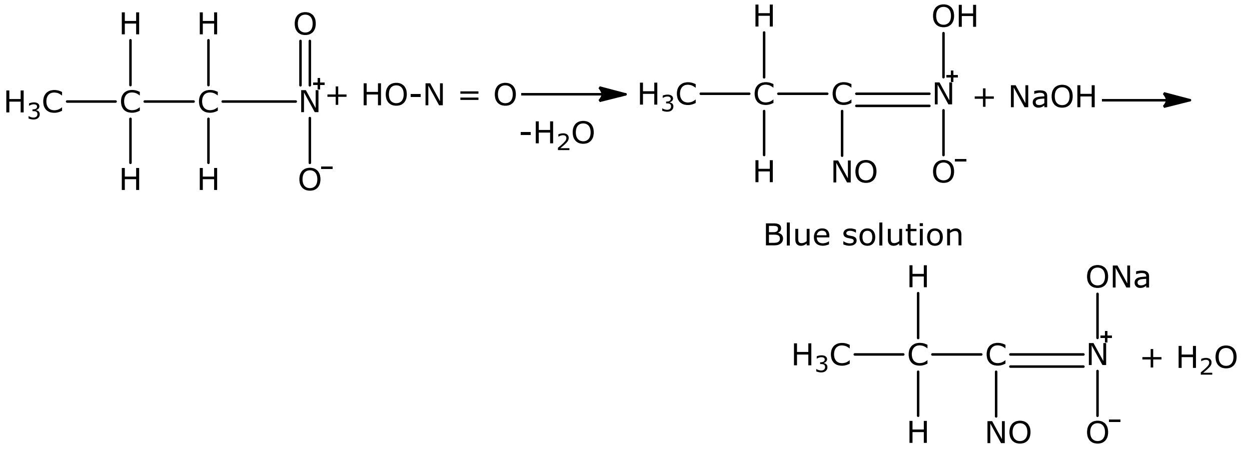
Structure of nucleoside:



Structure of nucleotide:

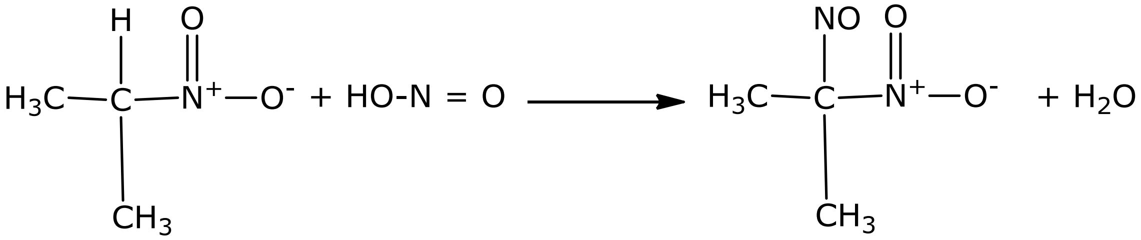


1-Nitropropane reacts with nitrous acid to form blue-coloured nitroso-nitroalkanes which dissolve in NaOH to give red solution.



Red solution

2-Nitropropane reacts with nitrous acid to form blue-coloured nitroso-nitroalkanes which are further insoluble in NaOH because of the absence of the alpha hydrogen atom.



2-nitropropane

2-Methyl2-nitropropane does not react with nitrous acid because it has no alpha-hydrogen atom.

8.

(i) (b) Finkelstein reaction

Alkyl fluorides are prepared by heating alkyl chlorides in the presence of metallic fluorides such as AgF, CoF_2 or SbF_3, and this reaction is known as Finkelstein reaction.

(ii) (d) p-Aminophenol

Electron-withdrawing substituents make the phenol more acidic, while electron-releasing substituents make the phenol less acidic.

p-aminophenol < p-cresol < p-chlorophenol < p-nitrophenol

(iii) (d) Propanoic acid

$CH_3CH_2C \equiv N + 2H_2O + HCl \xrightarrow{\Delta} CH_3CH_2COOH + NH_4Cl$

(iv) (a) Ethyl amine

Ethyl amine on heating with chloroform and alcoholic KOH gives foul smelling ethyl isocyanide.

$C_2H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3CH_2N \equiv C + 3KCl + 3H_2O$

(v) (d) Uracil

The heterocyclic bases in DNA are adenine, guanine, cytosine and thymine.

(vi) (c) PHBV

It is a copolymer and the monomers used are 3-hydroxy butanoic acid and 3-hydroxy pentanoic acid.

(vii) (d) Antidepressant

Phenelzine is used as an antidepressant.