Chemistry

Grade 12

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Ministry of Education, Science and Technology

Curriculum Development Centre

Sanothimi, Bhaktapur

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Preface

The curriculum is the central guide that determines what is essential for teaching and learning. A textbook is one of the main tools used to deliver the intent and the content of the curriculum. Therefore, it should present relevant, practical, and useful knowledge and help develop skills for the overall development of learners in accordance with curricular aims and objectives. This textbook**,** **'Chemistry, Grade 12',** has been prepared in line with the intent of the National Curriculum Framework for School Education, 2076 and developed in accordance with Secondary Level (Grade 11-12) Chemistry Curriculum, 2077.

This book has been developed by a team consisting of Mr. Hari Prasad Regmi, Mr. Khem Raj Bhatta, Mr. Naresh Prashad Bhatta, Mr. Pramatma Mishra and Mr. Lav Dev Bhatta. Several people, notably, the Director General Mr. Yubaraj Paudel and Dr. Kamal Prasad Acharya, Mr. Umanath Lamsal, Mr. Keshar Bahadur Khulal, Mr. Heramba Raj Kandel, Ms. Mina Shrestha, Mr. Purushottam Ghimire, Asst. Prof. Dr. Deval Prasad Bhattarai, Asst. Prof. Dr. Bhoj Raj Poudel, and Asst. Prof. Dr. Bhanu Neupane deserve special appreciation for their valuable contributions.

Efforts have been made to make the book activity oriented and interesting to the learners. All the contents of each lesson in this book are equally important. However, teachers can adapt to the contents and tasks according to the needs of their learners and classroom contexts. This book can be used as a major resource for classroom teaching; however, it should not be considered the only source of learning. The teachers are encouraged to explore additional resources and use them to supplement the curricular contents as outlined in the curriculum. The Curriculum Development Centre always welcomes constructive feedback and suggestions for the continuous improvement of its publications.

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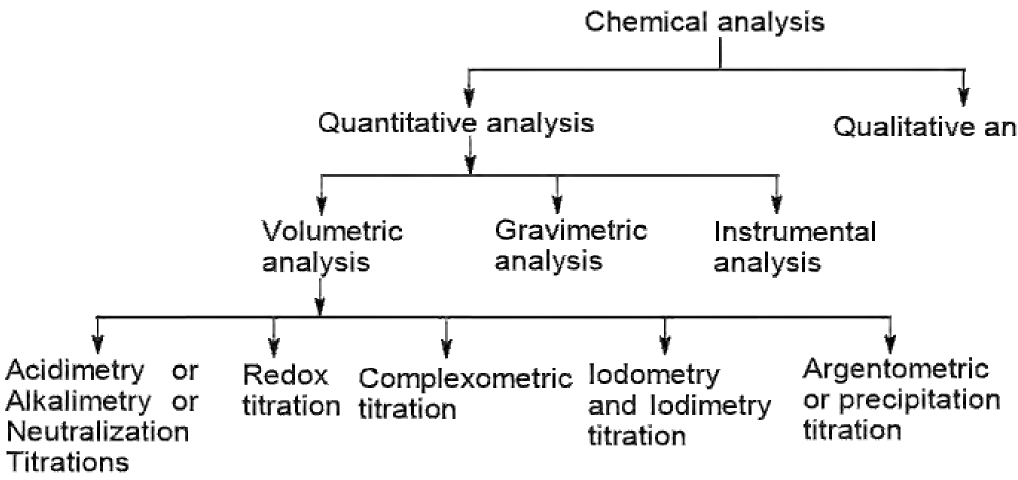
Volumetric Analysis



1.1 Introduction to gravimetric analysis, volumetric analysis and equivalent weight

Activity: 1

a. Identify the figure related to quality of substance and the figure that is related to quantity of the substance.
b. Identify the quantity that is measured and the quality that is observed.

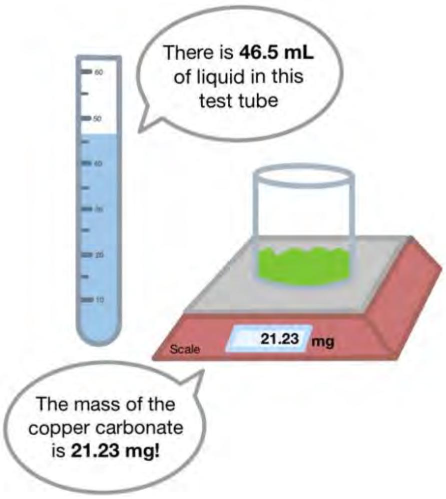


Figure A

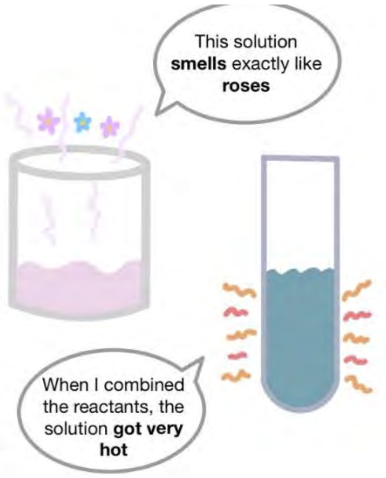


Figure B

In a chemistry laboratory, you may have observed the odors of gases produced or noted the colors of various solutions. These observations are part of **qualitative analysis**, which provides understanding into the characteristics or quality of a substance. In contrast, when we measure the mass or volume of the substance formed, we are engaging in **quantitative analysis**, which focuses on the quantity of the analyte being tested. The substance under investigation, whether analyzed qualitatively or quantitatively, is referred to as the **analyte**. Gravimetric analysis, volumetric analysis are examples of quantitative analysis.

1.1.1 Gravimetric analysis

Either in the food industry or even at home, it is important to monitor the moisture content to ensure the food is preserved and has the correct texture. A small sample of the food is weighed before and after drying. The difference in mass corresponds to the water content in the sample, as the moisture evaporates when heated. This is the example of a **gravimetric method** of determining moisture content. This technique depends on the principle of measuring changes in mass during a chemical or physical change.

The figure given below explains the **gravimetric analysis** by measuring the mass of the analyte.

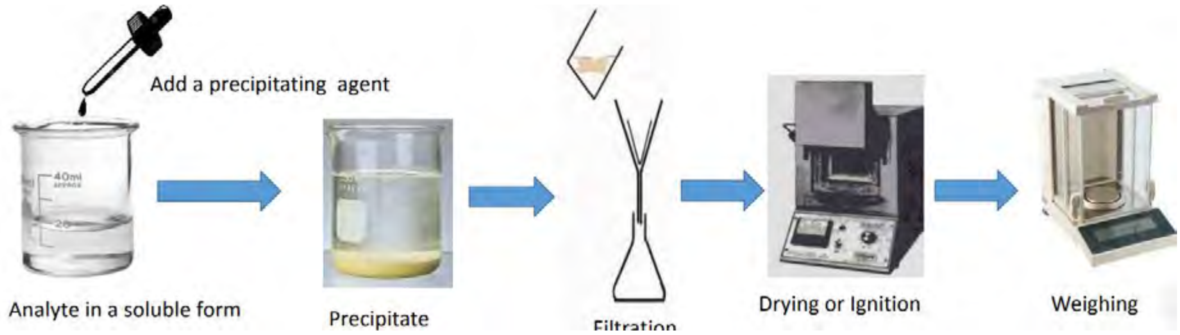


Figure 1.1. Diagrams illustrating the phenomena of gravimetric analysis

When the amount of analyte is determined by measuring its mass then that quantitative analysis is referred to as gravimetric analysis.

Do yourself

Add 1 mL of silver nitrate solution into a 5 mL of sodium chloride solution. Did you see any precipitate? Measure the mass of solid formed.

1.1.2 Volumetric analysis

Activity

Name the apparatus given below. Discuss in group about the common use of these apparatus and fill the table given.

Apparatus	Uses

Have you ever used beaker or any other instruments to measure the volume of the liquid? You may have seen the injection syringe measuring the certain volume of medicine. In volumetric analysis volume of liquid is measured using one of the instruments given above.

Volumetric analysis is based on the principles of stoichiometry, where the number of reactants and products in a chemical reaction are related by their molar ratios. The reaction must be known and should ideally be fast, complete, and with a clear endpoint.

Different apparatus is used in the chemistry laboratory to measure the volume of liquid or gas. For example, burette, pipette, measuring cylinder, volumetric flask etc. Burette and measuring cylinder can transfer desired volume whereas pipette and volumetric flask can transfer fixed volume of liquid as shown in the figure.

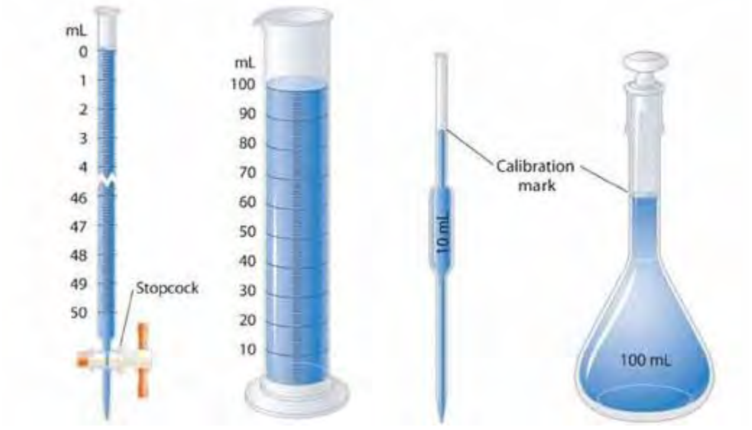


Figure: Glasswares for measuring volume of liquid (burette, measuring cylinder, pipette and volumetric flask)

Volume is usually measured in liter (L) or decimeter cube (dm^3), milliliter (mL). Higher units of volume are such as kiloliter (kL) and megaliter (ML) can also be used.

These days everyone is concerned with the quality of food, water, air, and pharmaceuticals. To ensure the quality of the products we need to find the composition and purity of the consumables. This brings the importance of chemical analysis which involves identifying, separating, and quantifying a substance in a sample. Chemical analysis may be qualitative or quantitative.

Qualitative analysis is the determination of elements and compounds that are present in a sample of unknown material whereas quantitative analysis is the determination of the amount or quantity of each element or compound present. To state it more clearly, qualitative analysis explores "what is it?" and quantitative analysis explores "how much is it?".

Quantitative analysis can be performed by chemical and physical methods. Physical methods involve the measurement of physical properties such as density, refractive index, and surface tension. Chemical methods rely on reactions like precipitation, neutralization, oxidation, etc. The frequently used analytical methods are gravimetric analysis, volumetric analysis, and instrumental analysis.

Volumetric analysis is a quantitative analytical method used to determine the concentration of an analyte (component of interest) in a solution by measuring the volume of the reactants.

Applications of Volumetric Analysis

a. Water Quality Testing: Determination of hardness of water, and water pollutants such as arsenic in drinking water
b. Pharmaceuticals: Quantitative analysis of active ingredients in medicine.
c. Food Industry: Measurement of acidity in food products like vinegar, juices, wine etc.
d. Environmental Monitoring: Analysis of pollutants, such as nitrate or phosphate levels

Test yourself

You have to measure 10 mL of water accurately. You are provided beaker, measuring cylinder, burette, and pipette. Which glassware you will use and why?

1.1.3 Equivalent weight

We can calculate the mass of any reactants or products in the balanced chemical equation using the concept of mole. But if the products are unknown or equation is not balanced, it is not possible to calculate the exact number of substances using the mole calculation. It is possible by using another concept of weight what we called equivalent weight. *Equivalent weight* of any substance is calculated with reference to hydrogen, oxygen or chlorine. Equivalent weight expressed in gram is called as *gram equivalent weight.*

In the early development of chemistry, hydrogen was chosen as the benchmark for measuring reactivity because it is the simplest element and has the smallest atomic mass. Oxygen was chosen as the standard because it is highly reactive and forms a wide variety of compounds. Chlorine is chosen because of its well-defined reactivity, especially its ability to react with metals and non-metals and its role as a halogen.

Equivalent weight is a crucial concept for understanding chemical reactions. It provides a way to simplify calculations involving the mass of substances that participate in reactions and determine the quantities of reactants and products involved.

Equivalent weight tells how much of a substance is equivalent to one mole of a standard substance in a given reaction.

Gram equivalent weight of a substance is the mass of the substance that can displace or combine 1.008 g of hydrogen or 8.0 g of oxygen or 35.5 g of chlorine.

For example, in the given reaction between Mg (24 g) and HCl to produce 2.016 g of hydrogen gas, we can calculate the equivalent weight of **Mg** using hydrogen as a reference.

$$Mg + HCl \rightarrow MgCl_2 + H_2$$

24 g $\qquad$ 2.016 g

$\frac{24}{2.016} \times 1.008 = 12$ g of Mg $\qquad$ 1.008 g

Therefore, equivalent weight of Mg =12 because it is equivalent to 1.008 part of hydrogen.

Equivalent weight of any element can be calculated as:

$$\frac{weight\ of\ element}{weight\ of\ hydrogen} \times 1.008 = \frac{weight\ of\ element}{weight\ of\ oxygen} \times 8 = \frac{weight\ of\ element}{weight\ of\ chlorine} \times 35.5$$

Test yourself

What is equivalent weight of: a) Na in NaH, b) Aluminum (Al) in Aluminum oxide Al_2O_3, c) Mg in $MgCl_2$?

1.2 Relationship between equivalent weight, atomic weight and valency

The atomic weight (A) of an element is the mass of one mole of its atoms, usually expressed in gram per mole.

Valency (**v**) indicates the combining capacity of an element. One of the most commonly used methods to find the combining capacity of an element is to find the number of hydrogen atoms that combines with one atom of the element.

It means **v** atoms of hydrogen ≡1 atom of the element
Or, mass of $v \times 1.008$ g of hydrogen ≡ mass of 1 atom (which is atomic weight, A)
Or, 1.008 g of hydrogen = **A/v**
The equivalent weight (**E**) of an element is defined as the mass of that element which combines with or displaces 1 mole of hydrogen atoms (1.008 g) in a chemical reaction.
Therefore,

$$\textbf{Equivalent weight (E)} = \frac{\textbf{atomic mass (A)}}{\textbf{valency (v)}}$$

1.2 Equivalent weight of compounds (acid, base, salt, oxidizing and reducing agents)

Fill the table as given

Name of the substance	Moleculecular weight	Acidity/basicity(n)	Molecular weight /n
HCl	36.5	1	36.5
H_2SO_4			
NaOH			
$Mg(OH)_2$			

Equivalent weight of compound refers to the mass of a substance that combines or displace one mole of hydrogen atoms (for acids), hydroxide ions (for bases), or a specific quantity of an oxidizing or reducing agent in a redox reaction. It can be understood in terms of the substance's ability to donate or accept protons (H^+), hydroxide ions (OH^-), or electrons.

The equivalent weight (E.W.) of a compound is given by the formula:

$$= \frac{\text{molar mass of a compopund (M)}}{factor\ (n)}$$

Where, n = number of ionizable or replaceable hydroxyl ions present in one molecule of a base (also called as acidity)

=number of replaceable hydrogen atoms present in a molecule of the acid (also called as basicity)

= total number of cationic or anionic charge per molecule of salt.

= total number of electrons that an oxidizing agent can accept in a redox reaction.

= number of electrons that a reducing agent can donate in a redox reaction.

a. Equivalent weight of an acid

Acids contain one or more replaceable hydrogen atoms. The number of replaceable hydrogen atoms present in a molecule of the acid is referred to as basicity. Equivalent mass of an acid is the number of parts by mass of the acid which contains 1.008 part by mass of replaceable hydrogen atom.

Equivalent weight of an acid = $\frac{\textbf{molar mass of an acid}}{\boldsymbol{number\ of\ replaceable\ hydrogen\ atom}} = \frac{\textbf{molar mass of an acid}}{\boldsymbol{basicity}}$

For example, the basicity of sulphuric acid is 2.

Equivalent weight of $H_2SO_4 = \frac{\text{Molar mass of H2SO4}}{\mathbf{2}}$ = 98/2 = 49

b. Equivalent weight of a base

Equivalent mass of a base is the number of parts by mass of the base which contains one replaceable hydroxyl ion, or which completely neutralizes one gram equivalent of an acid. The number of hydroxyl ions present in one mole of a base is known as the **acidity of the base**. Sodium hydroxide, potassium hydroxide, ammonium hydroxide are examples of monoacidic bases (acidity 1)

Equivalent weight of a base = $\frac{\textbf{molar mass of base}}{\textit{acidity}}$

For example, Equivalent Mass of $Mg(OH)_2 = \frac{58}{2}$

$= 29$

c. Equivalent weight of a salt

Salt contains positively charged cation and negatively charged anion. The total positive charge of cation or negative charge of anion is called **ion exchange capacity** of the salt. Equivalent mass of salt depends upon such capacity as given by the relationship.

Equivalent weight of a salt $= \frac{\text{molar mass of an acid}}{\textit{total positive or negetive charge}} = \frac{\text{molar mass of salt}}{\textit{ion exchange capacity of salt}}$

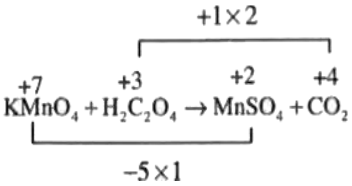
For examples,

Equivalent mass of NaCl $= \frac{58.5}{1} = 58.5$

Equivalent mass of $MgCl_2 = \frac{95}{2} = 47.5$

d. Equivalent weight of oxidizing and reducing agent

Activity: Study the following reaction between potassium permanganate ($KMnO_4$) and anhydrous oxalic acid ($H_2C_2O_4$).



a. Identify the oxidizing and reducing agents.
b. How many electrons are lost and gained per molecule in the reaction?

An oxidizing agent gains electrons whereas reducing agent donates electrons in a redox reaction. The number of electrons gained or lost equals to the **change in oxidation number**. These number determines the equivalent mass of these substances.

Equivalent weight of oxidizing agent = $\frac{\text{molar mass of compound}}{\textit{total change in oxidation number}}$

$= \frac{\text{molar mass of compound}}{\textit{total number of electrons gained}}$

Equivalent mass of $KMnO_4$ in the above equation $= \frac{158}{5} = 31.6$

Equivalent weight reducing agent = $\frac{\textbf{molar mass of compound}}{\textit{total change in oxidation number}}$

$$= \frac{\textbf{molar mass of compound}}{\textit{total number of electrons lost}}$$

Equivalent mass of $H_2C_2O_4$ in the above equation $= \frac{90}{2} = 45$

We can calculate the equivalent mass of compound using half equation as well

For examples,

the half reaction of $KMnO_4$ in neutral medium is

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

Equivalent mass of $KMnO_4 = \frac{158}{3} = 52.66$

In alkaline medium $MnO^-_4 + e^- \rightarrow MnO_4^-$

Equivalent mass of $KMnO_4 = \frac{158}{1} = 158$

In the same way the half reaction of $Na_2S_2O_3$ (reducing agent) in acidic medium can be written as

$S_2O_3{}^{2-} \rightarrow 1/2\ S_4O_6{}^{2-} + e^-$

Equivalent mass of $Na_2S_2O_3 = \frac{126}{1} = 126$

Equivalent mass of oxidant or reductant $= \frac{\text{molecular mass}}{\textit{total change in oxidation number}}$

Likewise, the equivalent weight of oxalic acid as reducing agent in the given reaction is

$$2MnO_4{}^- + 16H^+ + 5C_2O_4{}^{--} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

Equivalent weight $= \frac{126}{2} = 63$

e. Equivalent weight of radical

Radical are charged species. Equivalent weight of radicals depends on the number of charges that the radical carries.

Equivalent weight s of radical = $\frac{\textbf{molecular mass}}{\textbf{total number of charge per radical}}$

Equivalent Mass of $CO_3^{--} = \frac{12 + 16 \times 3}{2}$

$$= 30$$

Solved example

Calculate the equivalent weight of Ferric sulphate

a. as salt

b. as oxidizing agent

Solution,

a. ferric sulphate contains total 6 +ve charge

$$Fe_2(SO_4)_3 \quad \rightarrow \quad 2Fe^{+++} + 3SO_4^{--}$$

Equivalent weight of Ferric sulphate salt = $\frac{400}{6}$= 66.66

b. $Fe_2(SO_4)_3 \quad \rightarrow \quad FeSO_4$

Change in oxidation number per iron atom =1

Total Change in oxidation number =1×2 =2

Therefore, Equivalent weight of Ferric sulphate salt = $\frac{400}{2}$ =200

Test yourself

1. Calculate the equivalent mass of $AlCl_3$
2. What is the equivalent mass of $Na_2S_2O_3$ in the given reaction?
   $S_2O_3^{2-} + 10\ OH^- \rightarrow 2SO_4^{2-} + 5H_2O + 8e^-$
3. Find the equivalent weight of underlined compound in the given reactions
   a. $\underline{\mathbf{K_2Cr_2O_7}}$ + 8 H_2SO_4 → 2 $\underline{K_2SO_4}$ + 2 $\underline{Cr_2(SO_4)_3}$ + 8 H_2O + 3 O_2
   b. $\underline{\mathbf{H_3AsO_3}}$ + I_2 + H_2O → H_3AsO_4 + 2 H^+ + 2 I^-
   c. $\underline{\mathbf{CrO_4}^{-}}$+ 4 H_2O + 3 e^- → $Cr(OH)_3$ + 5 OH^-
   d. NaOH+ $\underline{\mathbf{H_3PO_4}}$→$NaH_2PO_4$+$H_2O$
   e. 2NaOH+ $\underline{\mathbf{H_3PO_4}}$→$Na_2HPO_4$+$H_2O$

Project work

Using chart or A4 sized paper complete the table below.

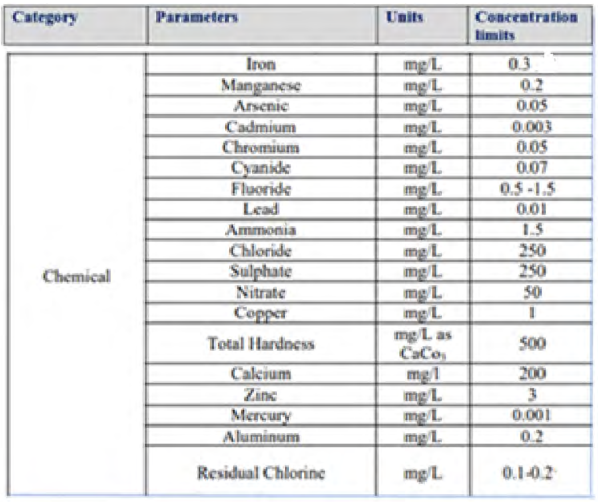
Compound	Molecular mass	Acid, base, salt, oxidizing agent or reducing agent	n-factor	Equivalent weight
$CaSO_4$	136	Salt	2	68
HCOOH				
H_2SO_4				
NH_4OH				
$Ca(OH)_2$				
$Al_2(SO_4)_3$				
Ag_2CrO_4				
$KMnO_4$ in neutral medium				
$K_2Cr_2O_7$ in acidic medium				

1.4 Concentration of solution and its units

Activity 1

The table includes different chemical parameters of National Drinking Water Quality Standards, 2062 issued by government of Nepal.

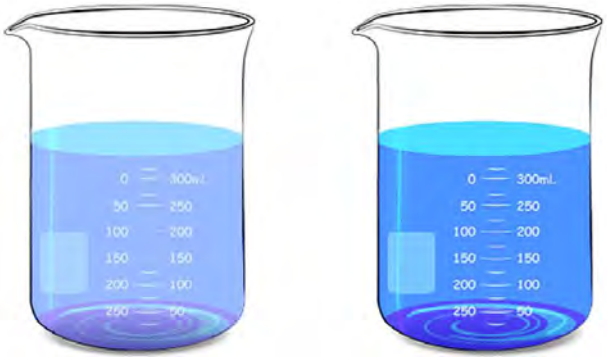
a. The permissible limit for lead is 0.01 mg/L. What does it mean?
b. Identify the metal having highest and lowest concentration limits in the drinking water.
c. Can you predict the toxicity of a metal based on the permissible concentration limit?



Category	Parameters	Units	Concentration limits
Chemical	Iron	mg/L	0.3
	Manganese	mg/L	0.2
	Arsenic	mg/L	0.05
	Cadmium	mg/L	0.003
	Chromium	mg/L	0.05
	Cyanide	mg/L	0.07
	Fluoride	mg/L	0.5 -1.5
	Lead	mg/L	0.01
	Ammonia	mg/L	1.5
	Chloride	mg/L	250
	Sulphate	mg/L	250
	Nitrate	mg/L	50
	Copper	mg/L	1
	Total Hardness	mg/L as $CaCo_3$	500
	Calcium	mg/l	200
	Zinc	mg/L	3
	Mercury	mg/L	0.001
	Aluminum	mg/L	0.2
	Residual Chlorine	mg/L	0.1-0.2

Activity 2

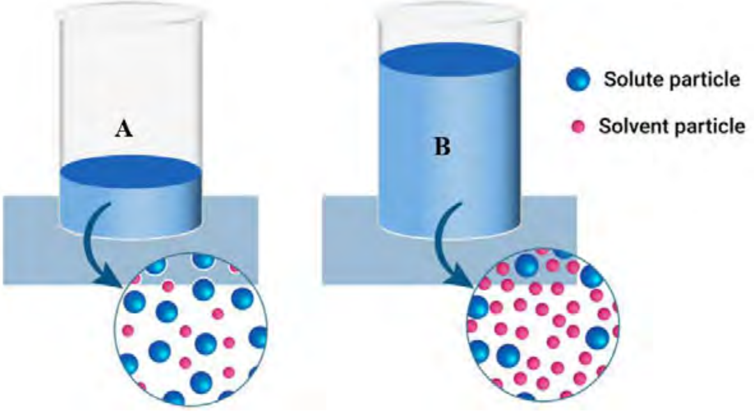
You are provided two beakers containing copper sulphate solution. Find the difference in terms of volume, color intensity, and concentration of the solution.



The concept of concentration is also applicable in cooking. If your curry is salty then it tells that concentration of sodium chloride in curry is high. You add water to make it less salty. The addition of water basically decreases the concentration of sodium chloride. Keep in mind that the amount of sodium chloride does not change on adding water in the curry.

The concentration of a solution is determined by the number of solute particles in a given volume. Beaker **A** contains a greater number of **solute particles** than **solvent particles** per unit volume of solution than the beaker **B**. It means beaker A contains more concentrated solution than the solution in beaker B.

In normal sense, the amount of solute present in given volume of solution is called concentration of that solution.



The amount of solute can be expressed either in mass or in mole fraction or in number of gram equivalent. So, there are various ways of expressing the concentration.

A. Percentage

When you see 98.3% on a bottle of H_2SO_4, it means the sulfuric acid has a mass percentage of 98.3%, with the remaining 1.7% typically consisting of water or other impurities. Percentage refers to the amount of a component in a total of 100 and can be expressed as either mass or volume percentage.

When amount of solution is in 100, it is called percentage. It may be expressed in terms of mass or volume percentage.

i. Percentage by mass (% w/w)

Commercial concentrated aqueous reagents such as acid and bases are often labeled in concentrations of weight percentage (abbreviated as % **w/w**) with the specific gravity also listed. If a bottle contains 40 grams of ethanol and 60 grams of water, then it contains 40% ethanol by mass.

The %w/w refers to the amount of solute (g) per 100g of solution. It is also called as percentage purity.

$$\text{Percent by mass} = \frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 100$$

ii. Percentage mass by volume (%w/v)

Normal saline solution (usually 0.9% w/v sodium chloride) is commonly used in to rehydrate patients who are dehydrated due to illness, surgery, or fluid loss. 0.9% w/v indicates 0.9 g of NaCl in 100mL of solution.

$$\%\text{w/v} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100$$

$$\%\text{w/v} = \text{w/w}\ \% \times \text{sp. gravity}$$

The %w/v refers to the mass of solute (g) dissolved per 100 mL of solution.

iii. Percentage by volume (%v/v)

A typical Beer contains about 5% ethanol by volume. This means every 100 mL contains 5 mL ethanol (ethyl alcohol).

$$\%\ \text{v/v} = \frac{\text{volume of solute (mL)}}{\text{volume of solution (mL)}} \times 100$$

The %v/v refers to the volume of solute present per 100 mL of solution.

Do you know?

Typically, in cold climate, a 35% (v/v) solution of ethylene glycol (well-known *antifreeze*) is used for preventing the water in a car's radiator from freezing during cold temperatures, ensuring the engine stays cool and doesn't overheat or crack due to ice formation.

Solved example

How would you prepare 250 mL of 70 % (v/v) ethanol [also called as rubbing alcohol] using pure ethanol?

Solution,

70 % v/v means 70 mL alcohol in 100 mL solution

$$\text{percentage by volume} = \frac{\text{volume of solute (mL)}}{\text{volume of solution (mL)}} \times 100$$

$$70 = \frac{\text{volume of alcohol (mL)}}{250} \times 100$$

$$\text{Volume of rubbing alcohol} = \frac{250 \times 70}{100} = 175\text{mL}$$

So, to make 250 mL of 70% (v/v) we would add 75 mL of water to 175 mL of pure ethanol.

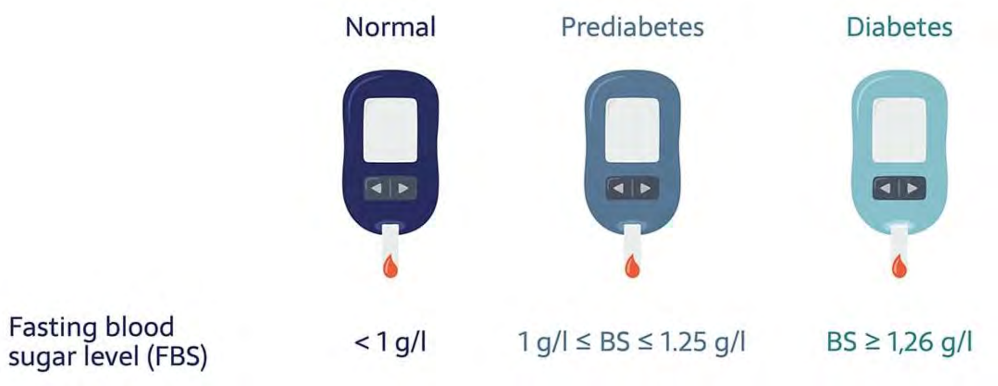
Test yourself

The %w/v and % v/v depend on temperature but not %w/w, why?

Gram per liter(g/L)

Do you know?

Easy to use glucose sensors are available in market to get preliminary information on sugar level of a patient. The sensors (see figure) normally give the glucose level in g per liter of blood.



The amount of solute in gram dissolved in one liter of solution is called gram per liter (g/L)

$$g/L = \frac{\text{amount of solute (g)}}{\text{volume of solution(mL)}} \times 1000$$

$$= \frac{\text{mass of solute(g)}}{\text{volume of solution(mL)}} \times 100 \times 10$$

$$= \%w/v \times 10$$

Gram per liter (g/L) is a unit of concentration that expresses the mass of a solute (g) present in one liter of solution.

B. Molarity (M)

It is one of the most commonly used unit in chemistry to quantify the concentration of a solution. It expresses the amount of solute in **mole** present in one liter of solution.

$$\text{Molarity (M)} = \frac{\text{number of mole of solute}}{\text{volume of solution(L)}}$$

$$= = \frac{\text{number of mole of solute}}{\text{volume of solution(mL)}} \times 1000$$

$$= \frac{\text{mass of solute(g)}}{\text{molecular mass of solute} \times \text{volume of solution(mL)}} \times 1000$$

$$= \frac{g/L}{\text{Molecular weight}}$$

When one mole of solute is dissolved in one liter of solution, it is called molar solution(M).

For example,

40 g of NaOH = 1 mole dissolved in 1 liter of solution =molar solution(M)

20 g of NaOH = 0.5 mole dissolved in 1 liter of solution = Semimolar solution(M/2)

0.4 g of NaOH = 0.1 mole dissolved in 1 liter of solution =Decimolar solution(M/10)

Molarity or molar solution is defined as the total number of moles of solute per liter or total number of moles of solute per cubic decimeter (dm^3) of solution.

Solved example

Calculate the molarity of solution containing 5 g of NaOH in 450 mL solution.

Solution,

Moles of NaOH = 5 / 40 = 0.125 mol

Volume of the solution in liters = 450 mL

$$\text{Molarity (M)} = \frac{\text{number of mole of solute}}{\text{volume of solution(mL)}} \times 1000$$

$$= \frac{0.125}{450} \times 1000$$

$$= 0.278 \text{ mol /L} = 0.278 \text{ M}$$

C. Molality (m)

Molality is ideal for experiments involving temperature changes because, unlike volume, mass does not change with temperature. This makes it a more reliable concentration unit when dealing with heating or cooling.

$$\text{Molality (m)} = \frac{\text{number of mole of solute}}{\text{mass of solvent (kg)}}$$

$$= \frac{\text{mass of solute} \times 1000}{\text{Molecular mass of solute} \times \text{mass of solvent (g)}}$$

If you dissolve 1 mole of sugar in 2 kg of water, the molality of the solution is:

$$\frac{1}{2} = 0.5\text{m}$$

Molality or molal solution is defined as the total number of moles of solute per kilogram of solvent.

D. Normality (N)

Normality is also known as the equivalent concentration of a solution or equivalent per liter. It is often used in titration calculations to find the concentration of an unknown solution. Amount of solute is expressed in number of gam equivalent instead of mole.

$$\text{Normality (N)} = \frac{\text{number of gam eqvt. of solute}}{\text{volume of solution(L)}}$$

$$= \frac{\text{number of gam eqvt. of solute}}{\text{volume of solution (mL)}} \times 1000$$

$$= \frac{\text{mass of solute (g)}}{\text{equivalent mass of solute} \times \text{volume of solution (mL)}} \times 1000$$

$$= \frac{\text{g/L}}{\text{equivalent mass}}$$

= w/v% ×10 ×equivalet mass

The number of gram equivalent weight of solute dissolved per liter of solution is called normality.

When one-gram equivalent weight of solute is dissolved in one liter of solution, it is called **normal solution**(N), whereas if 0.5-gram equivalent is dissolved it is called **semi normal solution(N/2).**

For example:

53 g of Na_2CO_3 (1 gram equivalent) in 1 liter of solution = **Normal solution(N)**

27.5 g of Na_2CO_3 (0.5 gram equivalent) in 1 liter of solution = **Seminormal solution(N/2)**

5.3 g of Na_2CO_3 (0.1 gram equivalent) in 1 liter of solution = **Decinormal solution(N/10)**

E. Mole fraction (χ)

Mole fraction (χ) is a way of expressing the concentration of a component in a mixture or solution. Unlike molarity or molality, the mole fraction is a dimensionless quantity, meaning it has no units.

mole fraction of solute ((χ_{solute}) $= \frac{\text{number of mole of solute}}{\text{total number of moles}}$

mole fraction of solvent ((χ_{solvent}) $= \frac{\text{number of mole of solvent}}{\text{total number of moles}}$

mole fraction of solute + mole fraction of solvent =1

let us consider a mixture of component A and B.

the mole fraction of A (χ_A) $= \frac{nA}{nA+nB}$

the mole fraction of B (χ_B) $= \frac{nB}{nA+nB}$

Mole fraction (χ) is the ratio of the number of moles of a particular component to the total number of moles of all components in the mixture.

Solved example

Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.
Solution:
Total mass of the solution = 100 g

Mass of benzene = 30 g.

∴ Mass of carbon tetrachloride = (100 - 30)g = 70 g

Molar mass of benzene (C_6H_6) = 78 g mol^{-1}

∴ Number of moles of C_6H_6 (nC_6H_6) = $\frac{30}{78}$ = 0.3846 mol

Molar mass of carbon tetrachloride (CCl_4) = 154 g mol^{-1}

∴ Number of moles of CCl_4($n\ CCl_4$) = $\frac{70}{154}$ = 0.4545 mol

Mole fraction of C_6H_6 = $\frac{n\ C6H6}{nCCl4 + n\ C6H6}$

$= \frac{0.3846}{0.3846 + 0.4545}$

= 0.45

F. Formality(F)

Formality is a measure of concentration that is similar to molarity. It is used to express the concentration of the ionic solids which do not exist as molecules but exist as network of ions.

It represents the total number of moles of solute (either whole molecules or dissociate into ions) per liter of solution. Formality is used when dealing with ionic compounds or substances that may dissociate in solution, and it helps describe the concentration before any dissociation occurs.

$$\text{Formality (F)} = \frac{\textbf{Total moles of solute (before dissociation)}}{\textbf{Volume of solution (L)}}$$

For example, if 1 mole of sodium chloride (NaCl) is dissolved in 1 liter of water, the formality of NaCl would be 1 F called **formal solution**.

Formality of a solution may be defined as the number of gram formula masses of the ionic solute dissolved per liter of the solution.

G. Parts per million (ppm) and parts per billion(ppb)

According to the EPA (environment protection agency), when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. It means when amount of lead reaches 15 **mg** in **1 liter of water**, it is harmful to human health.

Parts per million(ppm) **is** a unit of concentration commonly used to express very low concentrations of a substance in a solution or mixture.

For instance, concentration of pollutants in water or atmosphere is expressed in terms of micro gram per mL or ppm.

Mathematically,

$$\text{Parts per million (ppm)} = \frac{\text{mass of a solute}}{\text{mass of solution}} \times 10^6$$

It denotes the number of units of a substance present in one million units of the total mixture.

Parts per million can be defined as the ratio of number of parts of the component to the total number of parts of all components of the solution multiplied by 10^6.

Similarly, **parts per billion (ppb)** is used even for lower amount of solute i.e. the number of units of a substance present in one billion units of the total mixture.

Parts per billion (ppb)=$\frac{\text{mass of a solute}}{\text{mass of solution}} \times 10^9$

$$\text{ppb} = \text{ppm} \times 10^3$$

Do you know?

- Parts per million (ppm) is roughly equivalent to one drop of ink in a 40-gallon drum of water, or one second per 280 hours. Parts per billion (ppb) is roughly equivalent to one drop of ink in a canal lock full of water, or one second per 32 years.
- Air we breathe contains tiny dust particles. The particle having size at or below 2.5 micrometer are called as particulate matter 2.5 ($PM_{2.5}$). WHO guideline suggests, on 24 hours basis, air should not have more than 20 microgram of dust particles per liter (per m^3) of air we breathe (20 $\mu g/m^3$). However, due to increased air pollution, the particulate matter in urban air is higher than the WHO recommended concentration.

Test yourself

The w/v%, molarity and g/L depend upon temperature but molality and w/w% are independent to temperature, why?

Relation Between Normality and Molarity

Molarity is defined as the number of moles of solute per liter of solution. It is also known as **molar concentration**.
The formula of molarity is given as:
Molarity (M) = $\frac{\text{No.of moles of solute}}{\text{volume of the solution in litres}}$

Normality is defined as the number of **gam equivalent** of solute per liter of solution. It is also known as **normal concentration**.

Normality (N) =$\frac{\text{No.of gram eqivalent of solute}}{\text{volume of the solution in litres}}$

Nonetheless, they are related as follows:
Normality = [Molarity × Molar mass] / [Equivalent mass]

The ratio of Molar mass and equivalent mass can be written as valency factor (n)
Normality = molarity ×n
where the factor n = Acidity for base
=basicity for salt
=total number of positive charges per molecule for salt
=total change in oxidation number for oxidizing or reducing agent
To calculate the normality for acids we can make use of the following formula:

Normality = Molarity × Acidity
We can also convert molarity to normality by applying the following equation.
N = M × number of equivalents

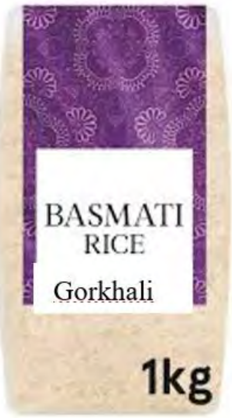
Test yourself

You are given 100mL of solution containing 4.0 g of caustic soda. Calculate the concentration of this solution in gram per liter, molarity, normality, ppm and ppb.

1.5 Primary and secondary standard substances

Activity

Primary and secondary standards are used in weighing. Using the primary or secondary standard we determine the determine the weight of unknown. Observe the following figure and identify primary standard, second standard, and the unknown.



primary standard	secondary standard	unknown

In order to prepare a solution, we need to dissolve solute in a certain volume of solution. If the solute used is readily soluble, highly pure and stable compound than is considered as a primary standard substance. These substances are used to prepare a solution of known concentration called primary standard solution. These solutions are used to **calibrate** or **standardize** solutions of unknown concentration.

The substances used as a primary standard should meet certain characteristics as mention:

a. **High Purity**: The substance must be pure enough so that the mass can be accurately measured without significant error. It must not contain any impurities that could affect the analysis.

b. **Stability**: The substance must remain stable under normal conditions and not degrade over time. It should not react with air or moisture.

c. **Non-Hygroscopic**: The substance should not absorb water from the atmosphere, as this could alter its mass and concentration.

d. **Solubility**: It should dissolve readily in a solvent (usually water) to allow for accurate and reproducible solution preparation.

Do you know?

Oxalis acetosella, common edible wild plant contains oxalic caid ($H_2C_2O_4$) which is used as primary standard substance.

Figure : Oxalis acetosella

Do yourself

Some other primary standard substances are given in the table. Complete the table .

Substance	Molecular formula	Molecular weight	Equivalent weight
Sodium carbonate			
Sodium oxalate			
Sulphamic acid	$NH_2\ SO_3H$		
Sodium tetraborate	$Na_2[B_4O_5(OH)_4]\cdot 8H_2O$		
Sodium dichroamte			
Potasium bromate			
Potasium hydrgoen iodate			
Ferrous ammonium sulphate (Mohr's salt)	$(NH_4)_2Fe(SO_4)_2(H_2O)_6$		

You might have used caustic soda (NaOH) pellets in laboratory. If you take few pellets of NaOH with spatula on a petri dish and leave it open for an hour you will find the pellets converted to semi-viscous form due to absorption of moisture i.e. caustic soda shows deliquescent property. In other words, NaOH is not stable. Not only that, if you touch NaOH pellets it will give burning sensation to skin. So, we have to handle it with care!

There are some chemical substances which are not found in pure form. They can have hygroscopic, deliquescence, and efflorescent properties. In other words, their composition can change over time limiting their application for longer use both in solid and in solution form. These substances are called **secondary standard substances**. Examples: NaOH, HCl, H_2SO_4, $KMnO_4$, $Na_2S_2O_3$

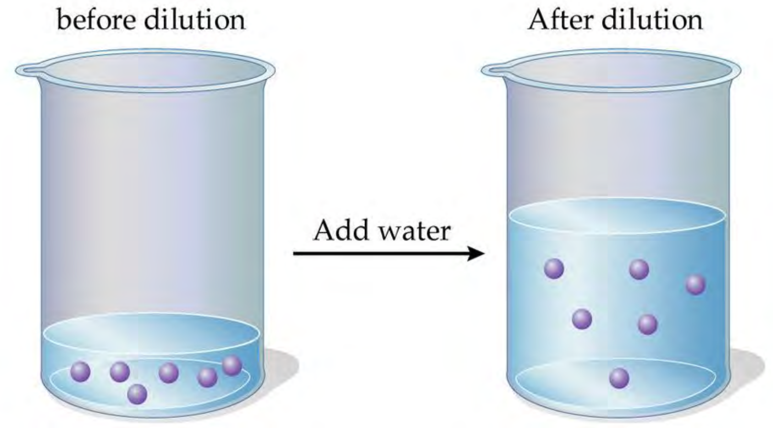
The solution prepared by dissolving known weight of primary standard solute in known volume of solution is called as primary standard solution. Similarly, the solution prepared by using secondary standard substance is called secondary standard solution. The exact concentration of secondary standard solution is determined by the help of primary standard solution.

1.6 Law of equivalence and normality equation

Activity

Observe the figure below and notice the following changes before and after dilution.

a. Mass of solute present
b. Mole of solute present
c. Number of gram equivalent
d. Concentration



One gram equivalent of one chemical substance reacts exactly with one gram equivalent of another substance. It means for a complete chemical reaction, number of gram equivalent of reacting substances is always equal. This is particularly useful in titrations, where the gram equivalents of a titrant (the solution in burette) react with gram equivalents of an analyte (solution in conical flask).

Let us consider a chemical equation,

$$aA + bB \rightarrow cC + dD$$

After the complete chemical reaction,

number of gram equivalent of A = number of gram equivalent of B= number of gram equivalent of C = number of gram equivalent of D

number of gram equivalent of any substances $= \frac{given\ mass\ of\ substance(g)}{equivalent\ mass}$

$$= \frac{normality \times volume\ (mL)}{1000}$$

therefore, $\mathbf{N_1V_1=N_2V_2}$

This equation is called **normality equation**. This equation also can be written as

$\mathbf{M_1n_1V_1 = M_2n_2 V_2}$

Where M= molarity of the solution, and n= valence factor

The *Law of Equivalence* states that in a chemical reaction, the number of gram equivalents of reactants is equal to the number of gram equivalents of products.

Theory of dilution

When water is added to a solution of definite concentration, the solution becomes comparatively of less concentration called dilute solution and the process is dilution. During dilution volume of solution increases, concentration decreases but the number of mole or number of gram equivalent of solute remains constant

Number of moles before the dilution = Number of moles after dilution

or $M_1V_1=M_2V_2$ [Molarity =number of mole/volume in liter]

where M_1=molarity of solution before dilution

V_1= volume of solution before dilution

M_2= molarity of solution after dilution

V_2 =volume of solution after dilution

Number of gram equivalent before the dilution = Number of equivalents after the dilution

or, $N_1V_1= N_2V_2$ [Molarity = number of gram equivalent/volume in liter]

Solved example

Calculate the molarity of half liter solution obtained by diluting 30 mL of 0.5 M H_2SO_4

Solution:

Number of moles before the dilution = Number of moles after dilution

or $M_1V_1=M_2V_2$

$0.5 \times 30/1000 = M_2 \times ½$

Therefore, molarity (M_2)= 0.03 M

Test yourself

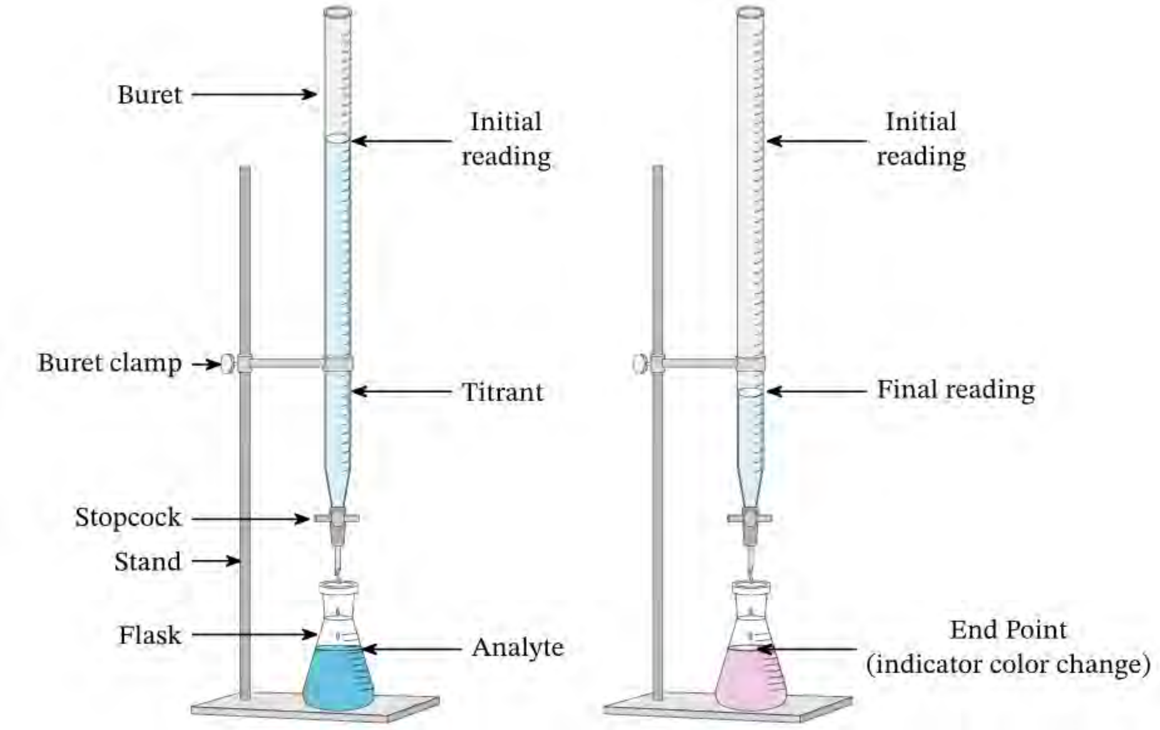
What is the amount of water required to be added in 1 liter of molar solution to make it centimolar?

1.7 Titration and its types: Acid-base titration, redox titration

Activity

Carefully, observe the following experimental set up.

a. Notice the change in burette reading and also the color in the conical flasks.
b. What could be the reason for color change?



A solution of known concentration of reactant is called standard solution, which is usually kept in a burette, is called as **titrant.** In a titration, a measured volume of titrant is added to a sample solution of known volume called **titrand or analyte.** The titration is complete when sufficient titrant is added to react with all the analyte.

An acid-base **indicator,** a substance that has distinctly different colors in acidic and basic media, is usually added to the reaction flask to signal about the completion of reaction practically. The point at which there is a sharp change in color of solution indicating the complete consumption of analyte is called **end point**.

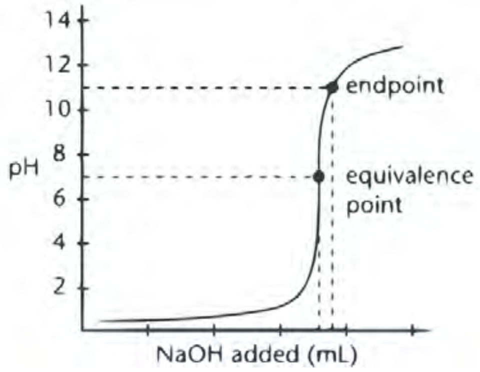
Titrations are widely used in various industries, including pharmaceuticals, environmental science, food, and beverages, as well as in academic research, to analyze the composition of chemicals.

Titration is a quantitative analytical technique in which concentration of unknown solution is determined by comparing it with a standard solution.

1.7.1 Endpoint and equivalence point

Activity 1

Observe the following graph and fill the table given .Which one do you think come first and why?



pH of end point	pH of equivalence point

While adding the titrant from the burette to the analyte in the titration flask, at one point the amount of titrant added is exactly enough to completely react with the analyte in the solution. This point is **stoichiometric point or equivalence point**. At this point, the number of gram equivalent of the titrant equals the number of gram equivalent of the substance being titrated (i.e. titrand) according to the stoichiometry of the reaction.

The point at which an indicator changes color is called as **end point**. Indeed, end point is practically measurable. In acid-base titration, the end point and equivalent points do not coincide.

The difference between end point and equivalence point is called the titration error.

The error in titration can occur due to:

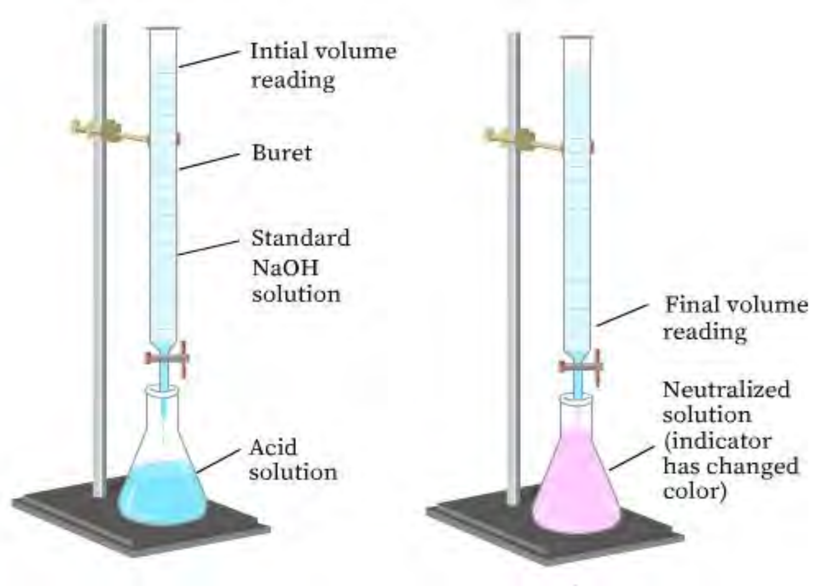
a. Due to defects in the experimental setup or method.
b. Variation in experimental parameters such as temperature, atmospheric pressure etc.
c. Failure in reading the meniscus level on the burette accurately.
d. Error in dilution or weighting.

The above errors can be minimized by using calibrated equipment, use of suitable indicator or by performing multiple titrations.
or solution occurs

A. Acid-Base Titration

Activity

Observe the figure given and fill the table below.



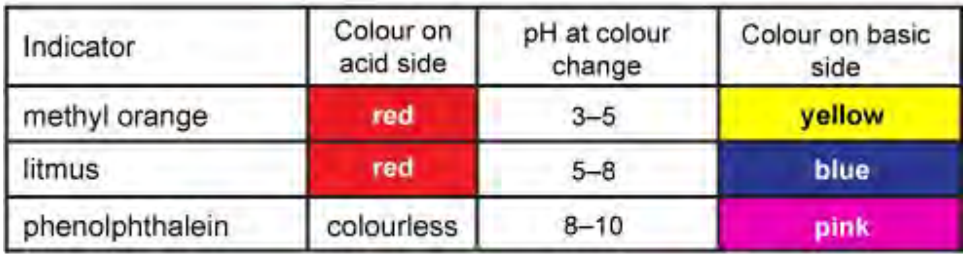
Analyte	Titrant	Colour before titration	Colour after titration

This titration aims to determine the concentration of either acid or base. When concentration of an acid is determined using a standard solution of a base then the process is called **alkalimetry**. In the same way, when strength of a base is determined with the help of a standard solution of an acid then the titration is known as **acidimetry**. The end point of this titration is monitored with the help of a pH indicator or acid – base indicator.

Acid-base reactions typically involve the exchange of protons (H^+) between the acid (HA) and base (BOH) to from salt (BA) and water.

$HA + BOH \rightarrow BA + H_2O$
In ionic from:
$H^+ + A^- + B^+ + OH^- \rightarrow B^+ + A^- + H_2O$
Or, $H^+ + OH^- \rightarrow H_2O$
The titration between acid and base is called acid- base titration or neutralization titration.

The acid-base indicators show different color in acidic and basic solution. The most commonly used indicators are phenolphthalein, methyl red, and methyl orange. The intensity of the color depends upon the pH of the solution.



Indicator	Colour on acid side	pH at colour change	Colour on basic side
methyl orange	red	3–5	yellow
litmus	red	5–8	blue
phenolphthalein	colourless	8–10	pink

We will learn the concept needed for the selection of indicator in unit 2 (ionic equilibrium).

B. Redox titration

Redox titration involves a redox reaction. Normally, redox titration requires an indicator that shows different color in reduced and oxidized forms; also called as **redox indicator**. At or near the equivalence point, a sharp change in the indicator's color will occur .

oxidizing agent+ reducing agent → reduced species + oxidized species

Test yourself

Find the oxidized and reduced species in the following redox reactions

a. $MnO_4^-+8H^++5Fe^{2+}\rightarrow Mn^{2+}+5Fe^{3+}+4H_2O$

b. $I_2+2S_2O_3^{2-}\rightarrow 2I^-+S_4O_6^{2-}$

c. $I_2+C_6H_8O_6$ (ascorbic acid) $\rightarrow 2I^-+C_6H_6O_6$(dehydroascorbic acid) + $2H^+$

When titration is done between oxidizing and reducing agent then the titration is called redox titration

Depending up on the reagent used, redox titration may be classified into following types

i. Permanganate titration or Permanganometry

Fig: Redox titration between potassium permanganate and oxalic acid solution

Since potassium permanganate is a strong oxidizing agent, it is widely used in redox titrations to determine the concentration of reducing agents like iron (II) salts, oxalates, hydrogen peroxide, and others in environmental, industrial, and biological samples.

$KMnO_4$ itself changes its color from distinct pink to colorless while reacting with any reducing agent, i.e. no external indicator is required. It means $KMnO_4$ is called **self-indicator or auto indicator**.

$$2KMnO_4 \text{ (pink)} + 16\ HCl + H_2C_2O_4 \rightarrow 2KCl + 2\ MnCl_2 \text{ (colorless)} + 5Cl_2 + 8H_2O + CO_2$$

In ionic form:

$$MnO_4^- + 8H^+ + C_2O_4^{--} \rightarrow Mn^{++} + 4H_2O + CO_2$$

Likewise, the redox reaction between potassium permanganate and a ferrous salt is represented as:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Permanganometric titration is a type of redox titration in which potassium permanganate ($KMnO_4$) is used as the titrant

ii. Dichromatometry

Potassium dichromate ($K_2Cr_2O_7$) is also a widely used oxidizing agent. It is a strong and stable oxidizing agent and can be obtained in a high state of purity, so is used as a primary standard substance.

The color change when chromium changes its oxidation state from +6 to + 3 is from orange to light green as shown by the equation.

$$Cr_2O_7^{2-} \textbf{ (orange)} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} \textbf{ (light green)} + 7H_2O$$

Since the color transition from orange to light green is difficult to follow for a normal human eye, it is difficult to find the end point without the use of additional indicator.

Dichromatometry is a type of redox titration in which potassium dichromate ($K_2Cr_2O_7$) as the oxidizing agent

Do you know?

Potassium iodate (KIO_3) is added in *Ayo noon* as iodine supplement. Nepal government mandates *Ayo noon* packet to have 50 ppm of iodine at the time of packaging. To determine iodine in the packet, KIO_3 present in the salt sample is to be titrated with sodium thiosulphate in acidic medium in presence of KI and starch as indicator. The titration is called as *iodometric titration*. The process involves two step reaction:

KIO_3 (from Ayo noon salt) $+KI+H_2SO_4 \rightarrow K_2SO_4+H_2O+I_2$

$I_2+Na_2S_2O_3 \rightarrow 2KI+Na_2S_4O_6$

Can you find oxidizing and reducing agents in the second reaction?

Project work

Find the concentration of acetic acid in different sample of vinegar

- Take standard NaOH (0.1N) solution and fill in the burette as a titrant.
- Take 25 mL of different brands of vinegar each in the conical flask and perform acid base titration using 2-3 drops phenolphthalein indicator.
- Record the volume of NaOH consumed and the concentration of acetic acid in each sample of vinegar in the table below.

Sample of vinegar	Volume of NaOH consumed /mL	Concentration of acetic acid in the sample $= \frac{0.1\ x\ volume\ of\ NaOH(mL)}{volume\ of\ vinegar(25mL)}$
A (25mL)		
B (25mL)		
C (25mL)		

Exercise

A. Multiple choice questions

1. Which of the following principle is used in gravimetric analysis?

a) Mass measurement

b) Volume measurement

c) Color change

d) Heat transfer

2. Ferrosoferric Oxide (commonly known as magnetite) is an iron oxide with the chemical formula $\mathbf{Fe_3O_4}$. What is the equivalent weight of iron in the oxide?

a) 56 b) 28 c) 18.6 d) 7

3. **Potassium Dichromate** ($K_2Cr_2O_7$) is an orange-red crystalline compound and a powerful oxidizing agent. What is the equivalent weight of this oxidizing agent having molecular weight M in the following ionic equation?

$$Cr_2O_7^{2-}aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

a) M b) M/2 c) M/3 d) M/6

4. If 1 ppm means one part per million, then what is the meaning of 1 ppb?

a) One part per ten billion

b) One part per billion

c) One part per thousand

d) One part per trillion

5. Which of the following is a primary standard substance used to prepare a standard solution in volumetric analysis?

a) Hydrochloric acid (HCl)

b) Sodium hydroxide (NaOH)

c) Oxalic acid ($C_2H_2O_4$)

d) Potassium permanganate ($KMnO_4$)

6. Which one of the following is NOT a characteristic of a good primary standard substances?

a) High stability

b) Low reactivity

c) High solubility in water

d) High hygroscopicity

7. The **Law of Equivalence** is a fundamental principle in chemistry, particularly in stoichiometry and titration. The law of equivalence states that at the endpoint of a titration:

a) The volume of acid equals the volume of base
b) The number of equivalents of acid equals the number of equivalents of base
c) The normality of acid equals the normality of base
d) The molarity of acid equals the molarity of base

8. If 25 mL of a Deci molar H_2SO_4 solution reacts completely with 50 mL of a NaOH solution, what is the Molarity of the NaOH solution?

a) 0.05 M

b) 0.1 M

c) 0.2 M

d) 0.25 M

9. In a redox titration involving potassium permanganate ($KMnO_4$) and oxalic acid ($C_2H_2O_4$), which of the following statement is true regarding KMnO4?

a) An oxidizing agent because it gains electrons

b) A reducing agent because it gains electrons

c) An oxidizing agent because it loses electrons

d) A reducing agent because it loses electrons

10. If 0.5 g of Na_2CO_3 is dissolved in 100 mL of solution, what is the molarity of the solution thus prepared? (Molecular weight of Na_2CO_3 = 106 g/mol)

a) 0.047 M

b) 0.094 M

c) 0.188 M

d) 0.235 M

11. You are asked to prepare a 0.25 M solution of NaOH using 20 g of it. What volume of solution can be made using this amount?

a) 0.5 L

b) 1.0 L

c) 2.0 L

d) 4.0 L

12. A 25 mL semi molar solution of HCl is titrated with 0.5 N Na_2CO_3 solution. What volume of titrant should be added from the burette for one fourth neutralization of the analyte in the conical flask?

a) 50mL
b) 25mL
c) 12.5mL
d) 6.25mL

13. You are given a solution of 0.2 M sulfuric acid (H_2SO_4). How many grams of H_2SO_4 are present in 500 mL of this solution?

a) 9.8 g

b) 19.6 g

c) 4.9 g

d) 2.45 g

14. A solution contains 20 g of NaOH in 500 mL of water. If the solution is 2 times diluted what is true in the diluted solution in compare to original solution?

a) Concentration of solution remain same
b) Mole of NaOH remain same
c) Volume of solution remain same
d) Corrosiveness of the solution remain same

15. A 0.7 g sample of an unknown monoprotic acid requires 35 mL of 0.1 M NaOH for complete neutralization. What is the equivalent weight of the acid?

a) 20
b) 40
c) 200
d) 400

16. You are tasked with preparing a solution of HCl. If you have 36.5 g of HCl and need to prepare 1 liter of a 0.5 N solution, what volume of water should be added to the HCl?

a) 1 L
b) 500 mL
c) 2 L
d) 250 mL

B. Short answer questions

17. Define and the differentiate the terms

a. Molarity and normality
b. Ppm and ppb
c. Molality and molality

- **d.** No of gram mole and no. of gram equivalent
- **e.** Primary and secondary standard substance
- **f.** Acid base and redox titration

18. Volumetric and gravimetric analysis are the types of quantitative analysis, both useful in chemical and industrial world.

- **a.** define volumetric analysis. How is it different from gravimetric analysis?
- **b.** What is the application of volumetric analysis in chemistry?
- **c.** Write any one limitation of volumetric analysis.

19. In gravimetric analysis, a sample of impure barium chloride weighing 0.500 g is dissolved in water and treated with excess sulfuric acid to precipitate barium sulfate. After filtration and drying, the precipitate weighs 0.434 g.

- **a.** Write the balanced chemical equation for the reaction.
- **b.** Calculate the percentage of barium chloride in the original sample.
- **c.** Explain why excess sulfuric acid is used.

20. Match the given list of secondary standard substances with their property so that it cannot be used as a primary standard substance.

HCl	it absorbs CO_2 and moisture from air
I_2	it is reduced by sunlight
H_2SO_4	it is a gas
NaOH	it absorbs moisture from air
$KMnO_4$	it sublimes

21.

- **a.** Define equivalent weight. write the relationship between equivalent weight, atomic weight and valency.
- **b.** Calculate the equivalent weight of underlined species given

$$\underline{\mathbf{H_3PO_4}} + KOH \rightarrow K_3PO_4 + H_2O$$

$$\underline{\mathbf{FeSO_4}}+7H_2SO_4+\underline{\mathbf{K_2Cr_2O_7}} \rightarrow 3Fe_2(SO_4)_3+K_2SO_4+Cr_2(SO_4)_3+7H_2O$$

22. Nitric Acid is a highly important inorganic acid known for its strong oxidizing properties and wide range of applications. Bottle of nitric acid is labeled with 68%(w/w) and specific gravity 1.4g/mL

- **a.** What do you mean by 68%(w/w)?
- **b.** Convert the given concentration in to w/v.
- **c.** Calculate the mass of HNO_3 dissolve in 1 liter of solution.
- **d.** Which of the concentration unit w/v or w/w depend upon temperature and why?

23. The Law of Equivalence is a fundamental concept in chemistry, particularly in stoichiometry and titration.

- **a.** State "law of equivalence". How is this law useful in titration?
- **b.** Use this law to calculate the mass of magnesium metal that is enough to react completely with 250mL of decinormal sulphuric acid.

24. Mohr's salt $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ is a double salt. It is widely used in analytical chemistry to prepare primary standard solution.

- **a.** What do you mean by standard solution? why such solution is important in volumetric analysis?
- **b.** Write any three chrematistics of Mohr's salt so that it is used as a primary standard substance.
- **c.** Why is this salt called double salt?

25. The normal range for glucose concentration in blood (fasting) is around 70–100 microgram per deciliter (mg/dL). If a person's blood found to contain 80 mg/dL. Convert this glucose amount into
- **a.** %w/v
- **b.** g/L
- **c.** ppm and ppb
- **d.** Molarity

26. A student is asked to prepare 500 mL of a 0.100 M solution of HCl. However, the only available HCl solution is 12.0 M.
- **a.** Calculate the number of mole present in 500 mL of a 0.100 M solution of HCl .
- **b.** How much volume of HCl solution should the student use to prepare the desired solution?
- **c.** What precaution should be followed during this work and why?

27. A 0.500 g sample of a mixture containing NaCl and NaBr is dissolved in water and titrated with 0.100 M $AgNO_3$.
- **a.** Name the type of titration. Why is it called so?
- **b.** If 25.00 mL of $AgNO_3$ is required to reach the endpoint, what is the percentage of NaCl in the mixture?

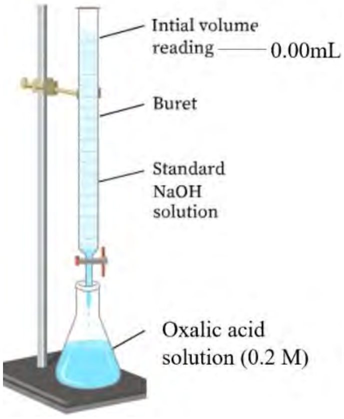
28. In a redox reaction, potassium permanganate ($KMnO_4$) is used to oxidize oxalic acid ($H_2C_2O_4$) in acidic medium.
- **a.** Write the balanced redox equation for the reaction between $KMnO_4$ and $H_2C_2O_4$.
- **b.** If 25 mL of 0.1 M $KMnO_4$ is required to completely oxidize 50 mL of oxalic acid solution, calculate the molarity of the oxalic acid solution.

C. Long answer questions

29. An industrial chemist needs to prepare 100 liters of a 0.5 N H_2SO_4 solution for a manufacturing process using a bottle of labelling 98% (w/w) and Density 1.84 g/mL.
- **a.** what do you mean by 0.5 N concentration of acid?
- **b.** Calculate the volume of concentrated sulfuric acid (H_2SO_4) required to prepare 100 liters of 0.5N?
- **c.** Discuss any safety concerns and precautions that must be taken when preparing and handling such concentrated acid solutions in large quantities

30. In biological research, a 2% (w/v) NaCl solution can be used as an isotonic solution to maintain osmotic balance for cells or tissues.
- **a.** What do you mean by 2% (w/v)?
- **b.** Calculate the molarity and normality of this solution if its density is 1.02 g/mL.
- **c.** why different units are needed for concentration measurement?

31. The given figure shows the titration between Deci molar caustic soda and Oxalic acid solution in acidic medium.



- **a.** Identify the type of titration, analyte and titrant in the figure.
- **b.** Write the chemical reaction involved.
- **c.** Calculate the volume of NaOH added from the burette for the complete reaction with 25 mL of Oxalic acid.
- **d.** What is the concentration of mixer in the conical flask when the oxalic acid is half neutralized?

32. 100 mL of 0.1 M HCl is mixed with 200mL of 0.2 M H_2SO_4 in a single container to make a mixture of acid

- **a.** What do you mean by 0.1MHCl?
- **b.** Find the volume of sulphuric acid required to prepare 200mL of 0.2 M from the bottle containing 98% (w/v) H_2SO_4 and has density of 1.8 g/L.
- **c.** Calculate the normality of acid mixture in the container.
- **d.** What happens to the concentration of the acid mixture when 700mL water is added ? Calculate the concentration of diluted solution.

33. A solution of $KMnO_4$ is standardized by titrating it against a known amount of oxalic acid in the presence of mineral acid in warm condition. The balanced equation for the reaction is:

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

- **a.** Why is it necessary to standardize a solution before using it in a titration?
- **b.** What is the end point color change in this titration keeping KMnO4 in the burette as titrant?
- **c.** Why is it necessary to warm the conical flask before the titration?
- **d.** If 25.00 mL of $KMnO_4$ solution is required to titrate 0.250 g of oxalic acid, what is the molarity of the $KMnO_4$ solution?

34. Potassium permanganate ($KMnO_4$) is used in a titration to determine the concentration of an iron (II) sulfate ($FeSO_4$) solution. In acidic conditions, $KMnO_4$ reacts with Fe^{2+} ions according to the equation:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

- **a.** What is the number of moles of $KMnO_4$ required to react with 1 mole of iron sulphate?
- **b.** Calculate the equivalent weight of $KMnO_4$ and $FeSO_4$ in the given equation (atomic mass of Mn=55, Fe=56).
- **c.** What is the indicator in the given titration and why?
- **d.** If 25.0 mL sample of iron (II) sulfate requires 20.0 mL of 0.02 M $KMnO_4$ for complete reaction. Calculate the concentration of the iron (II) sulfate solution.

35. Solve the given numerical problems

- **a.** A bottle of a tile cleanser contains 135 g of HCl and 775 g of water. What is the percent by mass of HCl in this cleanser?
- **b.** How many grams of $FeSO_4$ are present in a solution marked 0.35 M $FeSO_4$?

c. Calculate the concentration in grams per liter of bench hydrochloric acid whose concentration is 12 mol/L

d. Concentrated" hydrochloric acid is an aqueous solution of 37.2% HCl that is commonly used as a laboratory reagent. The density of this solution is 1.19 g/mL. What mass of HCl is contained in 0.500 L of this solution?

e. What volume of 0.01 M $KMnO_4$ solution will contain 5 g of $KMnO_4$

f. 1 g of caustic soda is added to 2 liter of X M sulphuric acid so that pH of the resulting solution is 7. Find the value of X

g. What volume of 12M and 2 M NaOH solution should be mixed to prepare 2 liter of 9 M solution?

h. Calculate the volume of 1M NaOH required to neutralize 200ml of 2N HCl. What mass of NaCl is produced from the neutralization reaction?

i. Two liters of molar H_2SO_4 is mixed with one liter of normal NaOH solution. Calculate the strength of the mixture and mass of salt produced from the reaction

j. 50 ml 2N H_2SO_4 is mixed with 30 ml 3N NaOH. Predict the solution is either acidic or basic or neutral. Also calculate the resulting strength of solution.

k. A 1.20 g of sample of lye (sodium hydroxide is sold commercially as solid lye) required 45.0 mL of 0.5M hydrochloric acid to neutralize .Calculate the percentage purity of NaOH in the sample.

l. 5.125 g of washing soda crystals are dissolved and made up to 250 mL.25.0 mL of this solution requires 35.8 mL of 0.05 M sulphuric acid for complete neutralization. Calculate the percentage of sodium carbonate in the washing soda crystals.

m. A blood alcohol level above 500mg per 100 mL, a person may die. What is the molar concentration of alcohol(ethanol) at the lethal level?

n. 8.492 g of salts having the formula $(NH_4)_2SO_4.nH_2O$ were dissolved and made up to 250 mL using dilute acid and water. A 25.0mL of this solution was titrated against potassium permanganate solution of concentration 0.015M, 22.5 mL was consumed at the end point. Calculate the value of n.

o. A commercial bleach solution contains 3.62 mass NaOCl in water. Calculate (a) the mole fraction and

(b) the molality of NaOCl in the solution

Unit 2

Ionic Equilibrium

Introduction to Acids and Bases

The word “acid” comes from the Latin word **“acere,”** which means sour. We have been using different types of acids and bases in our daily life . For example, curd contains lactic acid, and lemon contains citric acid. These acids are called as organic acids. They are weak and less corrosive as compared to mineral acids.

Probably the first acid to be produced in large quantities was acetic acid. Vinegar is a diluted aqueous solution of acetic acid. Some of the common examples of organic acids and their sources are given int the table below.

Acids	Source	Formula
Lactic acid	Milk	$C_2H_4OHCOOH$
Acetic acid	Vinegar	CH_3COOH
Citric acid	Lemon, orange	$HOC(CH_2COOH)_2$
Formic acid	Ant venom	$HCOOH$
Malic acid	Apple	$HOOCCHCH_2COOH$
Tartaric acid	Grapes	$HOOCCH(OH)CH(OH)COOH$

In the chemistry laboratory, you must have noticed bottle of HCl, H_2SO_4 and HNO_3. These acids are mineral or inorganic acids which do not contain carbon atoms. These acids are strong acids and highly corrosive in nature. These acids have wide range of applications as tabulated below.

Acids	Formula	Uses
Hydrochloric Acid	**HCl**	cleaning sinks and sanitary ware. purification of common salt.
Sulphuric Acid	**H_2SO_4**	car batteries manufacture of paints, drugs, dyes, and artificial silk
Nitric Acid	**HNO_3**	in the manufacture of explosives such as TNT (trinitrotoluene) for the production of fertilizers such as ammonium nitrate

Mineral acids are derived from minerals or non-living sources. Acids that contain carbon and are often derived from living organisms called organic acids

Do you know?

In 2022, the global production of sulfuric acid was approximately 265 million metric tons. Projections indicate that this figure will rise to around 321.4 million metric tons by 2030, driven by increasing demand in agriculture and industrial applications.

Activity

Observe the table given and fill the table

Base	Common name	Common use
NaOH	Caustic soda	Drain cleaner, making soap
$Mg (OH)_2$	Milk of magnesia	Antacid
$Ca (OH)_2$	Slaked lime	-----------
NaHCO3	--------------	Baking, cleaning
KOH	----------------	Soap, fertilizer

We use different types of bases in our daily life. For examples, caustic soda (NaOH) is used as a drain cleaner, milk of magnesia $Mg (OH)_2$ is used as antacid. These bases are widely used in industrial and engineering applications.

Figure: Antacid commonly used against acidity contains $Mg(OH)_2$ and drain cleaner contains NaOH

A base is a substance that gives hydroxide ions (OH^-) in an aqueous solution.
For example: $NaOH \rightarrow Na^+ + OH^-$

The simple concept of Acid and base was provided by Svante Arrhenius in 1884. According to this concept, base are the substances that give hydroxide ions (OH^-) in aqueous solution and acids are the substances that give hydrogen ions (H^+) in aqueous solution.

2.1. Limitation of Arrhenius concepts of acids and bases

Activity

Identify the acid and base in the following reactions. Also, find basic difference in the reactions.

a) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
b) $NH_3(g) + HCl(aq) \rightarrow NH_4Cl(s)$

The Arrhenius concept of acid and base has following limitations.

1. **Restricted to Aqueous Solution**
   The concept only applies to substances dissolved in water, but there are numbers of acid-base reactions in non-aqueous solvents or gaseous phases.
2. **Limited to explain the formation of hydronium ion rather than free H^+**
   It assumes all acids release free H^+ ions, while in reality, H^+ ions often exist as hydronium ions (H_3O^+) in solution.
3. **Limited to H^+ and OH^- Ions**

   It does not explain the acidic and basic nature of acids and base without H^+ and OH^- ions respectively. For example, ammonia is a base but does not contain OH^- and CO_2 has acidic nature but does not contain H^+.

4. **Does Not explain Amphoteric nature of Substances**
   Certain substances have amphoteric nature, i.e., show both acidic and basic properties. Arrhenius concept fails to explain it.

2.2 Bronsted –Lowry definition of acids and bases

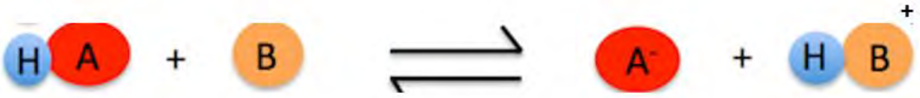
Johannes Nicolaus Brønsted (1879–1947) was a Danish physical chemist best known for his pioneering work in acid-base chemistry. He made significant advancements in the study of catalysis and chemical kinetics.

Thomas Martin Lowry (1874–1936) was a British physical chemist renowned for his contributions to acid-base chemistry. He worked also worked extensively on the optically active compounds under polarized light.

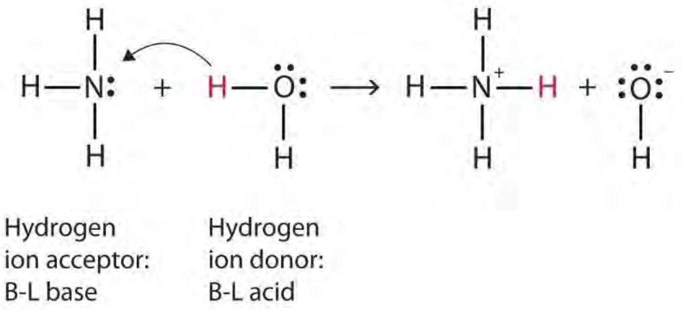
Activity

Observe general equation provided below.

a. Identify the species that gives proton (H^+) and the species that accept it.
b. Which of the reactant do you think acts as acid and why?



The **Bronsted–Lowry definition** of acids and bases was proposed by Johannes Nicolaus Bronsted and Thomas Martin Lowry in 1923. It is one of the most widely accepted concepts for explaining acid-base behavior. This definition focuses on the transfer of protons (H^+ ions) between molecules or ions.



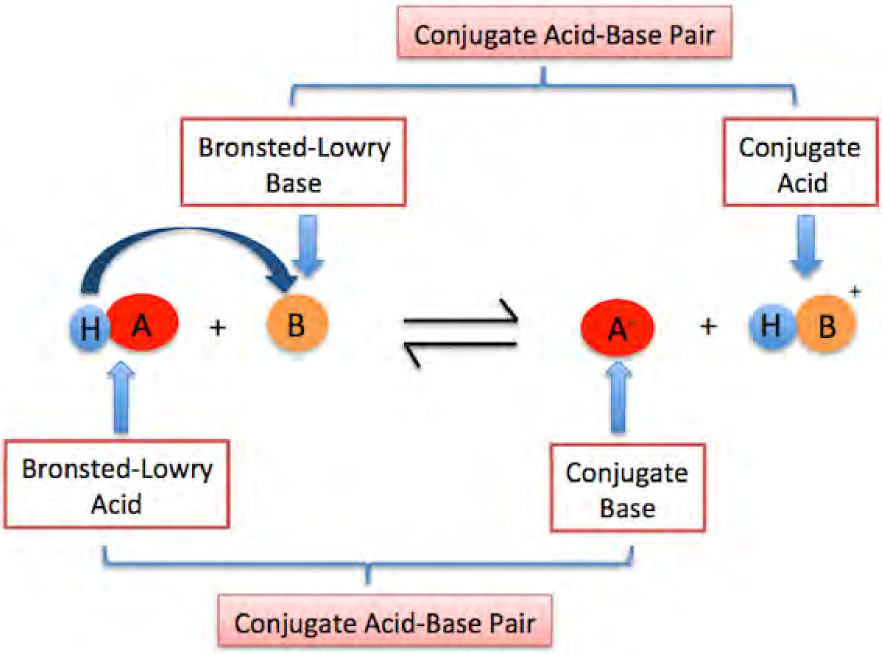
In the above reaction, water molecule donates proton and is a Bronsted-Lowry acid (B-L acid) whereas ammonia accepts the proton and is Bronsted-Lowry base (B-L base).

All Arrhenius acids are also Bronsted acid because they can donate protons. Acids with only one proton are called monoprotic acids. Likewise, acids with two protons are diprotic acids and acids with more than two protons are called polyprotic acids. For examples, HF and HCl are monoprotic acid, H_2SO_4 is a diprotic acid and H_3PO_4 is a polyprotic acid.

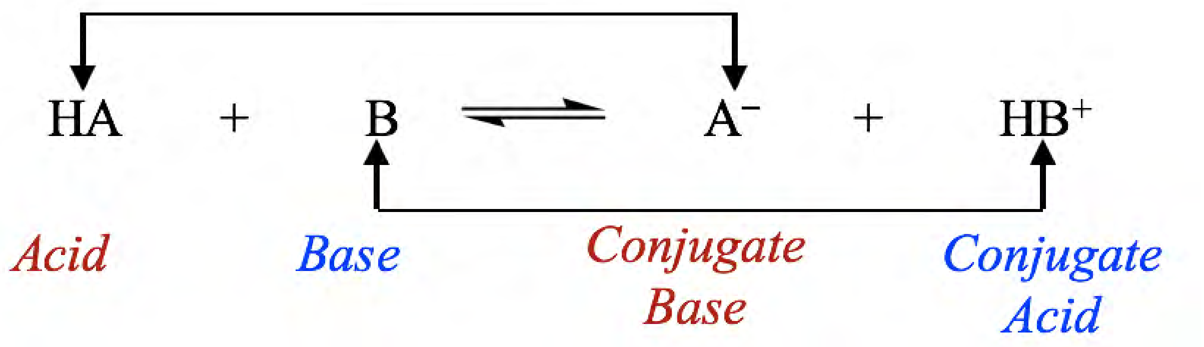
A Bronsted–Lowry acid is any species that can donate a proton (H^+) to another species.

A Bronsted–Lowry base is any species that can accept a proton from another species.

2.4 Conjugate acid –base pairs



The concept of conjugate acid–base pairs is a key element of the Brønsted–Lowry acid-base theory, which explains how acids and bases are interrelated through the transfer of protons (H^+ ions).



In the example provided, a Brønsted acid (HA) donates a proton to a base (B), transforming itself into its conjugate base (A^-). Similarly, the base (B) accepts the proton and becomes its conjugate acid (HB^+). A conjugate base is formed when an acid loses a proton, causing its positive charge to decrease by one. Conversely, a conjugate acid is formed when a base gain a proton, resulting in an increase of its positive charge by one. The original acid with its conjugate base and the original base with its conjugate acid is called **conjugate pair.**

The conjugate base of a Brønsted acid is the species that remains when one proton is removed from the acid. Conversely, a conjugate acid results from the addition of a proton to a Brønsted base.

Try yourself

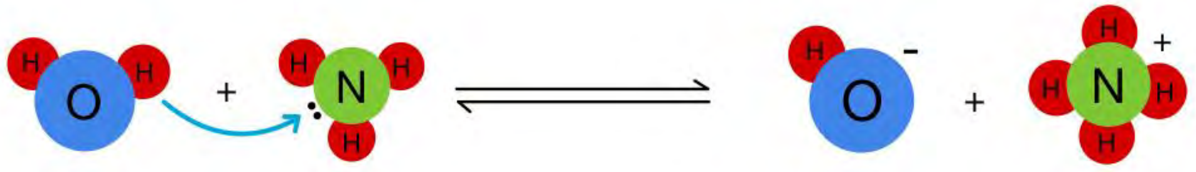
Complete the table below

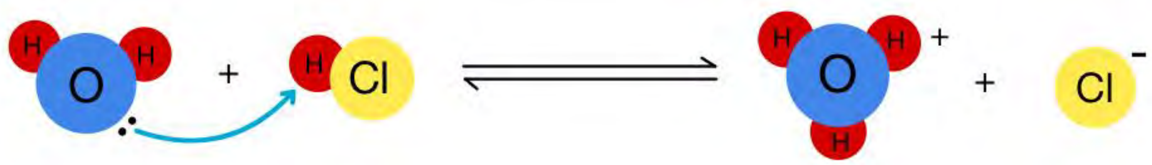
Bronsted acid	**Conjugate base**	**Bronsted base**	**Conjugate acid**
HCl	---------	NH_3	---------
CH_3COOH	CH_3COO^-	---------	H_2SO_4
	OH^-	H_2O	---------
H_2CO_3	---------	SO_4^{--}	HSO_4^-
NH_4^+	---------	HPO_4^{--}	---------
	$H_2PO_4^-$	HCO_3^-	---------

Amphoteric species

Activity

Using the Bronsted -Lowry concept of acid and base, discuss the differences found in the nature of water molecule in the reactions given below.





It is not always true that same substance always donates or accepts protons, it depends upon the nature of another species involved. Some substances can act as both acids and bases, depending on the reaction. These are called **amphiprotic species** (Greek work ***amphoteroi***, meaning "both) and the ability of a substance to act as both an acid and a base, depending on the chemical environment is termed as **amphoterism.** Since these substances have the ability to donate as well as the protons they are also called as **amphiprotic** species. Let us see following examples.

Example 1

$$Al(OH)_3+3HCl \rightarrow AlCl_3+3H_2O$$

$$Al(OH)_3+OH^- \rightarrow Al(OH)_4^-$$

Example 2

$$ZnO+2HCl \rightarrow ZnCl_2+H_2O$$

$$ZnO+2NaOH+H_2O \rightarrow Na_2[Zn(OH)_4]$$

Try yourself

1. Glycine (H_2NCH_2COOH) is an amino acid having both acidic ($-COOH$) and basic ($-NH_2$) groups, allowing it to act as amphoteric substances. Write the reaction of amino acid acting as acid and base.

2. Identify the Bronsted acid or base and their conjugates in the following.

   a. $CH_3O^{-}(aq) + H_2O(l) \rightarrow CH_3OH\ (aq) + OH^{-}\ (aq)$
   b. $NH_2^{-}(aq) + H_2O(l) \rightarrow NH_3(aq) + OH^{-}\ (aq)$
   c. $HClO_4\ (aq) \rightarrow H^{+}(aq) + ClO_4^{-}(aq)$
   d. $HNO_2 + H_2O \rightarrow NO_2^{-} + H_3O^{+}$
   e. $CN^{-} + H_2O \rightarrow HCN + OH^{-}$

2.3 Relative strength of acids and bases

The ionization of hydrochloric acid and acetic acid is provided below. Find the difference in ionization

$$\mathbf{HCl \rightarrow H^{+} + Cl^{-}}$$

$$\mathbf{CH_3COOH \rightleftharpoons H^{+} + CH_3COO^{-}}$$

The **relative strength of acids and bases** refers to their ability to donate or accept protons (H^{+}). This strength depends on how completely an acid or base ionizes (dissociates) in a solution or how readily it participates in proton transfer. The strength can be explained in detail using concepts such as degree of ionization, equilibrium constants, and the nature of conjugate acid-base pairs.

Relative Strength of Acids depends on how easily an acid donates a proton (H^{+}). If the acids completely dissociate in water and release all the protons, they are said to be **strong acids.** Examples: HCl, H_2SO_4, HNO_3, HI, HBr, and $HClO_4$. These acids have weak conjugate bases that are poor proton acceptors.

Weak acids have relatively stronger conjugate bases compared to strong acids.

The strength of acid also can be expressed in terms of acid dissociation constant (K_a) which measures the extent of ionization of an acid. Larger K_a means stronger acid (greater ionization) and smaller K_a indicates Weaker acid (lower ionization)

Base strength depends on how readily a base accepts a proton (H^{+}). Bases that completely dissociate in water and readily accept protons are strong bases

NaOH, KOH, $Ba(OH)_2$, and other alkali/alkaline earth metal hydroxides are strong bases .

$$\mathbf{OH^{-} + H+ \rightarrow H_2O}$$

Strong bases have very weak conjugate acids.

Bases that partially accept protons in water are weak bases. Weak bases have stronger conjugate acids compared to strong bases. Examples: NH_3, CH_3NH_2 (methylamine), $C_6H_5NH_2$ (aniline) etc.

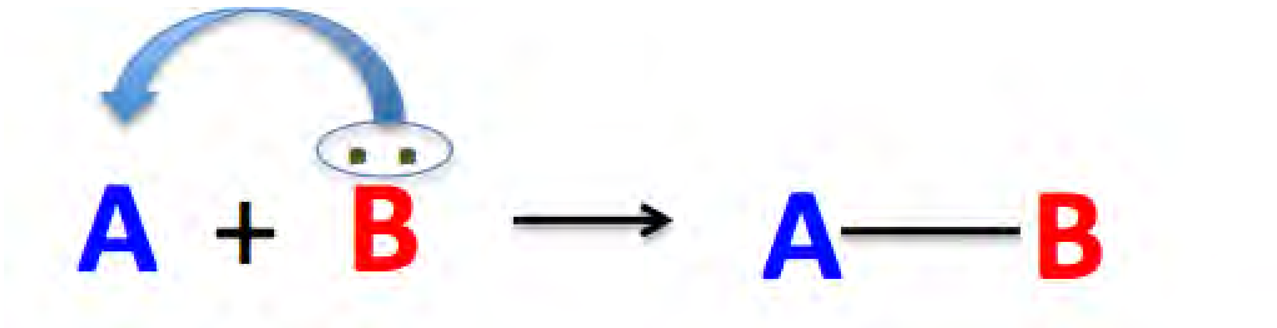
$$\mathbf{NH_3 + H_2O \rightleftharpoons NH_4^{+} + OH^{-}}$$

The relative strength of base can be compared in terms of Base **Dissociation Constant (K_b) which** measures the extent of ionization of a base. Larger K_b means Stronger base (greater ionization) and vice versa.

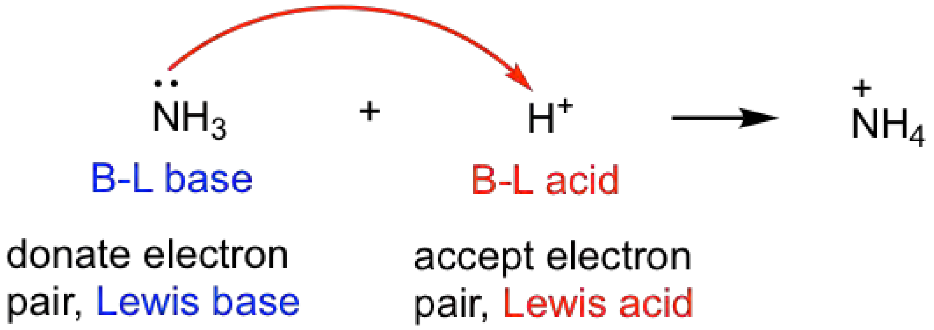
2.5 Lewis's definition of acids and bases

Activity

Identify the species that donates and accepts the pair of nonbonding electrons (lone pair of electrons).



The **Lewis concept of acids and bases**, introduced by Gilbert N. Lewis in 1923. The concept focuses on the transfer of electron pairs rather than the presence of hydrogen ions or hydroxide ions.



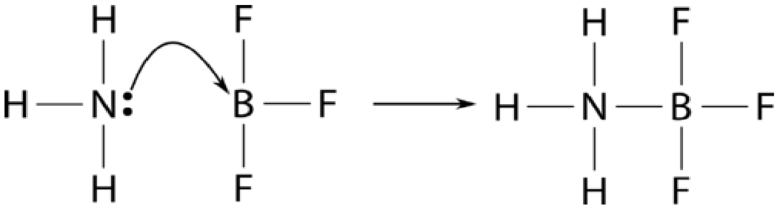
In the above reaction, a pair of electrons is donated by NH_3 acting as a Lewis base whereas hydrogen ion accepts the pair and becomes Lewis acid. Lewis Acids are Electrophilic in nature; i. e. they attract electrons. Some of the examples are listed below.

a. All cations are Lewis acids since they are able to accept electron pair. For examples, Cu^{2+}, Fe^{2+}, Fe^{3+}
b. An atom, ion, or molecule with an incomplete octet of electrons can act as Lewis acid. For examples, BF_3, AlF_3
c. Molecules that have multiple bonds between two atoms of different electro negativities. For examples, CO_2, SO_2

A Lewis acid is a chemical species that accepts an electron pair

Let us consider the following reaction between ammonia and boron trifluoride.

$NH_3 + BF_3 \rightarrow NH_3.BF_3$



In this reaction, NH_3 acts as Lewis base because it donates lone pair of electrons whereas BF_3 acts as Lewis acid as it accepts electron pairs.

A Lewis base is a chemical species that donates an electron pair

During Lewis acid base reaction, **acid base complex or complex ion** is formed due to the transfer of electron from donor to acceptor.
For example, in the reaction of aluminum ion with water molecule,

$$Al^{3+}(aq) + 6\,H_2O(l) \rightarrow Al(H_2O)_6^{3+}(aq)$$

In this reaction, Al^{3+} ion acting as a Lewis acid picks up six pairs of electrons from neighboring water molecules acting as Lewis bases to give an **acid-base complex**, or **complex ion (**$Al(H_2O)_6^{3+}$).

Limitations of Lewis Concept

1. **I**t does not explain the behavior of protonic acids such as HCl, H_4SO_4, and HNO_3
2. It does not predict the relative strength of acids and bases.

Try yourself

1. Classify the following species into Lewis acids and Lewis bases and give reason

   a. HO^- b. F^- c. H^+ d. BCl_3

2. Which of the following species acts a Bronsted-Lowry base?

   a. HCl
   b. HPO_4^{2-}
   c. H_3PO_4
   d. NH_4^+

2.6 Ionization of weak electrolyte (Ostwald's dilution law)

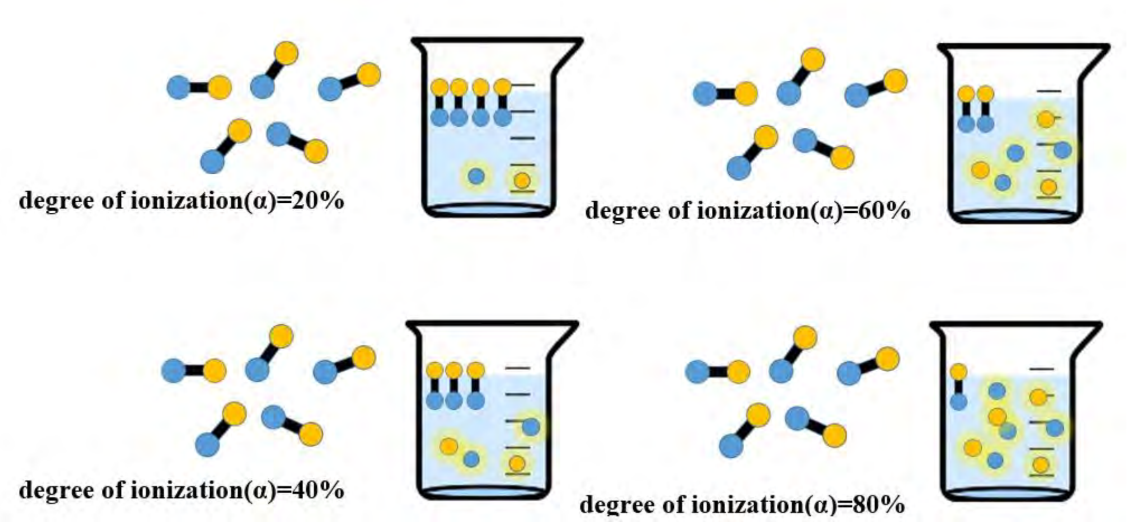


Figure: showing different degree of ionization of weak electrolyte

Weak electrolytes like acetic acid, (CH_3COOH) or ammonium hydroxide (NH_4OH) do not completely ionize in solution. Instead, they ionize partially or feebly in aqueous solution. The measurement of ionization is expressed in terms of **degree of ionization** denoted by **α.** It represents the fraction of the total number of molecules that get ionized in solution. At infinite dilution weak electrolytes get almost completely ionized. The value of **α** varies from 0 (no ionization) to 1 (complete ionization).

Let us consider a weak electrolyte (AB) which establish an equilibrium between their ionized and unionized forms:

$$AB \leftrightharpoons A^{+}+B^{-}$$

Let the initial concentration of the electrolyte be C mol/L. At equilibrium, the concentration of A^+ and B^- ions is also **Cα.** Then the concentration of the unionized electrolyte at equilibrium is **C(1−α).** The equilibrium constant for the equilibrium

$$K = \frac{A^{+} + B^{-}}{AB}$$

Substituting the equilibrium concentration in the above equation

$$K = \frac{C\alpha \ C\alpha}{c - C\alpha} = \frac{c^2\alpha^2}{c(1-\alpha)}$$

For weak electrolytes, $\alpha \ll 1$, Thus: $1 - \alpha \simeq 1$

$$K = \frac{c^2\alpha^2}{c}$$

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

$\boldsymbol{\alpha} = \mathrm{K.v}$

Where, V is the volume of solution (1/C). **The relation shows that, with the dilution of solution, the degree of ionization increases. This is called Ostwald's dilution law.**

Ostwald's dilution law is applicable for weak electrolyte only.

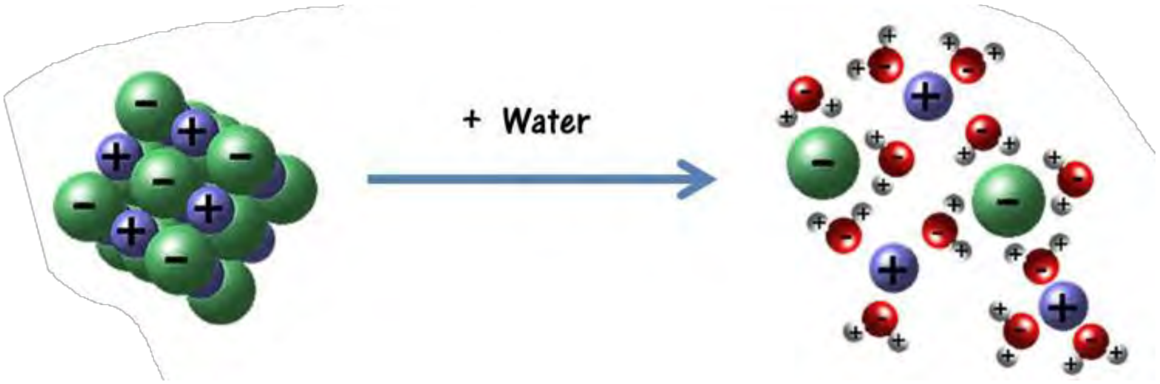
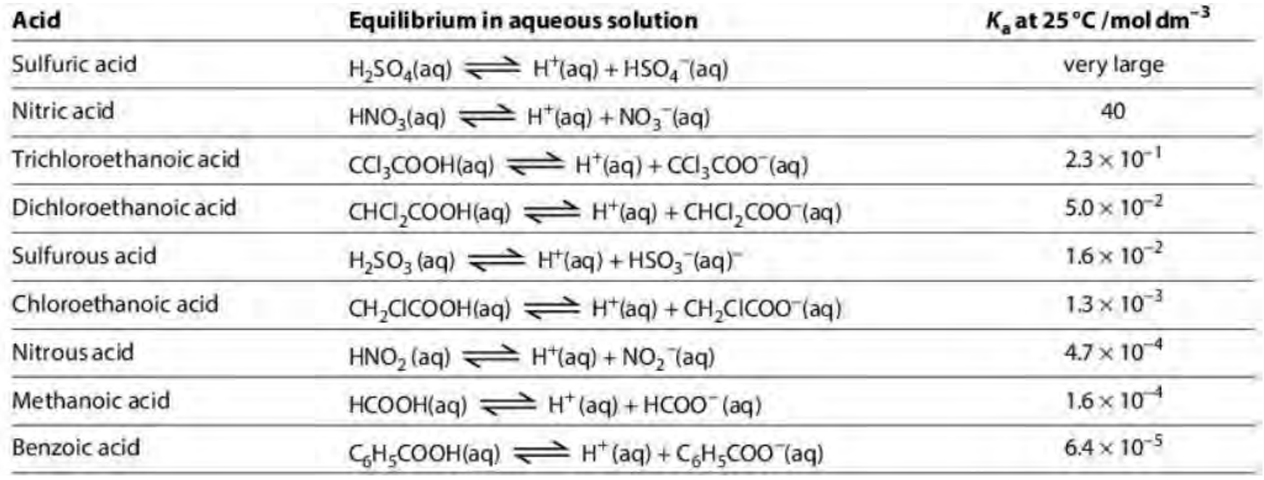


Figure: degree of ionization increases with the addition of water

Try yourself:

If Ka indicates the ionization constant of acid.

a. Using the table given, identify the strongest and weakest acid
b. Write the equilibrium constant for the equilibrium of sulphuric and nitrous acid

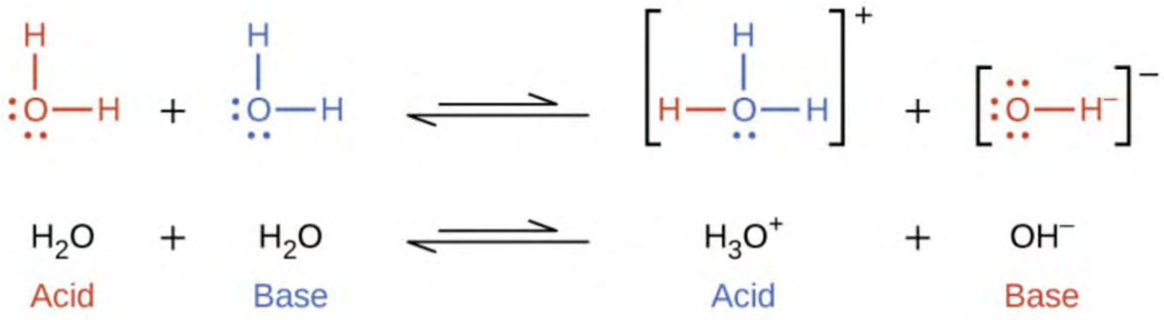


Acid	**Equilibrium in aqueous solution**	**K_a at 25 °C /mol dm^{-3}**
Sulfuric acid	$H_2SO_4(aq) \rightleftharpoons H^+(aq) + HSO_4^-(aq)$	very large
Nitric acid	$HNO_3(aq) \rightleftharpoons H^+(aq) + NO_3^-(aq)$	40
Trichloroethanoic acid	$CCl_3COOH(aq) \rightleftharpoons H^+(aq) + CCl_3COO^-(aq)$	2.3×10^{-1}
Dichloroethanoic acid	$CHCl_2COOH(aq) \rightleftharpoons H^+(aq) + CHCl_2COO^-(aq)$	5.0×10^{-2}
Sulfurous acid	$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq)^-$	1.6×10^{-2}
Chloroethanoic acid	$CH_2ClCOOH(aq) \rightleftharpoons H^+(aq) + CH_2ClCOO^-(aq)$	1.3×10^{-3}
Nitrous acid	$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$	4.7×10^{-4}
Methanoic acid	$HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$	1.6×10^{-4}
Benzoic acid	$C_6H_5COOH(aq) \rightleftharpoons H^+(aq) + C_6H_5COO^-(aq)$	6.4×10^{-5}

c. Consider the ionization of weak base (BOH) assuming the degree of ionization α, show the relation between ionization constant (K_b) with α.

2.7 Ionic product of water (Kw)

Let us consider the following reaction.



From the Bronsted and Lowry concept of acid and base, water can donate as well as accept the proton and behave as an amphiprotic substance.

The dissociation constant for the above equilibrium is represented by,

$$K = \frac{[H3O+][OH-]}{[H2O]}$$

As water is a pure liquid its concentration remains constant.

$K \times [H_2O] = [H_3O^+][OH^-]$

or, $Kw = [H_3O^+][OH^-]$

simply it can be written as

$\boldsymbol{Kw = [H^+][OH^-]}$

Where the new constant, *K*w is called ***the ionic product of water, which is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.***

At 25 °C, the concentration of H^+ and OH^- have been found out experimentally as 1.0×10^{-7} M (dissociation of water produces equal number of H^+ and OH^- ions).

$[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M.

At 25 °C, $Kw = [H^+][OH^-]$
$= (1 \times 10^{-7})^2 = 1 \times 10^{-14}$ mol^2 liter^{-2}

Like any other equilibrium constant, the value of K_W varies with temperature. The value of K_W increases with temperature because the autoionization of water is endothermic.

Whenever, $[H^+] = [OH^-]$ the aqueous solution is said to be neutral.

In an acidic solution, there is an excess of $[H^+]$ ions i.e., $[H^+] > [OH^-]$

In a basic solution, there is an excess of hydroxide ions, so $[H+] < [OH^-]$.

The autoionization of water (also called self-ionization) is a chemical process in which two water molecules react to form a hydronium ion (H_3O^+) and a hydroxide ion (OH^-).

Try yourself:

If $[H^+]$ of a solution at 25 °C is 1.0×10^{-6} mol L^{-1}, find the concentration of OH^- .

2.8 Dissociation constant of acid and base (K_a and K_b)

If we apply the Ostwald's dilution law in the case of weak acid (HA) which ionizes as

$$HA\ (aq) \rightleftharpoons H+(aq) + A^-$$

The ionization constant (K) can be written as,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

In the same way for the weak base which ionizes to give OH^- ions in aqueous solution can be written as

$$BOH\ (aq) \rightleftharpoons B+(aq) + OH^-$$

And the equilibrium constant (Kb)= $\frac{[B^+][OH^-]}{[BOH]}$

The constants **Ka** and **Kb** are called dissociation constant of acid and base respectively. Larger the value of **ka** indicates stronger the acid and higher the H^+ concentration at equilibrium. Similarly higher the value of **Kb** indicates stronger the base and higher the concentration of OH^- ions at equilibrium.

Try yourself:

Identify the strongest and weakest acid from the given table.

No.	**Acid**	K_a
1	Hydroiodic acid (HI)	3.16×10^{9}
2	Hydrobromic acid (HBr)	1.0×10^{9}
3	Hydrochloric acid (HCl)	1.0×10^{6}
4	Sulfuric acid (H_2SO_4)	1.0×10^{3}
5	Hydronium ion (H_3O^+)	55
6	Nitric acid (HNO_3)	28.2
7	Trifluoroacetic acid (CF_3COOH)	5.62×10^{-1}
8	Oxalic acid (HOOC–COOH)	5.37×10^{-2}
9	Acetic acid (CH_3COOH)	1.75×10^{-5}

2.9 Concept of pKa and pKb

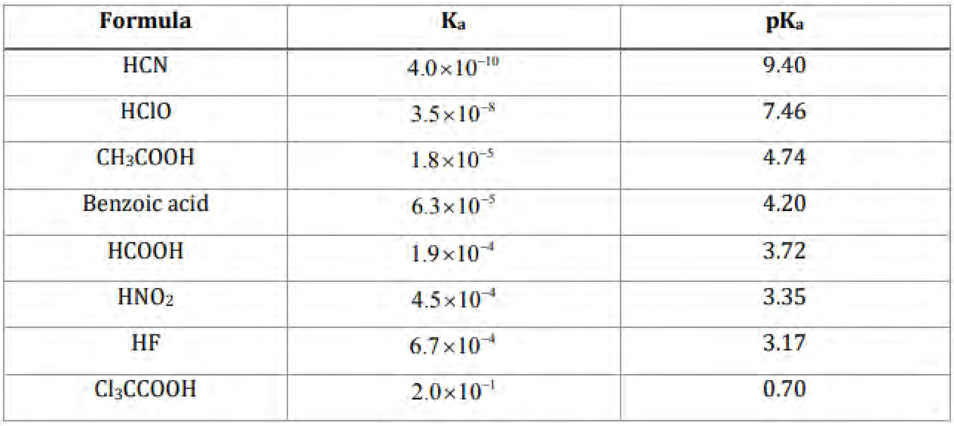
For most weak acids, **Ka** ranges from 10^{-2} to 10^{-14} and for most weak bases, **Kb** ranges from 10^{-2} to 10^{-13}.We convert these exponential numbers into a normal range by taking their negative logarithm in terms of pKa and pKb.

Both pKa and pKb are useful for predicting the behavior of acids and bases in various chemical reactions, including buffer solutions. They also help in understanding the relative strengths of different acids and bases in biological and environmental systems.

pKa is the negative logarithm (base 10) of the acid dissociation constant (Ka) of a solution. It quantifies the strength of an acid in solution.

$$pKa = -\log_{10}Ka$$

Like the **ka** , **pka** also measures the degree of dissociation of acid. A lower pKa value indicates a stronger acid, as it reflects a greater tendency to donate protons (H^+ ions). Conversely, a higher pKa value corresponds to a weaker acid.

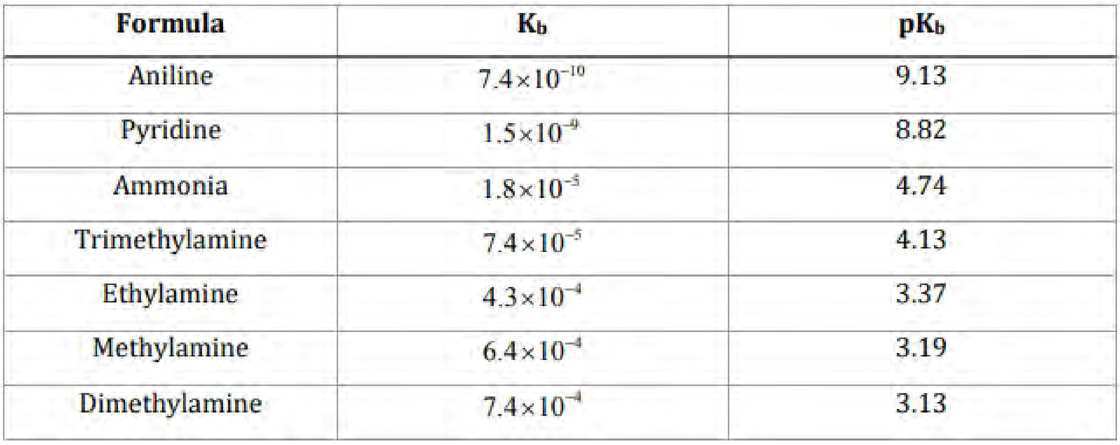


Formula	K_a	pK_a
HCN	4.0×10^{-10}	9.40
HClO	3.5×10^{-8}	7.46
CH_3COOH	1.8×10^{-5}	4.74
Benzoic acid	6.3×10^{-5}	4.20
HCOOH	1.9×10^{-4}	3.72
HNO_2	4.5×10^{-4}	3.35
HF	6.7×10^{-4}	3.17
Cl_3CCOOH	2.0×10^{-1}	0.70

pKb is the negative logarithm (base 10) of the base dissociation constant (Kb) of a solution. It quantifies the strength of a base in solution.

$$pKb = -\log_{10}Kb$$

A lower pKb value indicates a stronger base, as it signifies a greater tendency to accept protons. A higher pKb value reflects a weaker base.



Formula	K_b	pK_b
Aniline	7.4×10^{-10}	9.13
Pyridine	1.5×10^{-9}	8.82
Ammonia	1.8×10^{-5}	4.74
Trimethylamine	7.4×10^{-5}	4.13
Ethylamine	4.3×10^{-4}	3.37
Methylamine	6.4×10^{-4}	3.19
Dimethylamine	7.4×10^{-4}	3.13

Relationship Between pKa and pKb

For a given conjugate acid-base pair, the relationship between pKa and pKb can be described by the following equation:

$$pKa + pKb = 14 \text{ at } 25°C$$

This means that if you know the pKa of an acid, you can calculate the pKb of its conjugate base, and vice versa. For example, the pKa of NH_4^+ is 9.25, so the pKb of NH_3 is 14 - 9.25 = 4.75.

2.10 pH value: pH of strong and weak acids, pH of strong and weak bases

Activity:

Observe given information related to pH range of various substances and fill the table given.

Substance	pH range
Gastric juice	1 – 3
Vinegar	2.4 – 3.4
Tears	7.4
Human urine	4.8 – 8.4
Blood plasma	7.3 – 7.4
Boil water	6.56

Substance of highest pH	Substance of lowest pH	Most acidic substance	Most basic substance

You are aware about the acidic and basic solution. How do you measure the comparative strength of acidity or basicity?

It is inconvenient to measure the concentrations of H^+ and OH^- ions in aqueous solutions because the concentration is normally very small. A Danish Chemist ***Soren Sorensen*** in 1909 proposed a more practical measure of acidity and basicity in terms of pH of solution.

pH is negative common logarithm of hydrogen ion concentration.
Mathematically pH is expressed as

$$pH = -\log[H^+]$$
$$\text{Or, } H^+ = \log^{-1}(-pH) = 10^{-pH}$$

For example, the pH of 0.1 M HCl is

$$pH = -\log(0.1)$$
$$= 1$$

Similarly, the molar concentration of alkali (OH^-) is expressed as pOH

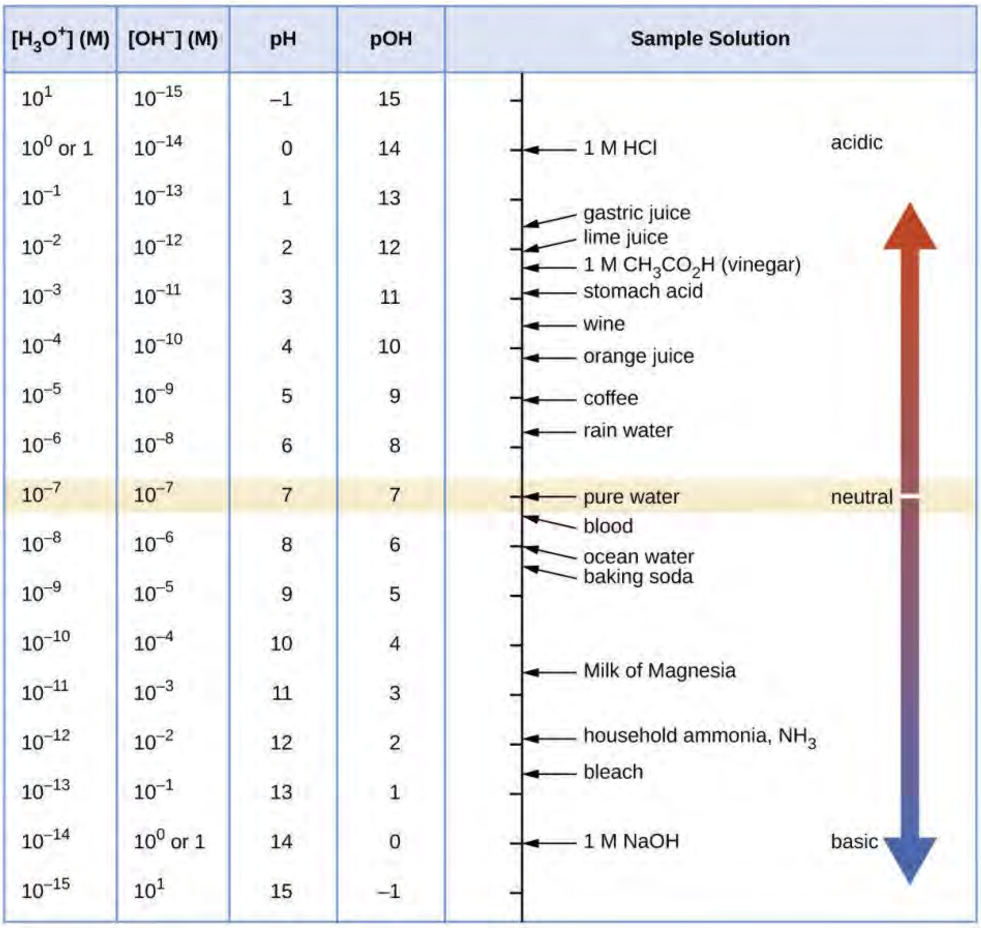
$$pOH = -\log[OH^-]$$

2.10.1 Relationship between pH and pOH

Activity:

Use the table given below and discuss in pair to find

a. The pH of rain water and milk of magnesia
b. The product of concentration of hydronium ion(H_3O^+) and hydroxide ion (OH^-)
c. The sum of pH and pOH



$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH	Sample Solution
10^1	10^{-15}	–1	15	
10^0 or 1	10^{-14}	0	14	1 M HCl acidic
10^{-1}	10^{-13}	1	13	gastric juice
10^{-2}	10^{-12}	2	12	lime juice 1 M CH_3CO_2H (vinegar)
10^{-3}	10^{-11}	3	11	stomach acid
10^{-4}	10^{-10}	4	10	wine orange juice
10^{-5}	10^{-9}	5	9	coffee
10^{-6}	10^{-8}	6	8	rain water
10^{-7}	10^{-7}	7	7	pure water neutral
10^{-8}	10^{-6}	8	6	blood ocean water
10^{-9}	10^{-5}	9	5	baking soda
10^{-10}	10^{-4}	10	4	
10^{-11}	10^{-3}	11	3	Milk of Magnesia
10^{-12}	10^{-2}	12	2	household ammonia, NH_3
10^{-13}	10^{-1}	13	1	bleach
10^{-14}	10^0 or 1	14	0	1 M NaOH basic
10^{-15}	10^1	15	–1	

The dissociation constant of water

$(K_w) = 1.0 \times 10^{-14}$ at 25°C

Or $[H^+][OH^-] = 1.0 \times 10^{-14} \ldots (1)$

Taking –log on both sides

$-\log[[H^+] - \log [OH^-] = \log 10^{-14}$

Or, pH + pOH = 14

In neutral water, concentration of H^+ and OH^- ions are equal.

i.e. $[H^+] = [OH^-]$

Then the equation (1) becomes

$$[H^+][H^+] = 1.0 \times 10^{-14}$$

$$\text{or } [H^+]^2 = 1.0 \times 10^{-14}$$
$$[H^+] = 1.0 \times 10^{-7}$$

Taking log on both sides

$$\text{Or, } \log[[H^+] = \log 10^{-7}$$
$$\text{Or, } -\log[[H^+] = 7 \log 10$$
$$\text{Or, pH} = 7$$

Likewise in acidic water, concentration of hydrogen ion is greater than hydroxide ion

$$\text{i.e. } [H^+] > [OH^-]$$
$$\text{Or } [H^+] > 10^{-7}$$
$$\text{pH} = -\log(>10^{-7})$$
$$\text{pH} < 7$$

Similarly for alkaline solution $[H^+] < [OH^-]$

$$\text{or, } [OH^-] > 10^{-7}$$
$$\text{pOH} < 7$$
$$\text{pH} > 7$$

Do you know?

a. pH value of an acid having H^+ concentration less than 10^{-7}, is always in between 6 and 7.
b. pH of solution is accurately measured by pH meter or emf method or roughly by pH paper or indicator paper.
c. pH can be zero for 1 N HCl solution.

Try yourself

Use the table given and find

a. The temperature at which water is most acidic
b. pH of neutral water at 50 °C
c. Concentration of hydroxide ion at 0 °C

Temperature (⁰C)	**Kw**
0	1.14×10^{-15}
25	1.00×10^{-14}
35	12.09×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}

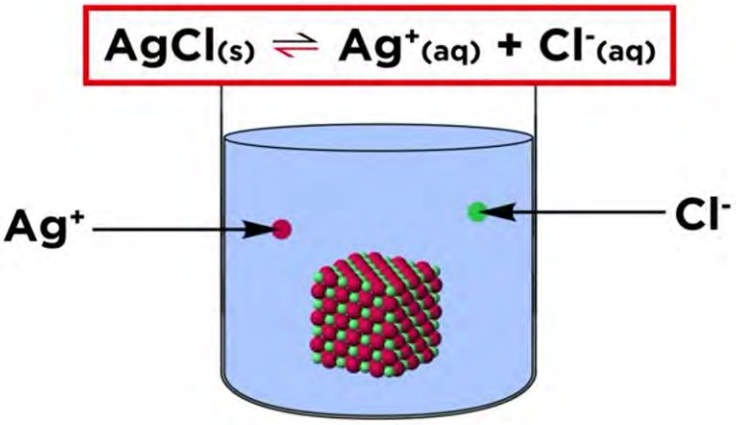
2.11 Solubility and Solubility product principle

Figure: Stalactites in Mahendra cave, Pokhara

Have you seen icicle-shaped (long, tapering) formations that hang from the ceilings of Mahendra cave in Pokhara? These hanging are called **Stalactites**. These are the results of deposits (precipitation) of calcium carbonate (calcite) over thousands of years.

Activity:

Identify whether the solution given in the beaker is unsaturated, saturated or supersaturated and name of substance that is precipitated in the beaker.



Precipitation or double displacement reaction gives different types of precipitates (water insoluble solid) which are useful in industry, medicine or in daily life. For example; precipitate of $BaSO_4$ is used in x-ray analysis to diagnose the disorders of alimentary tract and Na_2CO_3 precipitate is used as an important industrial chemical substance.

Concept of solubility product explains about the formation of these precipitates from ionic compounds. When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions as shown

$$\underset{\text{(solid)}}{AB} \rightleftharpoons \underset{\text{(aqueous)}}{A^+} + \underset{\text{(aqueous)}}{B^-}$$

Equilibrium constant $(K) = \frac{[A+][B-]}{[AB]}$

$\mathbf{K} \times [AB] = [A^+][B^-]$

since the activity (concentration) of solid is arbitrarily taken as unity.

$\mathbf{Ksp} = [A^+][B^-]$

where the new constant K_{sp} is called solubility product constant or simply solubility product.

Since it is a product of molar concentration of ions, the unit of Ksp depends upon the stoichiometric coefficient of ions.

$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2++}(aq) + 2PO_4{}^{3-}(aq)$

$Ksp = [Ca^{2+}(aq)]^3 [PO_4{}^{3-}(aq)]^2$

Unit of Ksp = $(Mol\ L^{-1})^3 (Mol\ L^{-1})^2 = Mol^5\ L^{-5}$

Some of the examples of solubility product constant (Ksp) are given below

$MgF_2 \rightleftharpoons Mg^{++} + 2F^-$	$Ksp = [Mg^{++}][F^-]^2$
$AgCl \rightleftharpoons Ag^+ + Cl^-$	$Ksp = [Ag^+][Cl^-]$
$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3{}^{--}$	$Ksp = [Ag^+]^2[CO_3{}^{--}]$

Lower value of Ksp indicates lower the solubility of the substance.

Solubility product of a compound is defined as the product of molar concentration of its constituent ions each raised to the power of its stoichiometric coefficient in the equilibrium equation.

Try yourself

The value of solubility product constant (Ksp) at constant temperature for particular salt as shown in the table below: Identify the solid that is highly soluble in water .

Ionic solid	Ksp at 25°C	Unit of Ksp
AgCl	1.6×10^{-10}	$Mol^2\ L^{-2}$
$BaCO_3$	2×10^{-9}	$Mol^2\ L^{-2}$
AgBr	5×10^{-13}	$Mol^2\ L^{-2}$
Ag_2CrO_4	2×10^{-12}	$Mol^3\ L^{-3}$

Ionic product (K_{ip})

The ionic product of a salt is the product of molar concentrations of the ions in solution each concentration term raised to the powers of stoichiometric coefficient. Solubility product is the ionic product when the solution is saturated.

For, $AgCl \rightleftharpoons Ag^+ + Cl^-$

Ionic product (K_{ip}) = $[Ag^+][Cl^-]$, where $[Ag^+]$ and $[Cl^-]$ are molar concentration of silver ions and chloride ions, respectively.

Solubility and molar solubility

Solubility of a substance is the weight of solute dissolved per hundred gram of solvent. However, solubility of a substance can also expressed in gram per liter (g/L) or mole per liter (M).

The relation be between gram per liter and mole per liter is given below.

$$\text{Molar solubility} = \frac{\text{g/L}}{\text{Molar mass}}$$

Relation between solubility and solubility product

let us consider a simple salt AB giving only two ions having solubility ‘S’ mole per liter.

	AB	$\rightleftharpoons A^+$	$+ B^-$
Initial solubility	‘s’	0	0
Solubility at equilibrium		‘s’	‘s’

Solubility product (Ksp) $= [A^+]\,[B^-]$

$= s \times s$

$= \mathbf{s}^2$

Or the molar solubility (s) $=\sqrt{Ksp}$

Solubility in gram per liter (g/L) = **s** × Molecular mass

Likewise for salt of the type AB_2 or A_2B giving 3 ions per molecule, the solubility equilibria are

	$\mathbf{AB_2}$	$\rightleftharpoons$	$\mathbf{A^{++}}$	$\mathbf{+\ 2B^-}$
initial solubility	‘s’		0	0
equilibrium solubility			‘s’	2‘s’

solubility product (Ksp) = $[A^+]\,[B^-][B^-]$

$= s \times 2s \times 2s$

$= 4s^3$

Or molar solubility (s)= $\sqrt[3]{\frac{K_{sp}}{4}}$

Solubility in gram per liter (g/L) = s × Molecular mass

Similarly

	$\mathbf{A_2B}$	$\rightleftharpoons$	$\mathbf{2A^+}$	$\mathbf{+ B^{--}}$
Initial solubility	‘s’		0	0
Equilibrium solubility			2 ‘s’	‘s’

Solubility product (Ksp) = $[A^+]\,[A^+]\,[B^-]$

$= 2s \times 2s \times s$

$= 4s^3$

Or molar solubility (s)= $\sqrt[3]{\frac{K_{sp}}{4}}$

For general ionic solid A_xB_y having solubility ‘S’, the solubilty equilibrium is

	A_xB_y	$\rightleftharpoons$	xA^{y+} +	yB^{x-}
Initial solubility	s		0	0
Equilibrium solubility	s		xs	ys

The solubility product constant (K_{sp}) = $[A^{y+}]^x\,[B^{x-}]^y$

The solubility product constant (Ksp) = $(xs)^x\,(ys)^y$

$= x^x y^y\, s^{(x+y)}$

Solved examples

1.The solubility of barium sulphate at 298 K is 1.05 × 10^{-5} mol L^{-1}. Calculate the solubility product.

$BaSO_4 \rightleftharpoons Ba^{++} + SO_4^{--}$

$[Ba^{++}] = 1.05\times10^{-5}$ mol L^{-1}

$[SO_4^{--}] = 1.05\times10^{-5}$ mol L^{-1}

Ksp= $[Ba^{++}]\,[SO_4^{--}]$

$= (1.05\times10^{-5})^2$ $mol^2\,L^{-2}$

$= 1.10\times10^{-10}$ $mol^2\,L^{-2}$

2.The solubility of magnesium hydroxide at 298 K is 1.71 × 10^{-4} mol dm^{-3}. Calculate the solubility product.

Solution,

$Mg(OH)_2 \rightleftharpoons Mg^{++} + 2\,OH^-$

For every mole of magnesium hydroxide that dissolves, you will get one mole of magnesium ions, but twice that number of hydroxide ions.

It means, if solubility of $Mg(OH)_2$ is ‘s’ then the molar solubility of magnesium ions

$[Mg^{++}] = s$ mol L^{-1}

and the molar solubility of hydroxide ion $[OH^-] = 2s$ mol L^{-1}

Ksp = $[Mg^{++}]\,[OH^-]^2$

$= s \times (2s)^2$

$= 4\,s^3$

$= 4\times(1.71\times10^{-4})^2\ mol^3L^{-3}$

$= 2.00\times10^{-11}\ mol^3L^{-3}$

Try yourself

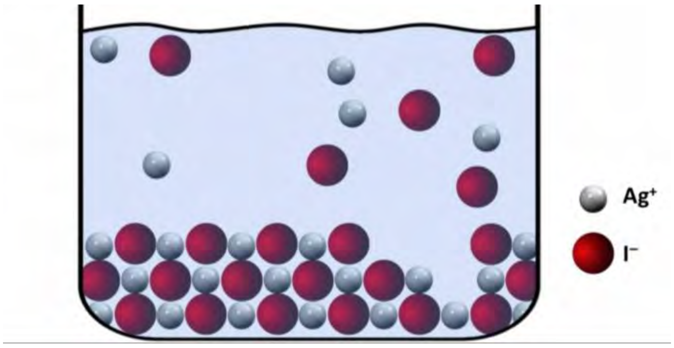
a. The solubility of silver chloride, AgCl, at 298 K is 1.34×10^{-5} mol L^{-1}. Calculate its solubility product at that temperature.
b. The solubility of strontium hydroxide, $Sr(OH)_2$, at 298 K is 0.0431 mol L^{-1}. Calculate its solubility product at that temperature.
c. The solubility product of strontium carbonate, $SrCO_3$, at 298 K is 1.10×10^{-10} mol^2 L^{-2}. Calculate its solubility in mol L^{-1} at this temperature
d. The solubility product of calcium phosphate, $Ca_3(PO_4)_2$, at 298 K is 1.0×10^{-26} mol^5 L^{-5}. Calculate its solubility in gram per liter at this temperature.

Solubility product principle

Activity

Observe the figure given

a. Identify the substance that is precipitated in the container
b. Write the expression of Ksp for the given substance



Solubility is the maximum amount of a solute that can dissolve in a solvent at a given temperature and pressure. It is usually expressed in terms of gram per liter. Higher solubility means higher amount of substance dissolved in the solution. Unsaturated solution contains comparatively less amount of solute than the saturated solution.

In a saturated solution of a salt, there exists a dynamic equilibrium between the excess of the solute and the ions furnished by that part of the solute which has gone in solution.

Let us consider, a sparingly soluble salt AB is kept in water where it ionizes as

$$\mathbf{AB(s) \rightleftharpoons A^+(aq) + B^-(aq)}$$

The solubility product (K_{sp}) is given by: $K_{sp} = [A^+][B^-]$

And ionic product $\mathbf{(K_{ip}) = [A^+][B^-]}$

The relationship between ionic product and solubility product depends upon the nature of solution whether it is saturated, unsaturated or supersaturated.

$K_{ip} < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
$K_{ip} = K_{sp}$. The solution is saturated and at equilibrium.
$K_{ip} > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

Consider, for example, the case when a sparingly soluble salt, like silver chloride, is added to water. A very small amount of salt gets dissolved and the rest of it remains in the solid state.

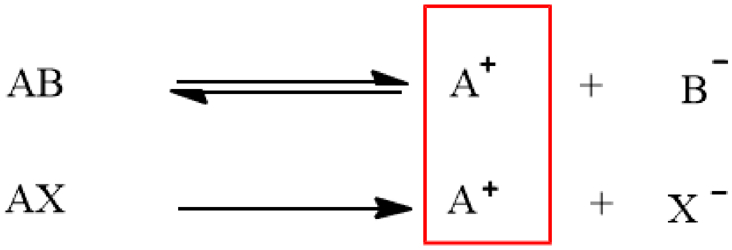
$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

Chemical precipitation is the formation of a solid in a solution during a chemical reaction. Precipitation lowers the solubility of the salt in the solution. The condition of precipitation is explained by **Solubility product** principle.

Solubility product principle states that for the precipitation to occur the ionic product of the ions must be greater than the solubility product.

2.12 Common ion effect

Activity:
Observe the ionization of weak and strong electrolyte given and fill the table to identify strong electrolyte, weak electrolyte and common ion .



Strong electrolyte	Weak electrolyte	Common ion

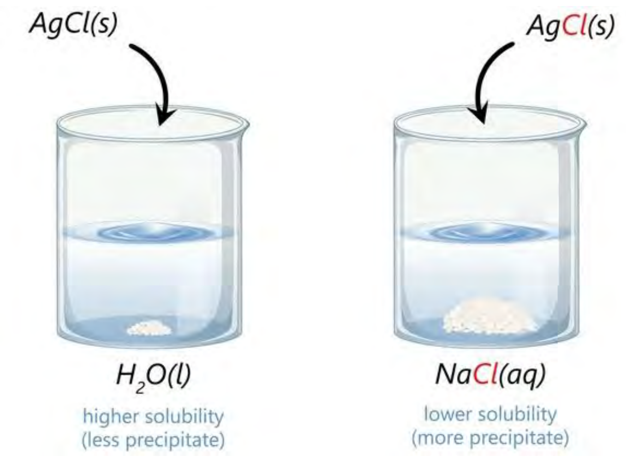
Let us consider a weak electrolyte AB is dissociated into A^{+} and $\mathbf{B}^{-}$ ions

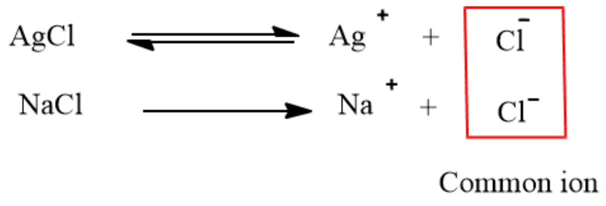
$$AB \rightleftharpoons A^{+}+B^{-}$$

If strong electrolyte AC is added

$$AC\rightarrow A^{+}+ C^{-}$$

The concentration of A^{+} increases and the equilibrium shift backward to maintain the equilibrium**.** Adding a common ion decreases solubility because the equilibrium shifts towards the unreacted molecule causing the precipitation. For example, when NaCl is added in AgCl solution, the ionization of AgCl decreases causing the precipitation.

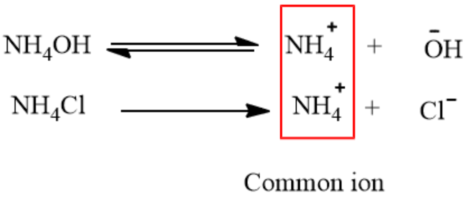




$$AgCl \rightleftharpoons Ag^+ + Cl^-$$
$$NaCl \longrightarrow Na^+ + Cl^-$$

Common ion

Likewise in the solubility of NH_4OH decreases in water after the addition of NH_4Cl .



$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

Common ion

The equilibrium shifts to the left, reducing the ionization of NH_4OH and lowering the concentration of $[OH^-]$. It makes the solution less basic (lower pH).

Common ion effect is defined as the suppression of degree of ionization of weak electrolyte by the addition of strong electrolyte having one common ion.

Try yourself

For any weak acid (HA), the ionization and the equilibrium constant (Ka) is given as

$$\mathbf{HA \rightleftharpoons H^+ + A^-}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

a. What happens to the concentration of A^- ion if another strong electrolyte having common H^+ ion is added?
b. In the above case, what will be the value of K_a?

2.13 Applications of Solubility Product and common ion in Qualitative Analysis

Figure: Salting out of soap is carried out by adding sodium chloride into the soap solution. This is one of the applications of solubility product principle and common ion effect.

Solubility-product constants can be used to devise methods for separating ions in a solution by selective precipitation. Selective precipitation is used to form a solid with one of the ions in solution without disturbing the other ions.

1) Qualitative Analysis of basic radicals

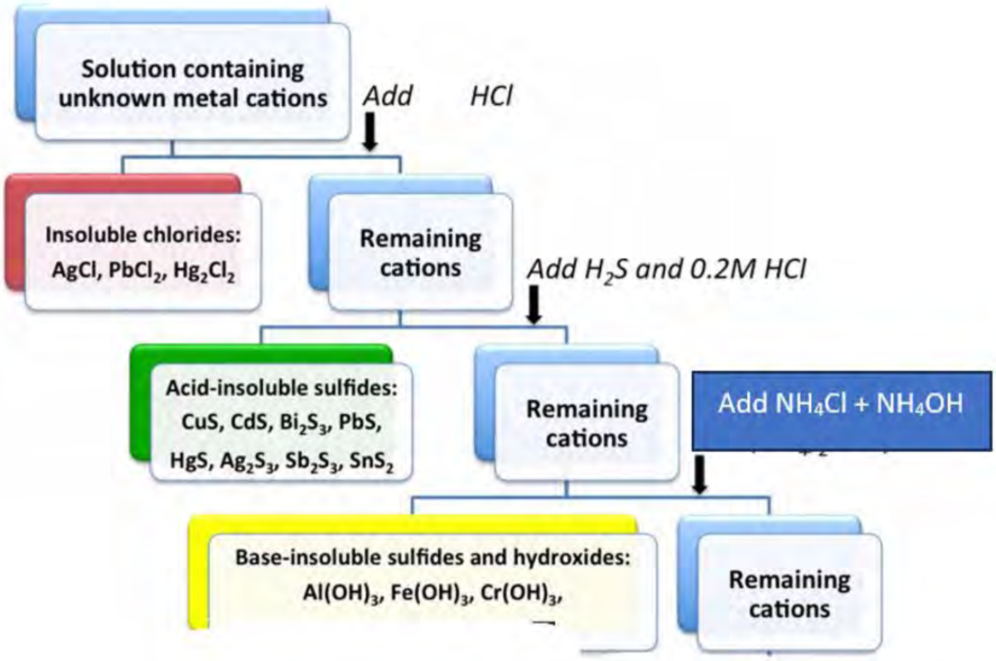
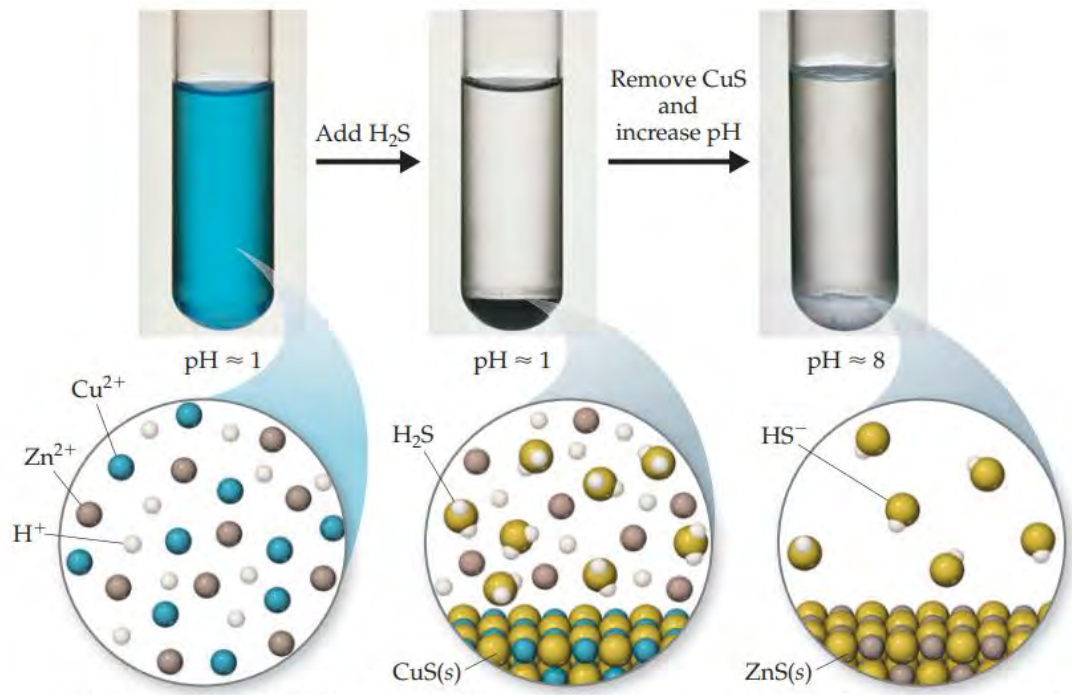


Figure: selective precipitation using H2S gas



Solution containing $Zn^{2+}(aq)$ and $Cu^{2+}(aq)$

When H_2S is added to a solution whose pH exceeds 0.6, CuS precipitates

After CuS is removed, the pH is increased, allowing ZnS to precipitate

Group II basic radicals (Cu^{++}, Hg^{++}, Pb^{++}, Cd^{++}, Sn^{++}, As^{+++}, Sb^{+++}, Bi^{+++}) are precipitated as their sulphides. Precipitation is carried out by passing HCl followed by the passage of H_2S gas through the solution. Being weak acid H_2S ionizes as

$$\mathbf{H_2S \rightleftharpoons 2H^+ + S^{--}}$$

HCl being a strong acid ionizes completely which increases the concentration of H^+ ions (common ion)

$$\mathbf{HCl \rightarrow H^+ + Cl^-}$$

Due to common ion effect, the equilibrium shifts backward suppressing the ionization of H_2S. It lowers the concentration of sulphide ions which are enough only to precipitate the group II cations (due to their low Ksp value of metal sulphide) leaving other group cations in the solution.

Group IIIA basic radicals (Fe^{+++}, Cr^{+++}, Al^{+++}) get precipitated as their metal hydroxides by adding NH_4Cl followed by NH_4OH. NH_4OH being weak base ionizes as

$$\mathbf{NH_4OH \rightleftharpoons NH_4^+ + OH^-}$$

Being strong electrolyte, NH_4Cl ionizes completely as

$$\mathbf{NH_4Cl \rightarrow NH_4^+ + Cl^-}$$

Due to common ion effect the equilibrium shifts backward lowering the concentration of hydroxide ion. The decreased concentration of OH^- ions are enough to precipitate only group IIIA ions .

3. Purification of common salt

Common salt solution consists of many insoluble and soluble impurities. Hydrogen chloride gas (HCl) is circulated through the saturated sodium chloride solution obtained from the salty sea water to obtain solid mass of salt.

HCl and NaCl dissociate into their respective ions as

$NaCl \rightleftharpoons Na^+ + Cl^-$

$HCl \rightarrow H^+ + Cl$

The concentration of Cl- ions increases considerably in solution due to complete ionization HCl. Hence, the ionic product $[Na^+]$ $[Cl^-]$ exceeds the solubility product of sodium chloride and therefore pure sodium chloride precipitates out form solution.

4. Salting out of soap

Soap is a sodium salt of higher acids, most common is $C_{17}H_{35}COONa$ (sodium stearate). From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride. Soap and sodium chloride are present in the form of ions.

$C_{17}H_{35}COONa \rightleftharpoons C_{17}H_{35}COO^- + Na^+$

$NaCl \rightarrow Na^+ + Cl^-$

Due to sodium ions the ionic product of salt of fatty acid i.e $[C_{17}H_{35}COO^-]$ $[Na^+]$ increases which exceeds the solubility product and soap precipitates.

Try yourself

a. In the manufacture of baking soda, CO_2 gas is passed through ammoniacal brine solution to precipitate out $NaHCO_3$. Is common in effect and solubility product principle applicable? How?

$NH_4OH + CO_2 \rightarrow NH_4HCO_3$

$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

b. Which one of the following salts is more soluble in water ?

$CaCO_3$: $Ksp = 2.8 \times 10^{-9}$

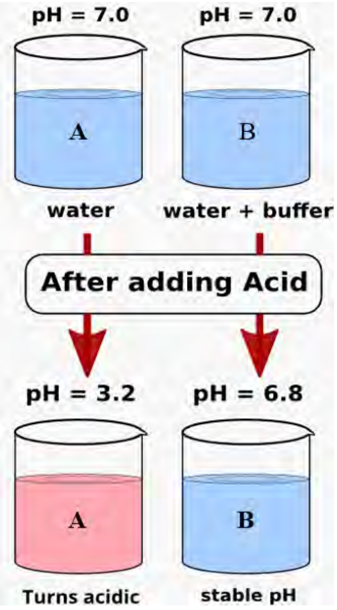
Ag_2CO_3: $Ksp = 8.1 \times 10^{-12}$

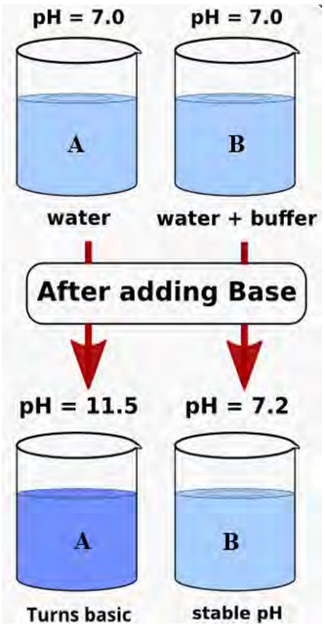
c. 25.0 mL of 0.002 M K_2CrO_4 is mixed with 75.0 mL of 0.000125 M $Pb(NO_3)_2$. Will a precipitate of $PbCrO_4$ form? Ksp of $PbCrO_4 = 1.8 \times 10^{-14}$

2.14 Buffer solution and its applications

Activity:

Two sets of beaker A (containing water only) and B (containing water and buffer) with few drops of indicators are given. Discuss in group and fill the table given.





Ph of water before	Ph of water +buffer before	Ph of water after adding acid	Ph of water after adding base	Ph of water+buffer after adding acid	Ph of water +buffer after adding base

Conclusion :
The pH of human blood is slightly alkaline (7.35-7.45) and it maintains almost constant even after the addition of small amount of acid or base. The carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) present in the blood helps to maintain the pH constant which is called buffer. In the same way, the different buffer components present in the different substances and their applications are given in the table below.

Examples	**Buffer components**	**Applications**
Carbonated drinks	carbonic acid and bicarbonate	Prevents the drink from becoming too acidic, which could alter the taste and texture
Eye Drops	Phosphate or borate buffers	Maintains the pH of tears (~7.4) to ensure the solution, doesn't irritate the eyes when applied, as pH changes can cause discomfort
Human Saliva	Phosphate ions ($H_2PO_4^-$/HPO_4^{2-}) and bicarbonate	Maintain the pH in the mouth (6.5-7.0) This helps prevent tooth enamel erosion
Creams and Lotions	Lactic acid and its salts	Maintain a pH that is close to the natural pH of the skin (~4.5-6). This prevents irritation and keeps the skin barrier intact, promoting skin health
Blood Buffer System	Carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-)	maintains a stable blood pH (~7.4). This buffer system prevents blood from becoming too acidic or basic, which is crucial for normal physiological function.

Buffer solution has the ability to resist the change in pH upon the addition of small amount of acid or base. Buffer solution maintains the pH which is important in both chemical and biological systems. The proper functioning of the enzymes as well as balance of osmotic pressure in the human body is due to the action of buffer.
A buffer solution should exhibit following characteristics:

1. Buffer solutions possess a definite pH value.
2. Their pH value remains constant on keeping for long time or on dilution.

A buffer solution is a solution that resists changes in its pH when small amounts of acid (H^+ ions) or base (OH^- ions) are added. Buffers are essential in maintaining stable pH conditions in biological, chemical, and industrial systems.

Types of buffers

A.Acidic buffer

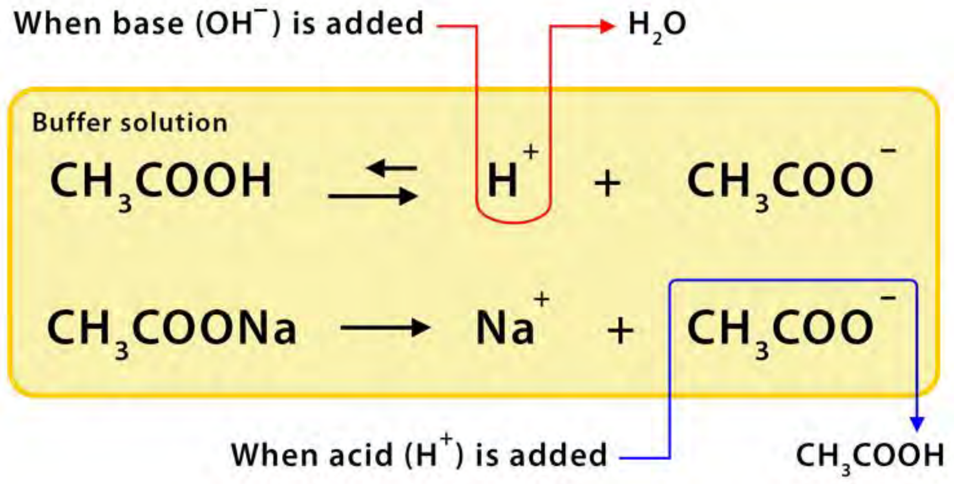


Figure: Mixture of weak acid(CH_3COOH) and its salt with strong base(CH_3COONa) which act as an acidic buffer

Weak acid partially dissociates in water, giving H^+ ions. For example, acetic acid (CH_3COOH). Conjugate Base is usually in the form of a salt of the weak acid, which provides the corresponding base. For example, sodium acetate (CH_3COONa).

Acidic buffer maintains pH less than 7. The sodium acetate –acetic acid buffer system is represented as CH_3COONa/CH_3COOH or CH_3COO^-/CH_3COOH.

Buffer action refers to the ability of a buffer solution to resist changes in its pH when small amounts of acid (H^+ ions) or base (OH^- ions) are added. A buffer maintains a relatively stable pH by neutralizing the added acid or base. This process is crucial in many biological, chemical, and industrial systems.

CH_3COONa is a strong electrolyte which dissociates completely in water

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

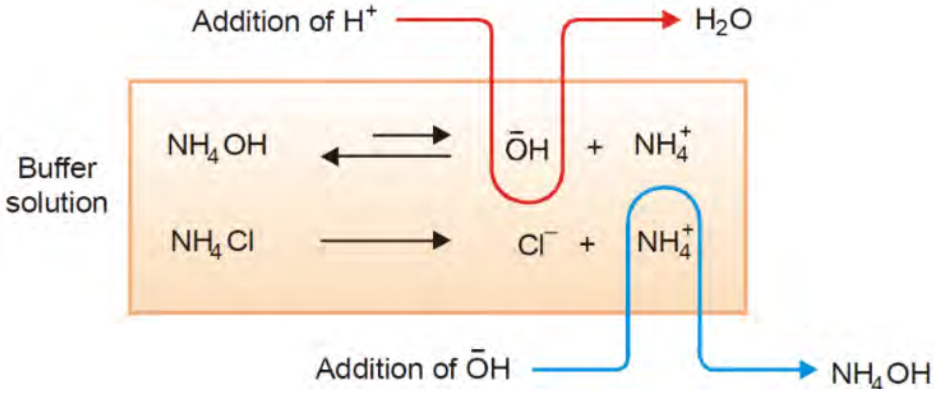
When acid is added, H^+ ion combines with conjugate base (CH_3COO^-) to form weak acid (CH_3COOH) which resists the change in pH of the solution.

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

When base is added, OH^- will be consumed by weak acid and maintain the pH almost constant.

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

B. **Basic buffer**



It is the mixture of weak base and its salt with strong alkali. It maintains pH greater than 7. For example, the mixture of ammonium hydroxide and ammonium chloride acts as basic buffer. This buffer system is represented as NH_4Cl/NH_4OH or NH_4^+/NH_4OH

When small amount of acid is added to the basic buffer, hydrogen ion given by acid combined with hydroxide ion of the buffer forming water thus neglecting the change in ph. Likewise when base is added to the basic buffer, hydroxide ion given combines with ammonium ion of the buffer forming weak ammonium hydroxide thus prevents the change in pH.

Calculation of PH of buffer solution

Let us consider a weak acid HA which remains in equilibrium with H^+ and A^- ions

$$HA \rightarrow H^+ + A^-$$

the equilibrium constant of the acid (K_a) = $\frac{[H+][A-]}{[HA]}$

taking -log on both sides $-\log K_a = -\log H^+ - \frac{\log A-}{[HA]}$

$$\text{or } pK_a = pH - \log \frac{[\text{salt}]}{[\text{acid}]} \ldots\ldots\ldots\ldots\ldots\ (1)$$

likewise for alkaline buffer the equation becomes

$$\text{or } pK_b = pH - \ log \frac{[\text{salt}]}{[\text{base}]} \ldots\ldots\ldots\ldots(\mathbf{2})$$

The equations (1) and (2) are called **Henderson-Hasselbalch** equations, these equations are useful for estimating the pH of buffer solution. It is also applicable to determine the amount of acid or base or their corresponding conjugate parts.

Applications of buffer

a. In biology, they are necessary for keeping the correct pH for proteins to work; if the pH moves outside of a narrow range, the proteins stop working and can fall apart.
b. A buffer of carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) is needed in blood plasma to maintain a pH between 7.35 and 7.45.
c. Industrially, buffer solutions are used in fermentation processes.

Solved examples

1. A buffer solution was made by dissolving 10.0 g of sodium acetate in 200.0 mL of 1.00 M acetic acid. Assuming the change in volume when the sodium acetate is not significant,

estimate the pH of the acetic acid/sodium acetate buffer solution. The K_a for acetic acid is 1.7×10^{-5}.

Solution,

concentration of CH_3COOH in mole per liter = 1.00 ×100/200.0 = 0.200 M

The concentration of salt in the solution = $\frac{10}{82.03} \times \frac{1000}{200}$

= 0.6095M

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$pK_a = pH - \log [salt]/[acid]$$

$$\mathbf{pH} = pKa + \log [salt]/[acid]$$

$$pH = -\log(1.7\times10^{-5}) + \log(0.2000/6095)$$

$$pH = 4.7696 + 0.4849$$

$$= 5.25$$

2. **Calculate the ratio of ammonium chloride to ammonia that is required to make a buffer solution with a pH of 9.00. The Ka for ammonium ion is 5.6×10^{-10}.**

solution,

$$pH = 9$$

$$[H^+] = \text{antilog}^{-pH}$$

$$= 1.0\times10^{-9}$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

$$K_b = [H_3O^+][NH_3]/[NH_4^+]$$

$$[H_3O^+] = [H^+] = ka\times[NH_4^+]/[NH_3]/$$

$$1 \text{ x } 10^{-9} = 5.6 \text{ x } 10^{-10}[NH_4^+]/[NH_3]$$

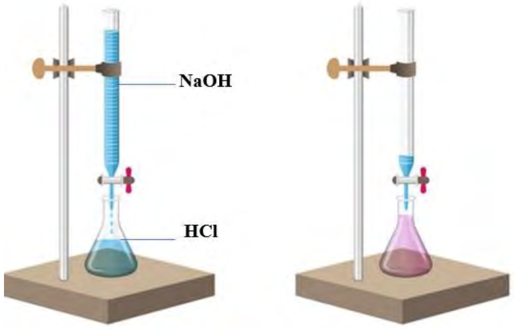
$$[NH_4^+]/[NH_3] = 1.786/1$$

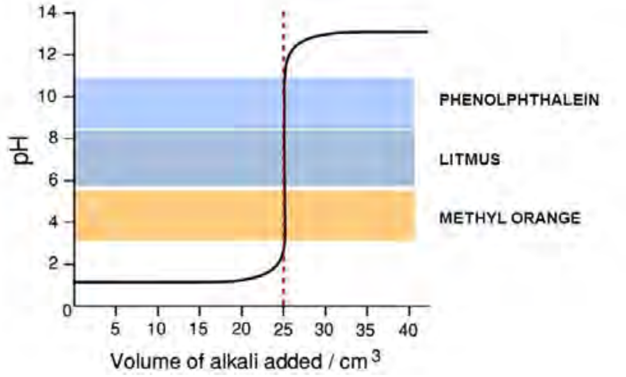
Try yourself

a. Calculate the pH of a buffer solution that initially consists of 0.0500 M NH_3 and 0.0350 M NH_4^+.
(Note: K_b for NH_4^+ is 5.6 x 10^{-10})
b. Formic acid buffer is prepared with 0.010M each of formic acid (HCOOH) and sodium formate . The Ka for formic acid is 1.8×10^{-4}. What is the pH of the solution? Find the pH if 0.0020 M NaOH is added to a liter of buffer. What would be the pH of the sodium hydroxide if the buffer concentration had been 0.10M instead of 0.010M?

2.15 Indicators and selection of indicators in acid base titration

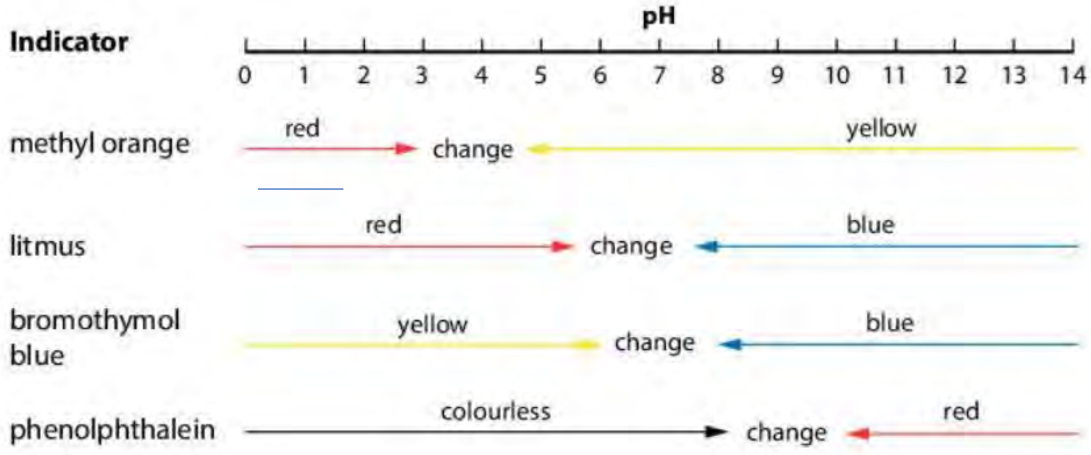
Activity: Acid base titration between NaOH and HCl and the corresponding change in pH of the solution with the addition of base is given in the below .Study the figure and graph and fill the table .

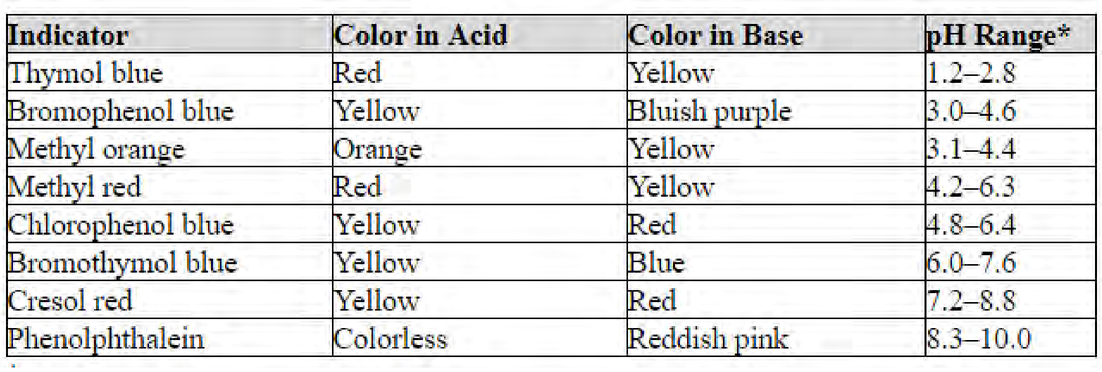




pH of acid before starting the experiment	pH of the solution after the complete reaction	Suitable indicator

An acid-base indicator is a weak acid or base that changes color over a specific pH range. It helps to determine the endpoint of a titration by a sharp change in its color when the reaction between the acid and base is complete. Depending upon the types of acid and base used in the titration, different types of acid base indicators can be used. Different indicators show different color in acidic and basic solution. There is a particular range of pH over which the color of specific indicator changes. This range is called **pH range**.





Indicator	Color in Acid	Color in Base	pH Range*
Thymol blue	Red	Yellow	1.2–2.8
Bromophenol blue	Yellow	Bluish purple	3.0–4.6
Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8
Phenolphthalein	Colorless	Reddish pink	8.3–10.0

A. Titration between strong acid and strong base

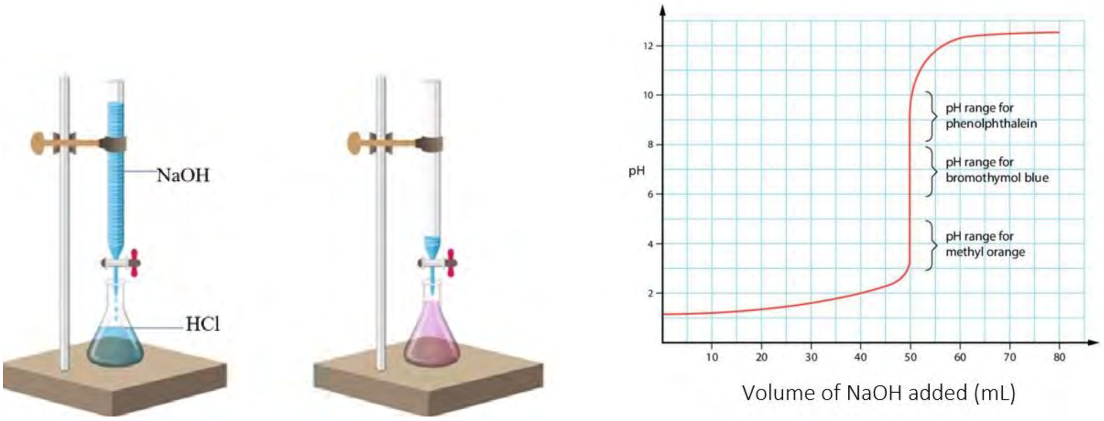


Figure: A graph of pH versus volume of alkali in the titration of strong acid and strong base

In a strong acid vs. strong base titration (e.g., HCl vs. NaOH), both the acid and base dissociate completely in water. For example:

$HCl \rightarrow H^+ + Cl^-$

$NaOH \rightarrow Na^+ + OH^-$

When mixed, the H^+ and OH^- ions neutralize each other to form water:

$H^+ + OH^- \rightarrow H_2O$

At the equivalence point, the moles of H^+ equal the moles of OH^-, and since both are from strong species, the resulting solution is neutral with a pH of 7 (at 25°C, assuming standard conditions).

When alkali is added from burette to the titration flask, initially, the pH of solution in conical flask gets increased slowly due to less amount of alkali. However, pH value changes rapidly at the equivalence point (~3.5 to ~9.5). The pH transition here is very steep jumping from highly acidic (e.g., pH 3) to highly basic (e.g., pH 11) over a tiny volume of titrant near the equivalence point. Since the pH jump is large, any indicators capable of changing its color within this range (methyl orange, phenolphthalein, bromothymol blue) can be used in this titration.

Titration of strong acid with weak base

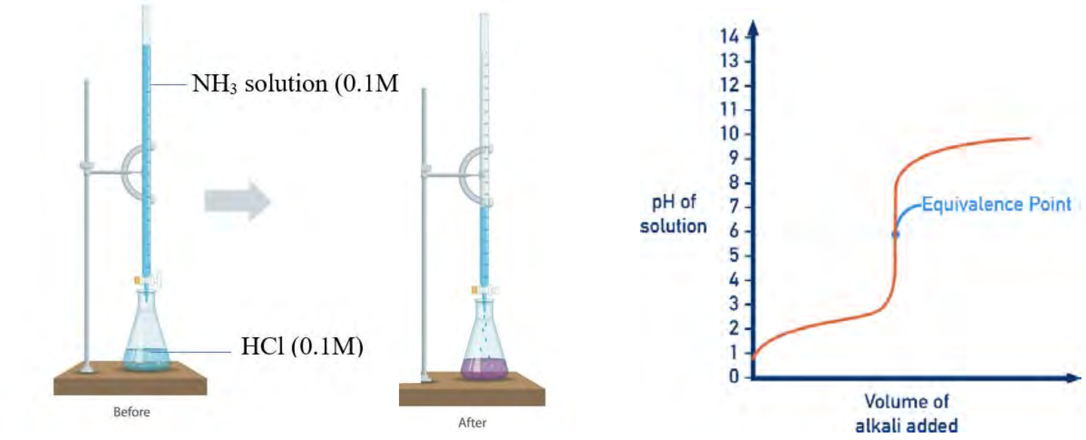
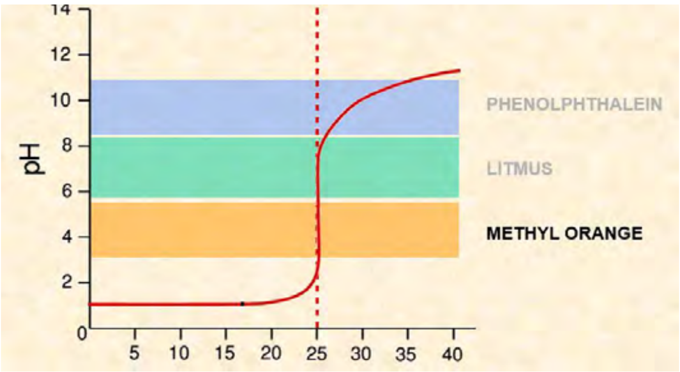


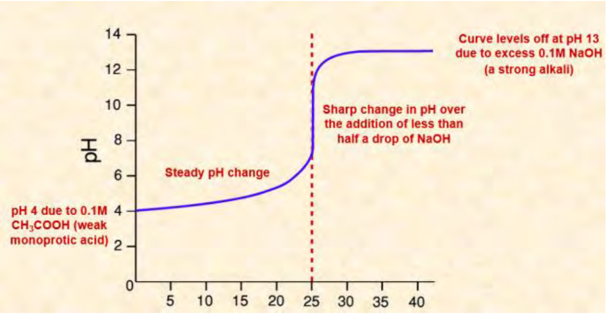
Figure: A graph of pH versus volume of alkali in the titration of strong acid and weak base

When weak base (NH_4OH) is dropped into the solution of strong acid kept in conical flask, there is a rapid change in pH from 3.5 to 7. Thus, any indicator which changes colour within this pH range will be suitable to indicate the equivalence point of this titration. Methyl orange or bromothymol blue can be used to indicate the end point of titration.



Titration for weak acid and strong base

The pH versus volume of alkali plot for the titration between acetic acid and sodium hydroxide is shown in the following figure.



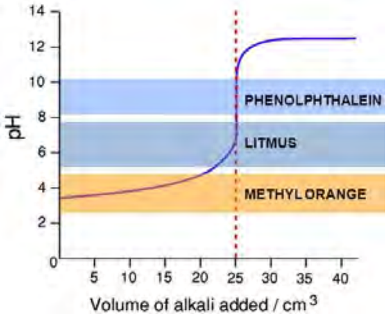
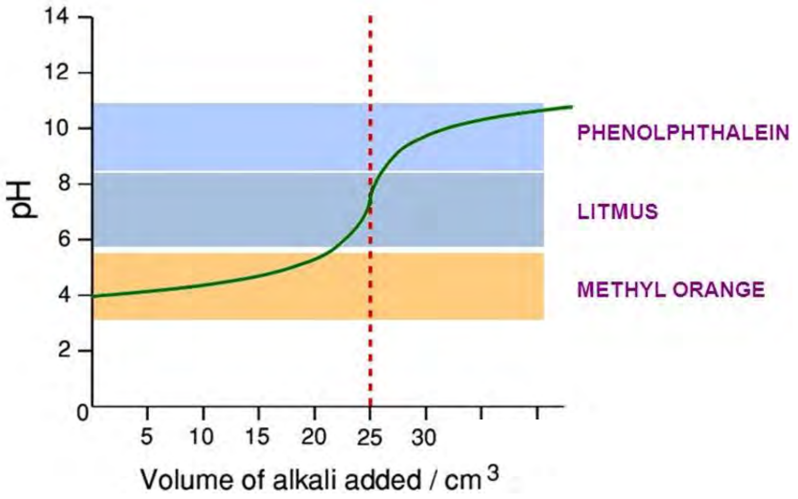


Figure: A graph of pH versus volume of alkali in the titration of weak acid and strong base

In this type of titration, sodium hydroxide solution is run form the burette into the solution of acetic acid in the titration flask. With the addition of alkali, the pH value of the solution in the conical flask gets increased and shows sharp change in the pH range of ~6 to ~9.5. Any indicator capable of changing its color within this range can be a suitable indicator for the determination of end point of the titration. Herein, phenolphthalein is suitable indicator.

Try yourself

The plot between pH and volume of alkali added for the weak acid (CH_3COOH) and weak alkali (NH_4OH) is given below. Why is there no suitable indicator to detect the end point of this titration?



2.16 Types of salts: Acidic salts, basic salts, simple salts, complex salts (introduction and examples)

Activity:

a) Add a spatula-full of $CuSO_4$, NaCl, and Na_2CO_3 in separate beakers, each containing 20 mL of distilled water.
b) Dip the universal indicator paper or pH meter in all three beakers and measure the pH of each solution.
c) Observe any color changes, fill the table and analyze the results.

Salt solution	colour	pH

Black salt (Birenoon)

Pink salt (Sidhenoon)

Alum (Fitkiri)

You are familiar with common salt in your kitchen. Besides these, there are other salts like potash alum (*fitkiri*), baking soda, black salt (*birenoon*), Himalyan Pink salt (*sidhe noon*) washing soda, etc. commonly used in our daily life. Each of these salts contains basic radical (cation) and acid radical (anion).

A salt is a compound formed by the combination of basic radical and acid radical.

Depending upon the nature and number of radicals present in salt, they are classified into different types.

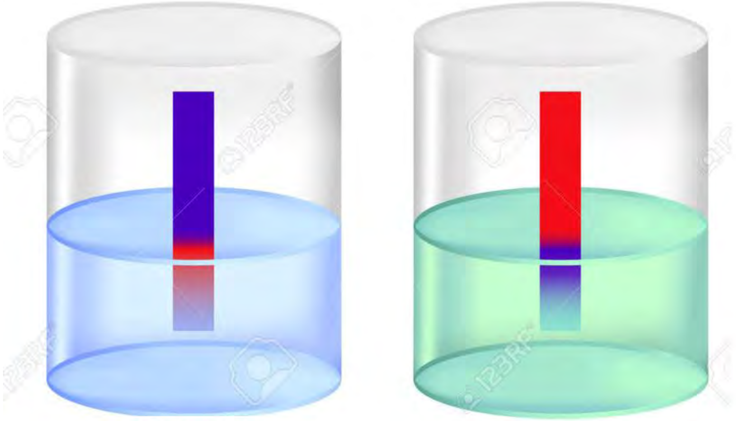
A. Simple salt

These salts consist of only one type of cation and one type of anion. Sodium chloride (NaCl), copper sulphate ($CuSO_4$), Sodium acetate (CH_3COONa), and ammonium acetate (NH_4COONa), are some examples of simple salt. Many simple salts are soluble in water, and they dissociate into their constituent ions when dissolved.

Simple salt refers to a type of salt that forms from the complete neutralization of an acid by a base.

Based on the pH of resulting solution, simple salt can be classified into

Acidic salt, basic salt and neutral salt.



$CuSO_4$ solution

Blue Litmus turns red

CH_3COONa solution

Red Litmus turns blue

Acidic salt: Salts such as copper sulphates, zinc nitrates, ammonium chloride, etc. gets dissolved in water. The resulting solution becomes acidic. These types of salts are called acidic salt.

$$CuSO_4 + 2H_2O \rightarrow Cu(OH)_2 + H_2SO_4$$

a. **Basic salt:** Salts such as sodium acetates (CH_3COONa), potassium formate ($HCOOK$), etc. gets dissolved in water. The resulting solution imparts the solution basic. These types of salts are called basic salt.

$$CH_3COONa + 2H_2O \rightarrow CH_3COOH + NaOH$$

b. **Neutral salt:** Salts such as sodium chloride ($NaCl$) and ammonium formate ($HCOONH_4$) gets dissolved in water. The resulting solution is neutral.

$$NaCl + H_2O \rightarrow Na^+OH^- + H^+Cl^-$$

There are some salts which are formed by incomplete neutralization of acid by base. Such types of salt still contain one or more replaceable hydrogen atoms. These types of salts are termed as acid salts. In the following reactions, $NaHSO_4$ is formed by the incomplete neutralization of sulphuric acid by sodium hydroxide. Therefore, sodium bisulphate ($NaHSO_4$) is acid salt. However, sodium sulphate is formed by the complete neutralization of sulphuric acid by sodium hydroxide.

$$H_2SO_4+NaOH\rightarrow\mathbf{NaHSO_4}+H_2O$$
$$H_2SO_4+NaOH\rightarrow\mathbf{Na_2SO_4}+H_2O$$

Uses of salts

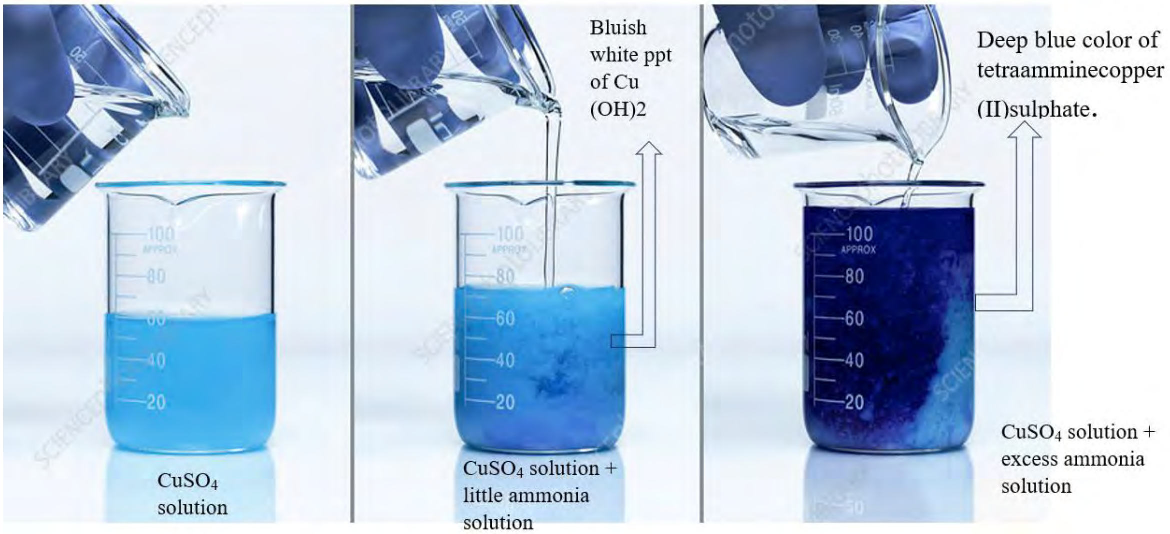
a. Sodium bicarbonate ($NaHCO_3$) is used as a leavening agent in baking. When mixed with an acidic ingredient, it produces carbon dioxide gas, helping baked goods rise.
b. Acidic salts like sodium bicarbonate and sodium hydrogen phosphate are components of buffer solutions, which are used in laboratories to maintain a stable pH in biological and chemical reactions.
c. Basic salts like basic copper carbonate are used as fungicides to protect plants from fungal infections.
d. Basic salts are used in industrial processes, especially in the **metal refining industry**. Zinc hydroxy chloride, for instance, is used in galvanization and other metallurgical processes.

B. Complex salt

When copper sulphate is treated with limited amount of ammonium hydroxide solution, there is a formation of bluish white precipitate of copper hydroxide.

$$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$$

Upon addition of excess of ammonium solution, the precipitate gets dissolved and gives deep blue colored solution of tetraamminecopper(II)sulphate.



Tetra ammine copper(II)sulphate, $[Cu(NH_3)_4]SO_4$ is complex salt. These types of complex salt contain at least one **complex ion** within its structure. Complex ions are formed when a central metal ion is coordinated by neutral molecules having lone pair of electrons or ions called **ligands**. The overall complex salt is an ionic compound that contains both a **complex ion** (the cation or anion) and a counterion of opposite charge to balance the overall charge.

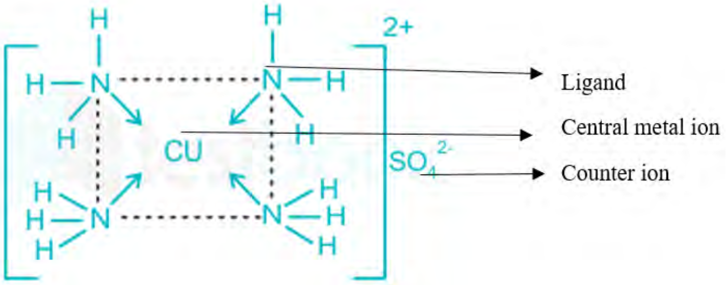
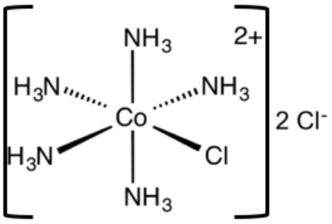


Figure: Structure of Tetraamminecopper (II)sulphate

Do you know complex salts like EDTA complexes are used to remove calcium and magnesium ions in water in water softening process.

Try yourself

Identify the ligand, central metal ion and counter ion in the given complex and write the molecular formula of the salt.



2.17 Hydrolysis of salt

Some of the common applications of hydrolysis are given :

a. **Alum** (Potassium Aluminum Sulfate - $KAl(SO_4)_2$) commonly called ***fitkir***i is used in pickling and water purification. When dissolved in water, the aluminum ion (Al^{3+}) undergoes hydrolysis, leading to an acidic solution. Aluminum reacts with water to form $Al(OH)_3$ and releases hydrogen ions (H^+), decreasing the pH .The resulting solution is acidic in nature and helps in the preservation of food (pickling).

b. **Sodium bicarbonate**, often used in cooking, undergoes hydrolysis in water. This leads to a mildly basic solution due to the bicarbonate ion (HCO_3^-), which reacts with water to produce hydroxide ions (OH^-) and carbonic acid (H_2CO_3).So that it can neutralize acids, making it a common home remedy for indigestion (heartburn).

c. **Soap** is one product created by hydrolysis. When a triglyceride or a fat is hydrolyzed, glycerin is produced as well as fatty acids. The glycerin then reacts with those fatty acids to turn them into a specific type of salt commonly known as soap.

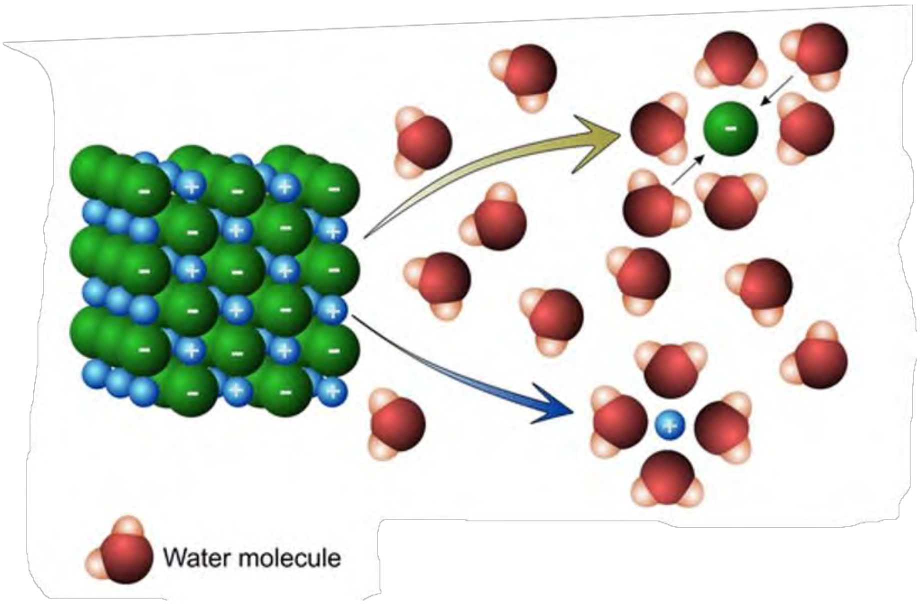


Figure: interaction of ions of salt with water.

Hydrolysis is reverse of neutralization.

Acid +Base → salt + water (neutralization)

Salt + water → Acid +Base (hydrolysis)

The process of interaction of cation or anion or both ions with water is called hydrolysis of the salt.

2.17.1 Hydrolysis of salt of strong base and strong acid

Salts formed by the neutralization of strong acid and strong base are **neutral** in nature as the bonds in the salt solution will not break apart. They generally get hydrated but do not hydrolyze. Such salts are neutral salts.

For Cati example: NaCl

NaCl + $H_2O \rightarrow NaOH + HCl$

or, $Na^+ + Cl^- + H_2O \rightarrow Na^+ + OH^- + H^+ + Cl^-$

Cancelling the common ion on both sides

$H_2O \rightarrow OH^- + H^+$

In this case $[OH^-] = [H^+]$. The solution is neither acidic nor basic i.e. it is neutral to litmus. Neither cation nor anion reacts with water. Hence **salt of strong acid and strong base does not undergo hydrolysis.**

2.17.2Hydrolysis of salt of weak base and strong acid

Salt of strong acid and weak base like NH_4Cl, $MgSO_4$, $CuSO_4$, etc. hydrolyze to give **acidic** solution.

For example, dissolving ammonium chloride in water results in its dissociation, as described by the equation

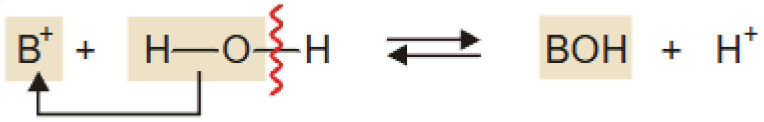
$NH_4Cl(s) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$

The ammonium ion is the conjugate acid of the weak base, NH_4OH

The acid hydrolysis reaction is represented by

$NH_4^+(aq) + H_2O(l) \rightleftharpoons H^+(aq) + NH_4OH\ (aq)$

Since the resulting solution contain excess of hydrogen ion, the solution is acidic in nature. As the cation (NH_4^+) interacts with water, it is referred as **cationic hydrolysis**.



2.17.3Hydrolysis of salt of strong base and weak acid

Salt of strong base and weak acid like CH_3COONa, $HCOONa$, etc. gets hydrolyzed to give basic solution.

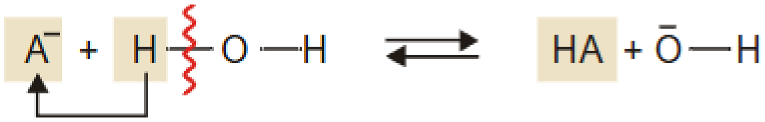
For example, dissolving sodium acetate in water results in dissociation

$NaCH_3CO_2(s) \leftrightharpoons Na^+(aq) + CH_3CO_2^-(aq)$

The acetate ion, $CH_3CO_2^-$ is the conjugate base of weak acetic acid (CH_3COOH). The anionic reaction is represented by

$CH_3COO^- + H_2O \leftrightharpoons CH_3COOH + OH^-$

The resulting solution contains excess of OH^- ions making the solution alkaline. As the anion of the salt interacts with water, it is **anionic hydrolysis.**



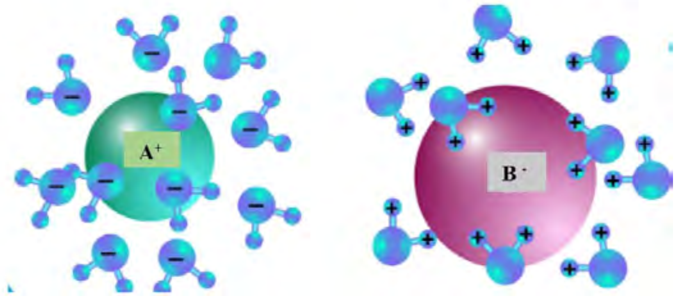


Figure: cationic and anionic hydrolysis

Try yourself:

Ammonium acetate is a simple salt. Whether its aqueous solution is acidic, basic or neutral?

Project work

1. Use A4 paper or chart paper, draw the table as given and define each term to fill the table

Acid	Base	Neutralization	Example
Arrhenius			
Bronsted			
Lewis			

2. Collect the different substances from your laboratory or kitchen and measure the pH using pH meter or universal indicator of each. Record the pH and compare their acidic and basic strength in the table below.

Substance	pH	pOH	Concentration of hydrogen ions
Curd			
Apple juice			
Vinegar			
HCl			
H_2SO_4			
NaOH			
KOH			
Na_2CO_3			
Tap water			
Rain water			
Underground water			

Exercise

A. Multiple choice questions

1. **Which of the following is a limitation of Arrhenius' concept of acids and bases?**
   a) It cannot explain acidic behavior of substances in non-aqueous solvents.
   b) It does not consider ionization of bases.
   c) It fails to differentiate between weak and strong acids.
   d) It defines acids and bases only based on pH.

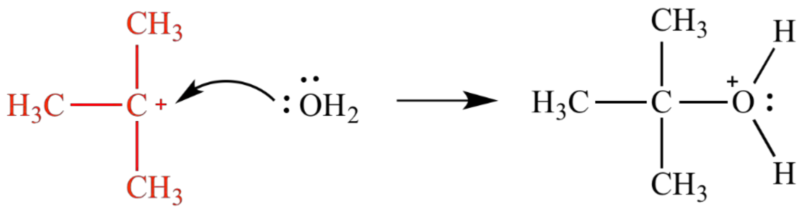
2. **Which of the following statements is in agreement with the Bronsted-Lowry concept?**
   a) A base is an electron-pair donor.
   b) Acids and bases are proton donors and acceptors, respectively.
   c) Acids and bases are substances that increase H^+ and OH^- in water.
   d) Acids and bases are proton acceptors and donors, respectively.

3. **Which of the following is the conjugate acid of NH_3?**
   a) NH_4^+
   b) NH_2^-
   c) NH_3
   d) OH^-

4. **The relative strength of an acid is affected by various factors. Which of the following best explains the relative strength?**
   a) Its pH value.
   b) The stability of its conjugate base.
   c) The amount of water it can dissolve.
   d) Both a and b.
5. **HCl is a stronger acid than HF. Which of the following statement gives the correct explanation?**
   a) HCl has a lower bond dissociation enthalpy.
   b) HCl ionizes more completely in water.
   c) HCl is less electronegative.
   d) All of these.

6. **Lewis acid is a lone pair acceptor. Which of the following is not a Lewis acid?**
   a) BF_3
   b) $AlCl_3$
   c) NH_3
   d) H^+
7. **A Lewis base must have:**
   a) An unshared pair of electrons.
   b) A proton donor capability.
   c) A hydroxide group.
   d) None of these.

8. The reaction between carbocation and water molecule is shown below .What is the reason of developing positive charge in the oxygen after the reaction ?



   a) Oxygen has gained lone pair electron
   b) Oxygen has lost protons
   c) Oxygen has gained protons
   d) Oxygen has lost lone pair electrons

9. **According to Ostwald's dilution law, which of the following is true about the degree of ionization of a weak electrolyte?**
   a) Inversely proportional to its concentration.
   b) Directly proportional to its concentration.
   c) Independent of its concentration.
   d) inversely proportional to temperature

10. **Which of the following statement explains the less ionization of acetic acid ?**
   a) It has a low dissociation constant.
   b) Its equilibrium constant is high.
   c) It cannot dissociate in water.
   d) It is an organic acid

10. **The ionic product of water (Kw) depends upon temperature .Which of the following can increases the value of kw?**
   a) Decreasing temperature because ionization of water decreases
   b) Increasing temperature because ionization of water decreases
   c) Decreasing temperature because ionization of water increases
   d) increasing temperature because ionization of water increases

11. **Which acid has the highest pKa value?**
   a) HCl
   b) HF
   c) HNO_2
   d) CH_3COOH

16. **Which solution has a highest pH value?**
   a) 10^{-2} M HCl
   b) 10^{-3} M NaOH
   c) Pure water
   d) 10^{-2} M NH_4OH

17. **Which of the following statement best describes the solubility product (Ksp) of a salt?**
   a) The product of the molar solubility of its ions.
   b) The equilibrium constant for the dissolution reaction.

c) The maximum concentration of solute in a solution.
d) Both a and b.

18. **Which of the following salts is least soluble in water at 25°C?**
a) AgCl (Ksp = 1.8×10^{-10})
b) $PbCl_2$ (Ksp = 1.6×10^{-5})
c) $BaSO_4$ (Ksp = 1.1×10^{-10})
d) $CaCO_3$ (Ksp = 4.9×10^{-9})

21. **Which of the following pairs can resist the change in pH even after the addition of 2 drops of NaOH ?**
a) HCl and NaOH
b) CH_3COOH and CH_3COONa
c) NaCl and NaOH
d) HNO_3 and NH_4OH

22. **The pH of a buffer solution is determined by:**
a) The concentration of acid and base.
b) The pKa of the weak acid used.
c) The volume of the solution.
d) Both a and b.

23. **Phenolphthalein is suitable for titrations involving:**
a) Strong acid and strong base.
b) Weak acid and weak base.
c) Weak acid and strong base.
d) Both a and c.

25. **Hydrolysis of salt can result acidic ,basic or neutral solution .Which of the following solutions will be acidic due to hydrolysis?**
a) NaCl
b) NH_4Cl
c) KNO_3
d) Na_2SO_4

26. **Which of the following is an acidic salt and why is it called so?**
a) Na_2SO_4 because of cationic hydrolysis
b) NH_4Cl because of anionic hydrolysis
c) KCl because of cationic hydrolysis
d) NH_4NO_3 because of cationic hydrolysis

27. **Solution of NaCl does not undergo hydrolysis. What is the correct reason behind it ?**
a) It is a salt of a weak acid and a strong base.
b) Both Na^+ and Cl^- are spectator ions.
c) The ionic product of water (Kw) is too low.
d) None of these.

28. **A complex salt is one that contains:**
    a) Two cations or two anions.
    b) A metal atom surrounded by ligands.
    c) Simple ions only.
    d) Both a and b.
29. **In the hydrolysis of a salt derived from a weak acid and strong base, the expression for the pH is:**
    a) $pH=7+0.5(pKa-\log C)$
    b) $pH=7+0.5(pKb-\log C)$
    c) $pH=7-0.5(pKa+\log C)$
    d) $pH=7-0.5(pKb+\log C)$

B. Short answer questions

1. **Define the term with one example of each**
    a. **Bronsted acid**
    b. **Bronsted base**
    c. **Lewis's acid**
    d. **Lewis's base**
    e. **Conjugate acid**

2. **Write any two differences between**
    a. **Conjugate acid and conjugate base**
    b. **Ka and kb**
    c. **Hydrolysis of sodium acetate and hydrolysis of ammonium chloride**
    d. **Solubility and solubility product**
    e. **Acidic salt and basic salt**

3. **Give reason for the following statement**
    a. **Water is an amphoteric substance**
    b. **Phosphine (PH_3) is a Lewis base**
    c. **pH of 10^{-7} M HCl is not 7**
    d. **Ostwald's dilution law is not applicable for strong electrolytes**
    e. **HCl is added before passing H2S gas in the salt analysis of group II metal ions**

4. **Ammonia can act as Bronsted as well as Lewis base.**
    a. **give reason why is NH3 act as a Lewis base?**
    b. **Write an equation to show that ammonia is a Bronsted base and show the conjugate acid as well**
    c. **With the help of suitable chemical equiation explains the reaction of ammonia with water where water acts as a Bronsted base**

5. Laboratory-grade concentrated sulfuric acid is 98% pure and density is approximately 1.84 g/mL.
    a. What do you mean by concentrated acid?

b. What is the concentration of given acid in gram per liter and molarity?
c. Calculate the pH of this acid

6. Ostwald's dilution law relates to the dissociation of weak electrolytes in a solution. It provides a relationship between the dissociation constant, the concentration of the electrolyte, and the degree of dissociation (α).
    a. Derive the **derive the relationship between the dissociation constant (Ka) and the degree of ionization (α) for a weak acid.**
    b. **How does dilution affect the ionization of the acid?**
    c. **What is the limitation of this law?**

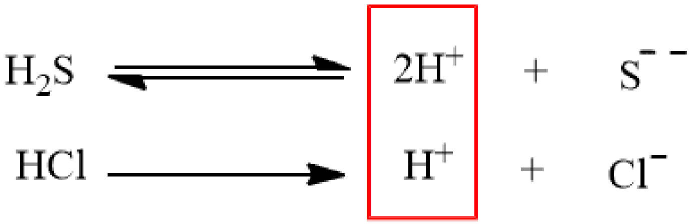
7. **A container contains 0.01 M solution of acetic acid (Ka = 1.8×10^{-5})**
    a. Why is acetic acid considered as a weak acid?
    b. What do you mean by dissociation constant (ka) of the acid?
    c. Calculate the pH of the given acid.

8. **Define the ionic product of water (Kw). Discuss how Kw changes with temperature and explain its significance in determining the pH of neutral water at different temperatures.**

9. The **solubility product constant** (Ksp) provides a quantitative measure of a compound's solubility in water.
    a. **Define the term solubility product constant and write Ksp value for the binary salt like AgCl**
    b. **Calculate the solubility of AgCl in water if** Ksp=1.8×10^{-10}**at 25°C.**
    c. Why is temperature mentioned while expressing solubility product value ?

10. For a salt like $Al_2(SO_4)_3$ which gives 5 ions upon dissociation.
    a. Write the equation of dissociation of this salt
    b. Write the ksp equation for this salt
    c. Calculate the solubility of $Al_2(SO_4)_3$ if its Ksp = 2×10^{-8} mol per liter at room temperature

11. The given example illustrates common ion effect and is applicable in the qualitative salt analysis of metal cation



    a. Define the term common ion effect . Expalin how does this effect affect the ionization of H_2S in the example above?
    b. **How is this effect applicable in salt analysis?**

12. Hydrolysis of salt may produce an acidic, basic, or neutral solution, depending on the nature of the salt. One of the hydrolysis reactions is given below.

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

   a. **Define the term hydrolysis**
   b. **What type of solution is produced in the example given above and why?**
   c. **What is the application of salt hydrolysis?**

13. **Describe the hydrolysis of salts with examples of:**
   a. A strong acid and a strong base.
   b. A weak acid and a strong base.
   c. A weak base and a strong acid. How does hydrolysis affect the pH of the solution in each case?

14. An acid base titration between oxalic acid and sodium hydroxide can be carried out using suitable acid base indicator
   a. What is the meaning of acid base indicator? Give two examples of such indicators
   b. Name the indicator suitable for the above titration and why is it suitable?
   c. What happens to the accuracy of titration if another indicator is used ?

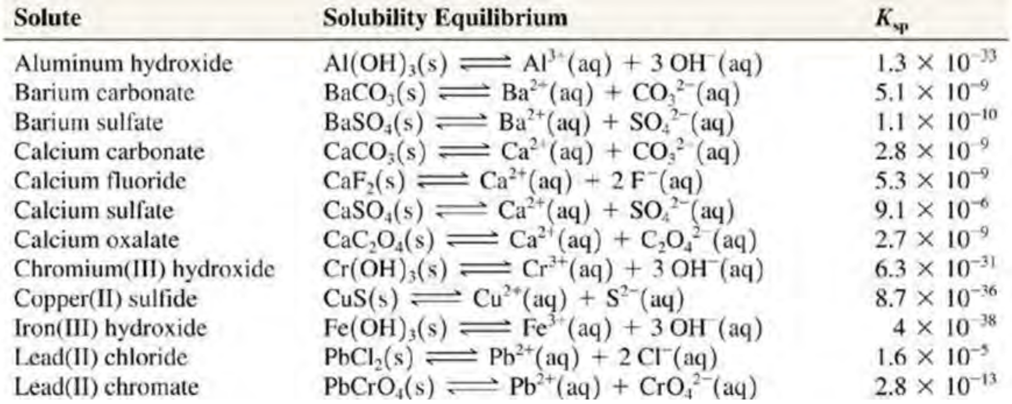
15. **Discuss the role of indicators in acid-base titrations. How do you select a suitable indicator for:**
   a) A strong acid-strong base titration.
   b) A weak acid-strong base titration?

16. **Explain the types of salts (acidic, basic, and neutral) with two examples for each. Discuss how the nature of the parent acid and base influences the properties of the salt**

C. Long answer questions

1. **The mixture of acetic acid and sodium acetate is an example of acidic buffer**
   a. **What do you mean by acidic buffer? Give another example of such buffer system.**
   b. **What is the application of buffer in human body?**
   c. **What is the mechanism of the buffer action for the given buffer ?**
   d. **Calculate the pH of this buffer using Henderson-Hasselbalch equation ($K_a = 1.8\times10^{-5}$)**

2. Solubility product of some sparingly soluble salts is given in the table
   a. Define the term solubility product and sparingly soluble salt.
   b. Calculate the solubility of $CaSO_4$ and Fe $(OH)_3$ in mole per liter and gram per liter.
   c. Using the information given compare the solubility of $CaCO_3$ with $BaSO_4$



Solute	Solubility Equilibrium	K_{sp}
Aluminum hydroxide	$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\,OH^-(aq)$	1.3×10^{-33}
Barium carbonate	$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$	5.1×10^{-9}
Barium sulfate	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	1.1×10^{-10}
Calcium carbonate	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	2.8×10^{-9}
Calcium fluoride	$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$	5.3×10^{-9}
Calcium sulfate	$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$	9.1×10^{-6}
Calcium oxalate	$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$	2.7×10^{-9}
Chromium(III) hydroxide	$Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3\,OH^-(aq)$	6.3×10^{-31}
Copper(II) sulfide	$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$	8.7×10^{-36}
Iron(III) hydroxide	$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\,OH^-(aq)$	4×10^{-38}
Lead(II) chloride	$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$	1.6×10^{-5}
Lead(II) chromate	$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$	2.8×10^{-13}

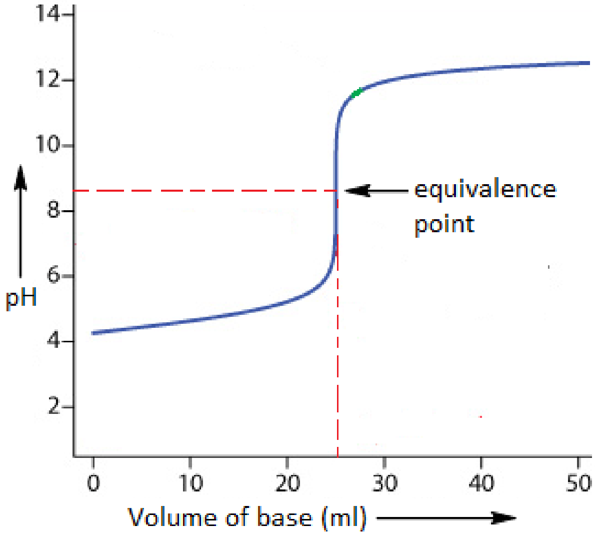
3. The given graph shows the change in pH of acid with the addition of base from the burette.

a. What is the trend of change in pH with the addition of base and why is this trend observed with the addition of base ?

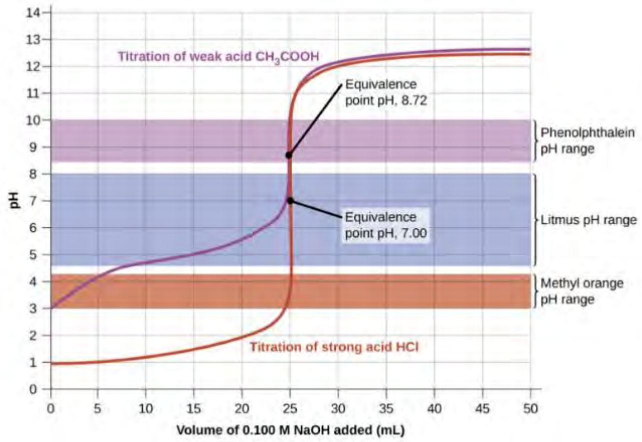
b. What is the starting pH of the solution and what does this indicate about the nature of acid?

c. Name the indicator suitable for this titration and give reason behind.

d. Draw the graph for the same solution keeping acid in the burette instead of titration flask.



4. pH versus volume of alkali added for different titrations are given in the graph below,

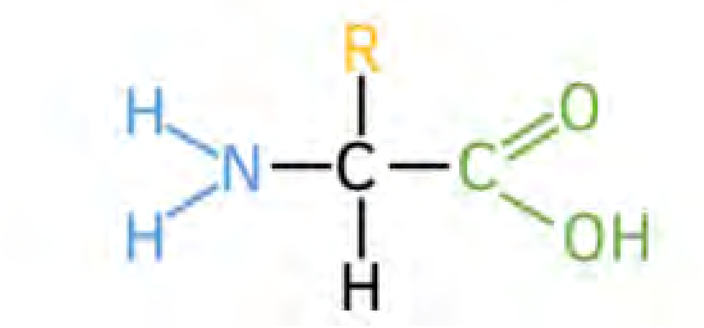


a. what is the starting pH of HCl and why does pH increase with the addition of NaOH?

b. Find out the pH at which there is a sharp change in pH for the titration of HCl with NaOH.

c. Name the indicator that is suitable for the titration of acetic acid with NaOH and why ?

5. **Amino acids** are organic molecules that serve as the building blocks of proteins. These acids are amphoteric in nature. Structure of amino acid molecule is given:



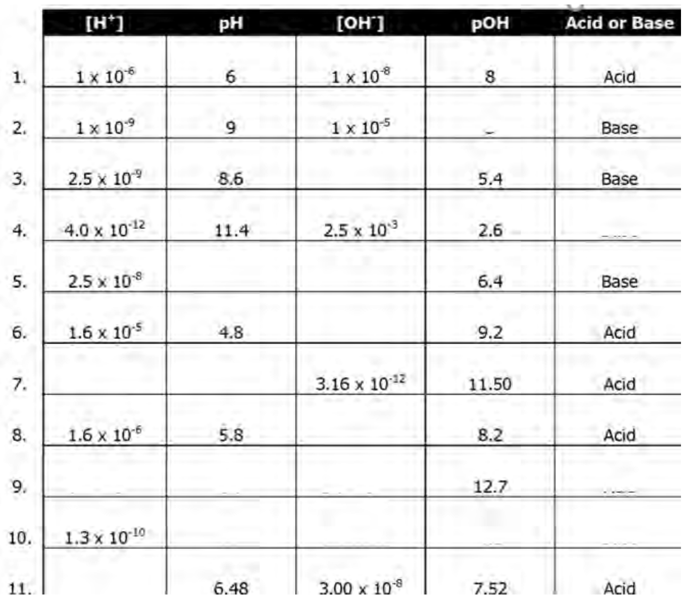
a. What is the meaning of amphoteric substance?
b. What could be the reason so that the molecule of amino acids are amphoteric
c. Write the reaction of this acid with hydrogen ion and hydroxide ion showing amphoteric nature.

6. A buffer solution is made by mixing 0.050M acetic acid and 0.050M sodium acetate.
   a. What do you mean by buffer solution what is the role of buffer in human body?
   b. Calculate the pH of the given buffer.
   c. Calculate the change in pH when 0.001 mole of hydrochloric acid is added to one liter of solution, assuming the volume increases upon adding the HCl is negligible.
   d. Compare this pH if the same amount of HCl is added to a liter of pure water

7. A buffer solution is prepared by mixing 0.1 M formic acid (HCOOH) and 0.05 M sodium formate (HCOONa).
   a. What is an acidic buffer, and how does the formic acid-sodium formate system qualify as one? Provide another example of an acidic buffer.
   b. Explain the role of buffers in maintaining pH stability in biological systems, such as blood.
   c. Calculate the pH of this buffer using the Henderson-Hasselbalch equation, given that the Ka of formic acid is 1.77×10^{-4}.

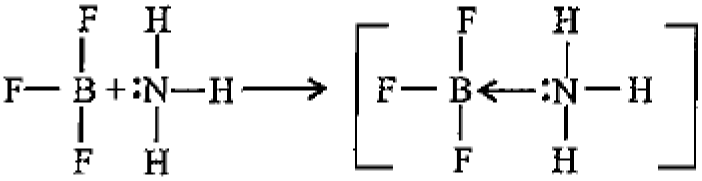
8. The solubility product constants (Ksp) of some sparingly soluble salts are as follows: $BaSO_4$ (1.1×10^{-10}) and Ag_2SO_4 (1.2×10^{-5}).
   a. What do you mean by solubility product and sparingly soluble salt?
   b. Write down the expression of solubility product of BaSO4 and $Ag_2(SO_4)$.
   c. Calculate the solubility of $BaSO_4$ and $Ag_2(SO_4)$in moles per liter and grams per liter in pure water.
   d. Based on your calculations, determine which of the salts will precipitate first in their solution and why?

9. A table with concentration of hydrogen ion, hydroxide ion pH and pOH are given below.
   a. Define the terms pH and pOH and write their relationship.
   b. Complete the table given below .



	$[H^+]$	pH	$[OH^-]$	pOH	Acid or Base
1.	1×10^{-6}	6	1×10^{-8}	8	Acid
2.	1×10^{-9}	9	1×10^{-5}		Base
3.	2.5×10^{-9}	8.6		5.4	Base
4.	4.0×10^{-12}	11.4	2.5×10^{-3}	2.6	
5.	2.5×10^{-8}			6.4	Base
6.	1.6×10^{-5}	4.8		9.2	Acid
7.			3.16×10^{-12}	11.50	Acid
8.	1.6×10^{-6}	5.8		8.2	Acid
9.				12.7	
10.	1.3×10^{-10}				
11.		6.48	3.00×10^{-8}	7.52	Acid

10. One of the acid base reactions is given below:



a. Identify the acid and base in the reaction given and give reason why are they called so?
b. Name the concept by which it explains the above reaction
c. Write the similar reactions with NH_3 and water and BF_3 and water
d. What is the limitations of this concept?

11. Solve the given numerical problems

a. Calculate the solubility product constant for $PbCl_2$ (mw = 278.1), if 50.0 mL of a saturated solution of $PbCl_2$ was found to contain 0.2207 g of $PbCl_2$ dissolved in it.
b. A solution is 0.010M in barium chloride and 0.020M in strontium chloride. Can either Ba^{2+} or Sr^{2+} be precipitated selectively with concentrated sodium sulfate solution? Which ion will precipitate first?
c. Estimate the molar solubility of Ag_2CrO_4 in pure water if the solubility product constant for silver chromate is 1.1×10^{-12} ?

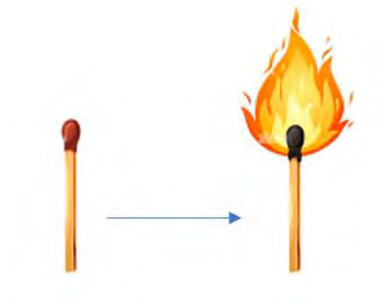
Unit 3
Chemical Kinetics

3.1 Introduction

Activity:

The figures given below shows the chemical change. Observe the figures in pair and

a. Identify which one is slow and which one is fast process?
b. Discuss about the product formed in each case



Do you know? Conversion of carbon to diamond under high pressure and temperature in the Earth's mantle takes millions of years. Likewise, conversion of some isotopes like (uranium-238), to another radioactive species takes millions to billions of years.

These processes are said to be very slow processes. In the other hand there are some processes which are very fast and occur almost instantaneously, often in fractions of a second.

Precipitation reactions occur very fast forming the precipitate. Explosive reactions are also very fast reactions occur in microsecond releasing large amount of energy.

Chemical kinetics is the branch of chemistry that studies the rates of chemical reactions, the factors affecting those rates, and the mechanisms by which reactions occur.

The answer of following questions can be obtained from the study of chemical kinetics.
why some reactions are slow and other are fast?

What makes a particular reaction slow and fast?

How a reaction takes place?

Chemical kinetics helps to monitor the rate of reaction and control the product formation. These are key factors in industrial chemistry to pharmaceuticals.

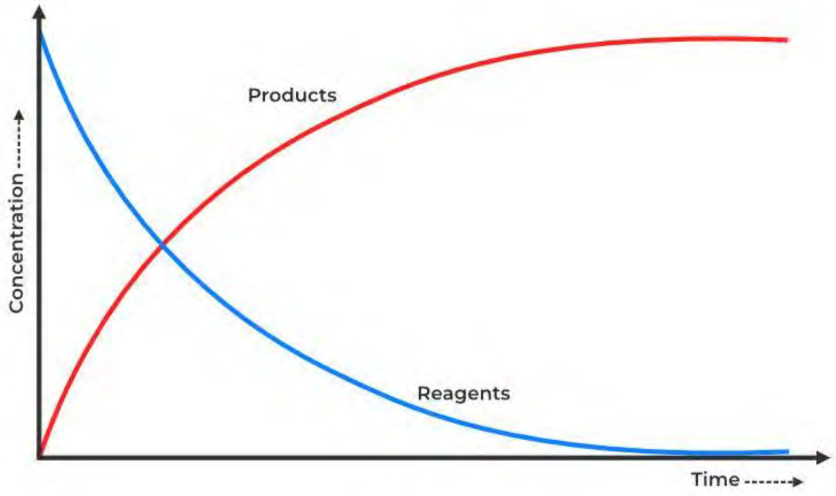
Figure: precipitation reaction is an example of fast reaction

Do you know?

a. Electron transitions between energy levels occur on the order of femtoseconds (10^{-15} s) to attoseconds (10^{-18} s)
b. The reaction between NaOH and HCl occurs within milliseconds to a few seconds.
c. The rusting of iron occurs over a timescale ranging from a few hours to several months, depending on environmental conditions.
d. The formation of petroleum products takes millions of years.

3.2 Rate of reactions: Average and Instantaneous rate of reactions

Activity: Analyze the given graph and identify the species whose concentration decreases and the one whose concentration increases over time. Discuss in pair behind the cause of these changes.



Chemical reactions proceed at extensively different speeds depending on the nature of the reacting substances, the type of chemical transformation, the temperature, and other factors. The speed at which reactants are converted into products is rate of reactions. If the conversion is at higher speed than is to be faster reaction or higher rate of reaction otherwise is called slow reaction or rate of reaction is less. Rate are usually expressed as the change in concentration of a reactant or product per unit time,

e.g., rate= −d[Reactant]dt

Rate is usually expressed as mol per liter per second or **Mol L^{-1} S^{-1}**

Average Rate of Reaction:

The average rate of reaction measures the change in the concentration of reactants or products over a finite time interval. It provides an overall picture of how fast a reaction occurs during that period.

$$\text{Average Rate} = \frac{-\Delta[\text{Reactant}]}{\Delta t} = \frac{\Delta[\text{Product}]}{\Delta t}$$

Where, Δ[Reactant] is the change in reactant concentration.

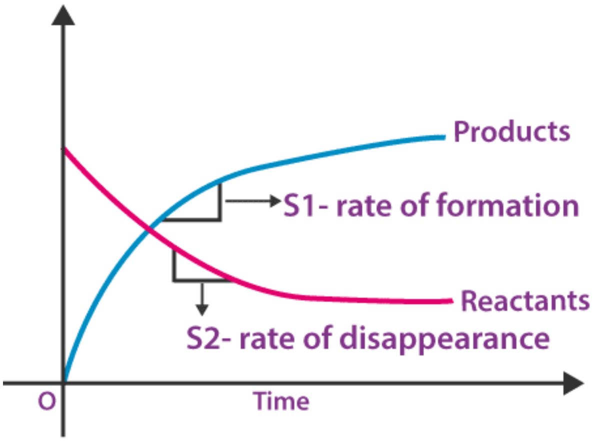
Δ[Product] is the change in product concentration.

Δt is the time interval.

Negative sign indicates that the concentration of the reactant is decreasing whereas positive sign indicates that the concentration of the product is increasing

In the reaction A→B, if the concentration of A decreases from 0.5 M to 0.3 M over 10 seconds, the average rate is:

$$\text{Average Rate} = \frac{-(0.3 - 0.5)}{10} = 0.02\,\text{M/s}.$$



Average rate of reaction can be calculated from the slope of the graph (concentration vs time) .

Remember that the change in concentration of reactant or product during the chemical reaction can be measured experimentally by monitoring the change in properties of the chemicals involved. Examples

a. change in pH (for acid base reactions) s
b. change in conductivity (for reactions involving electrolytes)
c. change in mass or volume (for reactions involving solids or gases)
d. change in color (for reactions involving transition metals or other colored compounds).

Instantaneous Rate of Reaction:

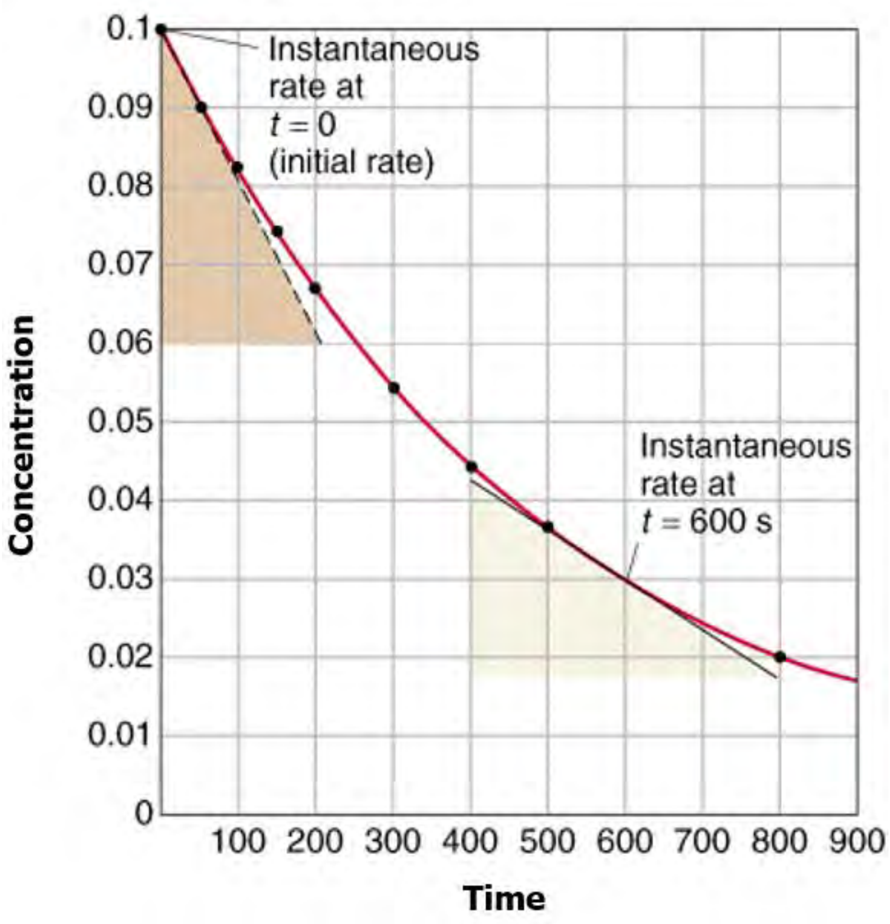


Figure: the tangent of the slope of the graph gives the instantaneous rate

In the Average Rate of Reaction, when the change in the time interval is very less i.e., $\Delta t \rightarrow 0$ then the rate of reaction is termed as **Instantaneous Rate of Reaction.**

Let us suppose that the small change in concentration is dx in the small interval of time **dt**. Then the rate of reaction at that instant is given by $\frac{dx}{dt}$. It represents the slope of the tangent to the concentration-time curve at a particular point.

The instantaneous rate of reaction is the rate at a specific moment in time.

$$\text{Instantaneous Rate} = \left|\frac{d[\text{Reactant}]}{dt}\right| = \frac{d[\text{Product}]}{dt}$$

Where d[Reactant]is the derivative of reactant concentration with respect to time.

Both rates are useful for understanding reaction dynamics: the average rate offers a broader perspective, while the instantaneous rate captures the reaction's behavior at a specific moment.

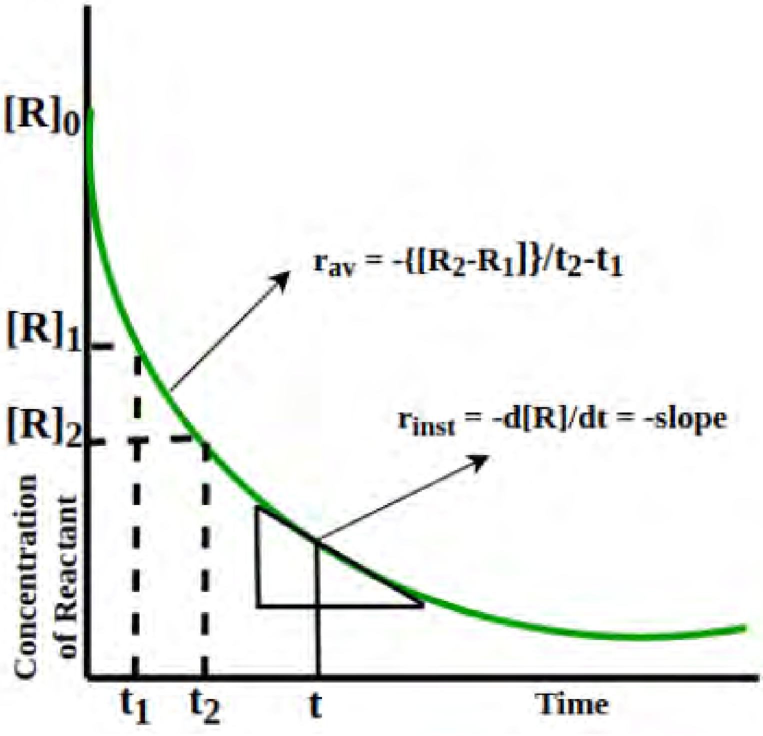


Figure: average and instantaneous rate of reaction

Initial rate means the instantaneous rate of reaction at t = 0

Try yourself

Complete the missing information in the table given:

Aspect	Average Rate	Instantaneous Rate
Time Interval	Over a finite time, interval (Δt)	………………………….
Representation	………………..	Slope of a tangent line on the graph
Accuracy	………………	……………………..

Relative Rates of Reaction

The rate of a reaction may be expressed as the change in concentration of any reactant or product. For any given reaction, these rate expressions are all related simply to one another according to the reaction stoichiometry. For example:

$$2H_2O \xrightarrow{\text{Electricity}} 2H_2 + O_2$$

There are three ways by which the rate of the given reaction can be monitored i.e., rate of decomposition of water or the rate of formation of either H_2 or O_2. The rate of decomposition of water using electricity is equal to rate of production of hydrogen gas but is double that of formation of oxygen gas. These different rates are related to each other as

$$\text{Rate} = -\frac{1d\ [H2O]}{2\ dt} = \frac{1d\ [H2]}{2\ dt} = \frac{1d\ [O2]}{dt}$$

For a general chemical equation,

a A + b B → c C + d D

$$\text{Rate} = -\frac{1d\ [A]}{a\ dt} = -\frac{1d\ [B]}{b\ dt} = \frac{1d\ [C]}{cdt} = \frac{1d\ [D]]}{ddt}$$

Try yourself

For the given equation write the possible rate expression in terms of reactants and products and use the stoichiometry to equalize the different rates

$$N_2 + 3H_2 \rightarrow 2NH_3$$

3.3 Rate law and its expressions

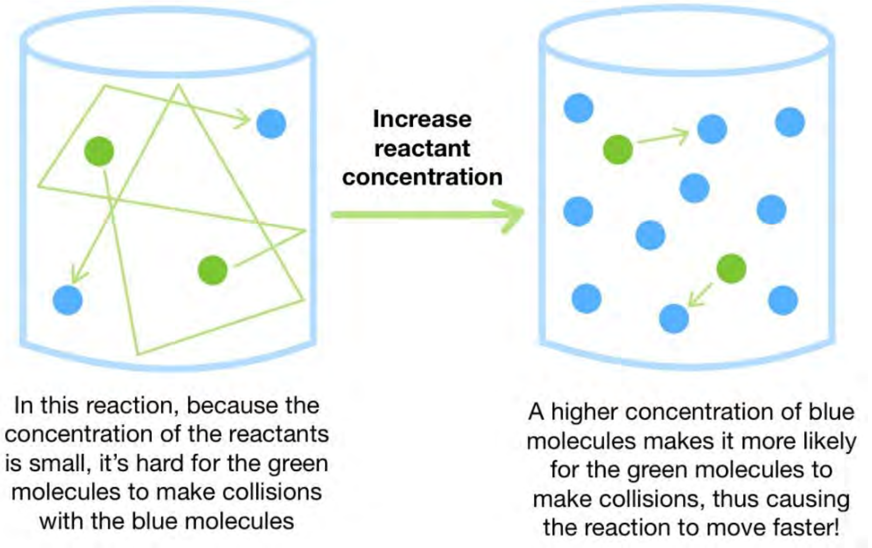
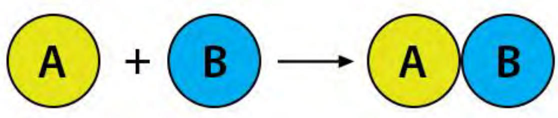


Figure: Effect of concentration on the rate of reaction

You know that concentrated HCl reacts faster with zinc metal than the dilute HCl. The figure above explains how rate of reaction increases with increasing the concentration of reactant. Let us consider a reaction between A and B to form AB.



The rate of reaction depends up on the concentration of both A or B.

$$Rate \propto [A]\,[B]$$

$$Or\ Rate = K\,[A]^x\,[B]^y$$

This relation is called **rate law equation.** The constant **K** is termed as rate constant and the square bracket indicates the molar concentration of reactants. **x** and **y** in the equation are called **order of the reaction**. Detail of order will be given later.

Let us consider a reaction of nitrogen dioxide with carbon monoxide which is second order in NO_2 and zero order in CO at 100 °C.

$NO_2(g)+CO(g) \rightarrow NO(g)+CO_2(g)$

the rate law for the reaction

$Rate = K\,[NO_2]^2\,[CO]^0$

$Rate = K\,[NO_2]^2$

The rate law expresses the relationship between the rate of a chemical reaction and the concentration of its reactants. It is determined experimentally and provides insight into the reaction mechanism.

Significance of Rate Law:

a. Rate law provides clues about the steps involved in a reaction mechanism. The slowest step (rate-determining step) often dictates the rate law.
b. Rate law helps in determining how changing reactant concentrations will affect the reaction speed.
c. Rate law helps in optimizing reaction conditions in processes like catalysis, polymerization, and combustion.

Try yourself

Write down the rate law expression for the given reaction indicating 2nd order with respect to NO and 1st order with respect to H_2.

$$H_2(g)+2NO(g) \rightarrow N_2O(g)+H_2O(g)$$

3.4 Rate constant, Its unit and significance

For any reaction of first order

A → product

rate = k [A]

The constant(k) is termed as rate constant. Its value depends on the nature of the reaction and the temperature but is independent of reactant concentrations. The reaction rate constant is also known as the **reaction rate coefficient**.

The rate constant (k) is a proportionality factor in the rate law that relates the reaction rate to the concentrations of reactants.

Unit of rate constant (k) depends upon the order of reaction

For example, let us consider a third order reaction

$A + B \rightarrow A + B$,

$Rate = k[A][B]^2$

Unit of k can be calculated as
$Mol\ L^{-1}\ s^{-1} = k\ (mol\ L^{-1})\ (mol\ L^{-1})^2$

$k = L^2 mol^{-2} s^{-1}$

Rate law expression and units of k for different order reaction are summarized in the table:

Reaction Order	Rate Law	Units of k	Explanation
Zero-order	Rate =k	$mol\ L^{-1}s^{-1}$	Rate is independent of reactant concentration.
First-order	Rate=k[A]	s^{-1}	Rate is proportional to one reactant concentration.
Second-order	$Rate=k[A]^2$	$L\ mol^{-1}s^{-1}$	Rate depends on the square or product of concentrations.
Third-order	$Rate=k[A]^2[B]$	$L^2mol^{-2}s^{-1}$	Rate depends on the cube of concentrations.

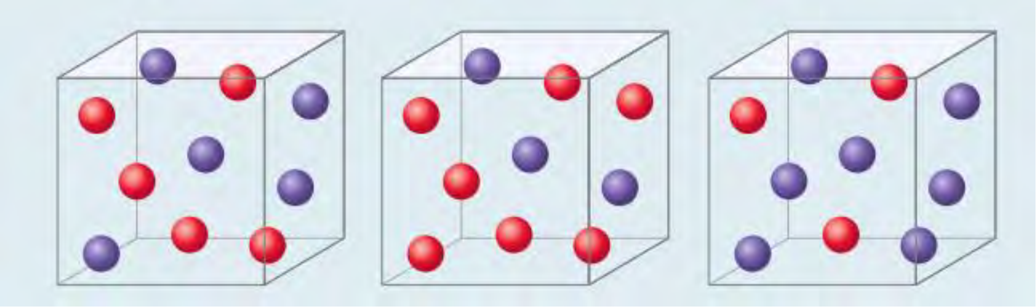
General Formula for Units of k

$$\textbf{Units of k} = \frac{\textit{unit of rate}}{(\textit{unit of concentration})\ \textbf{overall reaction order}}$$

3.5 Order and molecularity

Activity 1:

Observe the given boxes containing two different molecules (A = red) and (B=blue). Calculate the rate of reaction in each box and fill the table below.

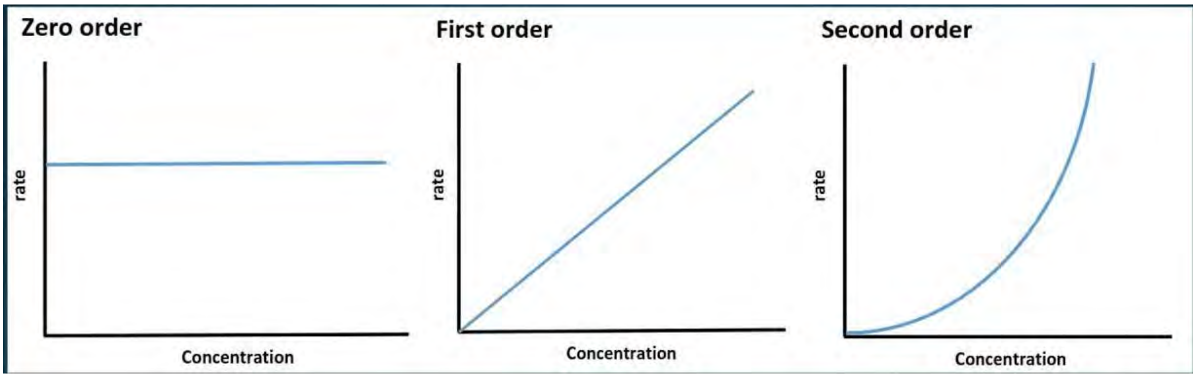


	First box	Second box	Third box
No. of red molecules(A)			
No. of blue molecules(B)			
Rate =[A] $[B]^2$			

Activity 2:

Observe the graph given and identify

a. The order in which rate of reaction increases linearly with concentration
b. The order in which rate is independent to concentration



Let us consider an example,

$$aA + bB \rightarrow Products$$

the rate law can be written as:

Rate = $k[A]^x[B]^y$

Where k is the rate constant, x and y are called **order** with respect to A and B respectively and overall order of reaction =x+ y

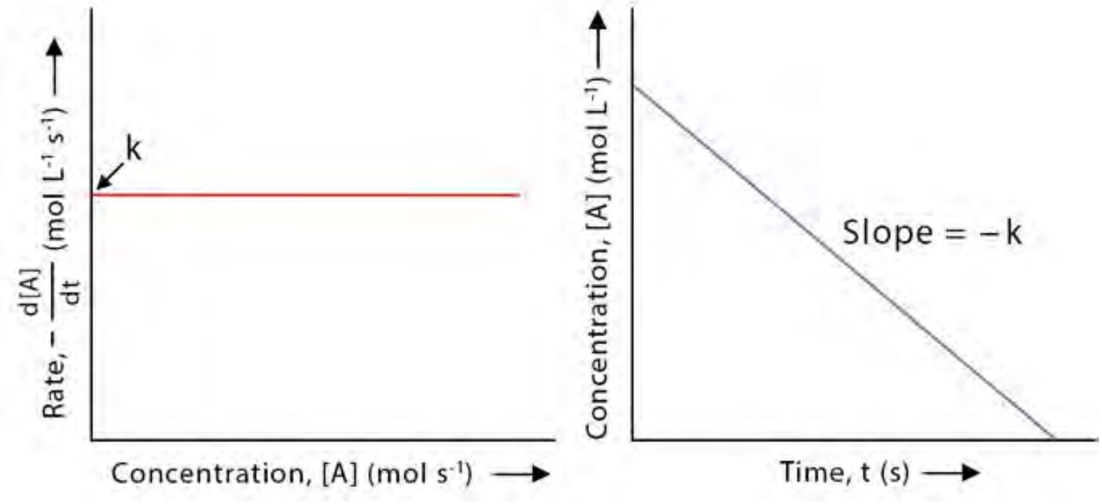
The order of a reaction is an experimental value. Its value is zero, positive, negative (whole number or even in fraction.) A positive order means that the concentration of that species has a direct influence on the rate of a reaction. A negative order means that the concentration of a species affects the rate of a reaction inversely.

The order of a chemical reaction is defined as the summation of the powers of the concentration of the reactants in that chemical reaction's rate equation

Zero Order Reactions

Activity:

Analyze the graph for zero order reaction given below



a. What is the relationship between rate of reaction and concentration?
b. Which of the given graph has highest slope?

A **zero-order reaction** the rate does not change when the concentration of the reactants increases or decreases. As a result, the rate of the specified reactions is always equal to the rate constant of these reactions.

In reality, zero order reaction kinetics are rare. As a result, reactions that follow zero order reactions are frequently referred to as pseudo-zero-order reactions. The most common type of zero-order reaction occurs when a gas undergoes decomposition on the surface of a solid

A zero-order reaction is one in which the rate of reaction is independent of concentration of reactant.

Examples of Zero Order Reaction

The reactions listed below are a few examples of zero order reactions that are not affected by the concentration of the reactants.

1. Photochemical Reaction – The reaction of hydrogen with chlorine is known as the photochemical reaction.

$H_2 + Cl_2 \rightarrow 2HCl$

$\text{Rate} = k[H_2]^0\,[Cl_2]^0$

$\text{Rate} = k$

2. Decomposition of nitrous oxide over a hot platinum surface –

$N_2O \rightarrow N_2 + 1/2\ O_2$

$\text{Rate}\ [N_2O]^0 = k[N_2O]^0 = k$

$d[N_2O] / dt = k$

3. Iodization of Acetone –

$CH_3COCH_3 + I_2 \rightarrow ICH_2COCH_3 + HI$

Unit of rate constant for a Zero Order Reaction

A unit of zero order reaction is equivalent to a unit of reaction speed. The rate constant of the reaction is denoted by k. The rate constant of a zero-order reaction is given as concentration/time or M/s, where 'M' is the molarity and 's' is one second.

$\text{Rate}\ (k) = dC/dt = \text{concentration/time} = \text{mol}\ L^{-1}/s = \text{mol}\ L^{-1}\ s^{-1}$

Characteristics of zero order reaction

a. The concentration of the reactant has no effect on the rate of a zero-order reaction.
b. The concentration of product increases linearly with time.
c. The rate constant is equal to the rate of reaction at all concentrations.
d. The unit of zero-order reaction is mol $L^{-1}sec^{-1}$

The concentration of the reactants does not change over time, and the rate of concentration remains constant. The enzyme-catalyzed oxidation of CH_3CH_2OH (ethanol) to CH_3CHO (acetaldehyde) is one example of a reaction. Some other examples of zero order reactions are given:

$H_2(g)$	$+$	$Cl_2(g)$	$\longrightarrow$	$2\ HCl\ (g)$
Hydrogen		Chlorine		Hydrogen chloride

$2\ N_2O\ (g)$	$\longrightarrow$	$2\ N_2\ (g)$	$+$	$O_2\ (g)$
Nitrous oxide		Nitrogen		Oxygen

CH_3COCH_3	$+$	I_2	$\longrightarrow$	ICH_2COCH_3	$+$	HI
Acetone		Iodine		Iodoacetone		Hydrogen iodide

First-Order Reactions

Activity:

Some of the examples of first order reactions are given below. Use the rate law equation

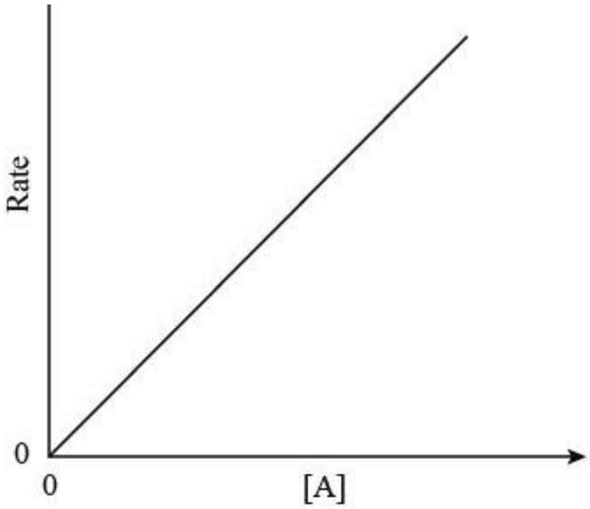
Rate =K[A], what happens to the rate of reaction when

a. Concentration of SO_2Cl_2 is increased 2 times
b. Concentration of H_2O_2 is decreased by 3 times

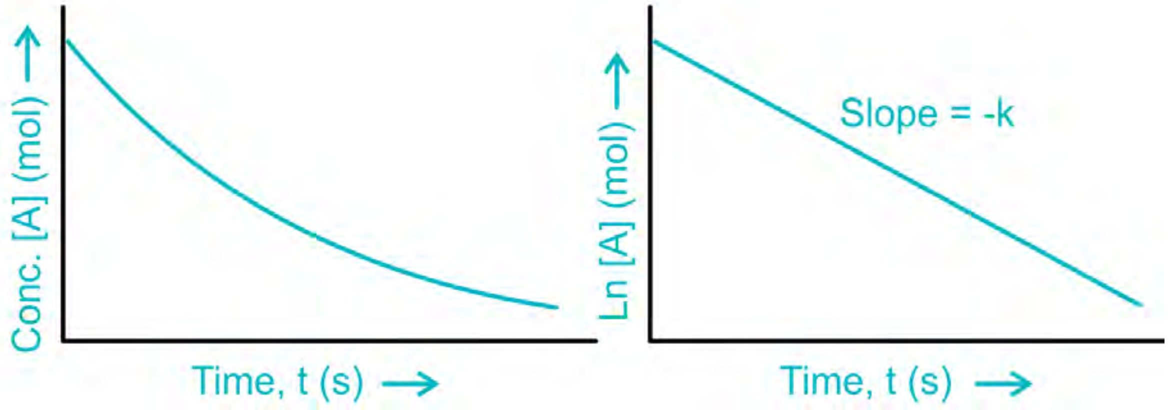
$SO_2Cl_2\ (l)$	$\longrightarrow$	$Cl_2\ (g)$	$+$	$SO_2\ (g)$
Sulfuryl chloride		Chlorine		Sulfur dioxide

$2\ H_2O_2\ (l)$	$\longrightarrow$	$2\ H_2O\ (l)$	$+$	$O_2\ (g)$
Hydrogen peroxide		Water		Oxygen

In these reactions, the rate of reaction is determined solely by the concentration of one component. The reaction can involve many reactants, but only the concentration of one reactant impacts the pace of the reaction. This means that as the concentration of the reactant changes, the rate of the reaction changes proportionally. The relationship between rate and concentration can be represented as



In first order reactions , concentration of reactant decreases with time as shown in the graph.



Example,

$2H_2O_2 \rightarrow 2H_2O + O_2$

Rate = $k[H_2O_2]$

A first-order reaction is a type of chemical reaction where the rate of the reaction is directly proportional to the concentration of a single reactant

Pseudo-First Order Reactions

The concentration of one component remains constant in a pseudo-first-order reaction. The reactant with a constant concentration is either present in excess relative to the other reactant or acts as a catalyst. Example,

$CH_3I + H_2O \rightarrow CH_3OH + H^+ + I^-$

Rate of reaction = k $[CH_3I][H_2O]$

Because methyl iodide is also utilized in an aqueous solution, the concentration of water is significantly greater than that of methyl iodide.

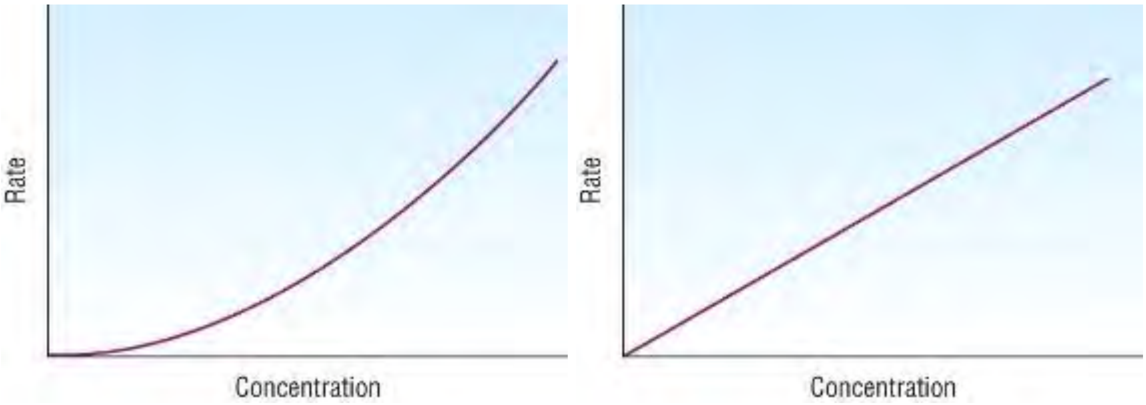
$[CH_3I] <<< [H_2O]$

As a result, the concentration of water does not change considerably and can be approximated as constant or no change.

Now, the Rate of reaction = k $[CH_3I]$

Second-Order Reactions

Activity:



Which of the graph has more slope and what does it indicate?

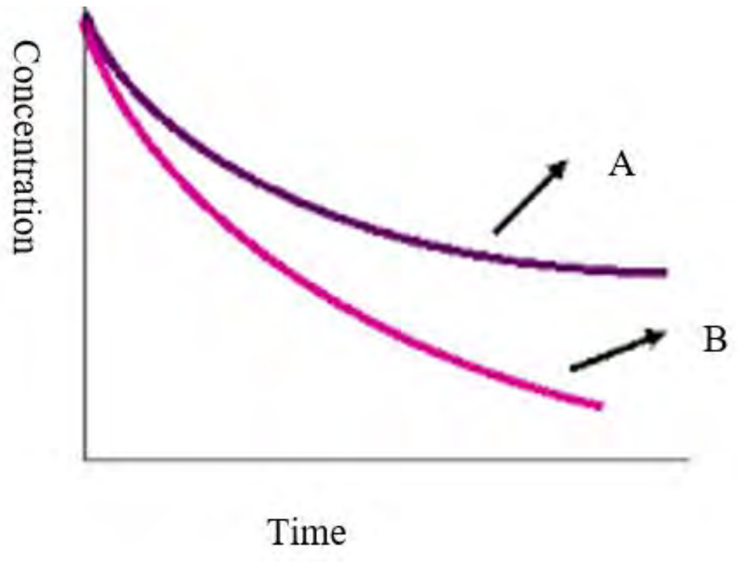
When the order of a reaction is 2, it is referred to as a second-order reaction. Rates like $r = k[A]^2$ or $R = k[A][B]$ can be identified. It means rate of reaction increases more with increasing the concentration of reactants than in the first order reaction. In these reactions when the concentration of reactant is increased by two times rate of reaction increases by 4 times. Example,

$2NO_2 \rightarrow 2NO + O_2$

Rate = k $[NO_2]^2$

Try yourself:

Identify the order A and B in the given graph:



Methods to Determine the Order of Reaction

There are numerous approaches that can be taken in order to identify the order of reaction. Some of these methods are described below.

a. Differential Method

This is the simplest way for determining the order of the reactions. The rate of a reaction is first expressed as Rate = k $[A]^x$. The reaction's final order is given by x.

b. Initial Rates Method

First, we extract the power law's natural log form as **ln rate = ln k + x.ln[A]**

If the partial order of A is found, the rate equation's power-law form now becomes

ln rate = x.ln[A] + C,

where C is a constant

By plotting the graph of 'ln rate' as a function of ln[A], the corresponding slope is x ,the order of reaction.

Solved example:

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2NO(g)+Cl2(g) \longrightarrow 2NOCl(g)$$

Trial	**[NO] (mol/L)**	**[Cl_2] (mol/L)**	**initial rate (molL^{-1}s^{-1})**
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Rate law can be written as
rate=k[NO]^m[Cl_2]^n

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

Or 2.25 = $(1.5)^m$
ln(2.25)= m ln(1.5)
0r m= 2
Likewise

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k(0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

1.5=(1.5)n
n=1
therefore, the rate law equation is
rate=k[NO]^m[Cl_2]^n
to calculate the value of rate constant, value of order of reaction can be kept in any of the experiment above.

0.00300 ==k$(0.10)^2(0.10)^1$
k= 3.0mol^{-2}L^{2}s^{-1}

c. Integral Method

This method is commonly used to validate the order of reaction derived from the initial rates method. The rate law for the first-order reaction is verified by determining if the value of ln[A] is a linear function of time.

A first-order reaction's integrated rate equation is as follows**: In[A] = -kt + In [A]^0**

Molecularity

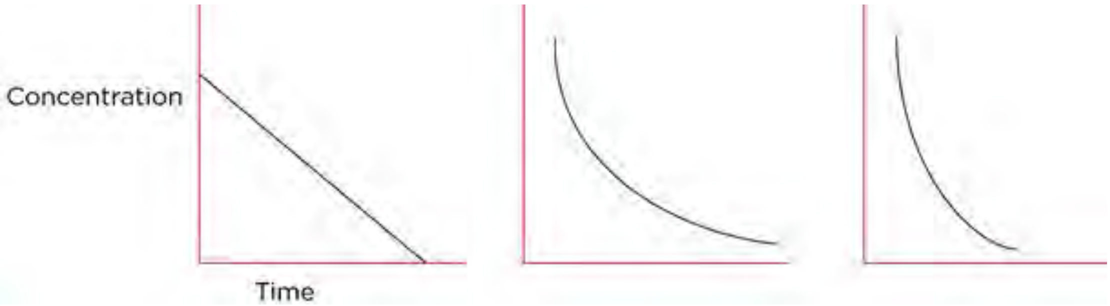
Activity:

An example of chemical reaction given in the equations below:

a. Find out the number of species that collide in each reaction
b. What is the difference between these two reactions?

Try yourself

The graph provided illustrates the relationship between concentration and time for various reactions. Identify the order of each and suitable reason behind.



3.6 Integrated rate equation for zero and first order reaction

A zero-order reaction is one in which the rate of the reaction is proportional to the 0th power of the reactant concentration.

Let us consider a general zero-order reaction.

$$A \rightarrow \text{Products}$$

If 'a' be the initial concentration of reactant and 'x' be the concentration consumed at time 't'

Initially concentration At time t=0	a	0
At time, t	(a-x)	x

The rate of the zero-order reaction is;

Rate = $K_0 [A]^0$

$$\frac{dx}{dt} = K_o$$

The differential Rate Equation for the zero-order reaction is;

$$\frac{dx}{dt} = K_o(a-x)^o$$

$$dx = K_o dt$$

Now, integrating the above equation we get,

$$\int dx = K_o \int dt$$

$$x = K_o t + I \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

Where, I = integration constant

When t=0, x=0, then I=O

Substituting the value of I in equation (i), we get

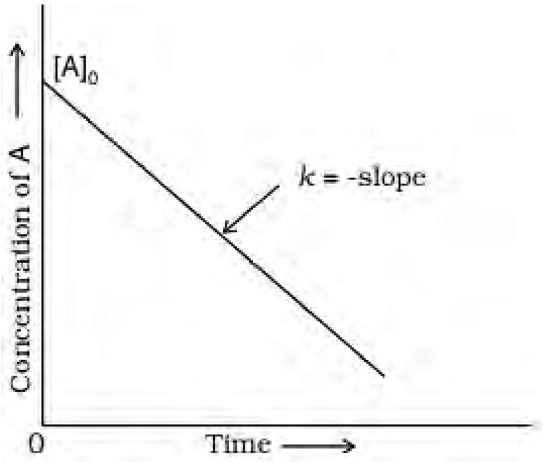
$x = K_0 t$

$K_0 = x/t$……………………. (ii)

Equation ii is the integrated rate equation of the zero-order reaction.

When we compare the above-derived equation with the equation of a straight line, $y = mx + c$, if we plot [A] against t, we get a straight line with slope = – k and intercept equal to $[A]_0$

When the rate of reaction is plotted against concentration and time, the below graph is obtained.



Integrated rate equation for 1st order reaction

Let us consider a general reaction;

$$A \rightarrow \text{Products}$$

If ‘a’ be the initial concentration of reactant and ‘x’ be the concentration consumed at time ‘t’

Initially concentration At time t=0	a	0
At time, t	(a-x)	X

The rate law equation can be written as ;

$$\frac{dx}{dt} = K_1[A]^1$$

$$\frac{dx}{dt} = K_1[a - x]^1$$

$$\frac{dx}{a-x} = K_1 dt \text{ .... (i)}$$

Integrating both sides we get,

$$\int \frac{dx}{a-x} = \int K_1 dt$$

$$-\text{In }(a\text{-}x) = K_1t + C\text{.......... (ii)}$$

When t=0, x=0 then;

$-\text{In } a = C$ ………………… (iii)

Substitute value of **C** in equation (ii)

$-\text{In }(a\text{-}x) = K_1t - \text{In } a$
$\text{In } a - -\text{In }(a\text{-}x) = K_1t$

$$K_1t = \text{In}\frac{a}{a-x}$$

$$K_1 = \frac{1}{t}\text{In}\frac{a}{a-x}$$

$$K_1 = \frac{2.303}{t}\log\frac{a}{a-x} \text{ .... (iv)}$$

Equation (iv) is called the integrated equation of the first-order reaction.

This equation can be rearranged as

$$K_1t = 2.303[\log a - \log(a\text{-}x)]$$

$$\frac{K_1 t}{2.303} = [\log a - \log(a\text{-}x)]$$

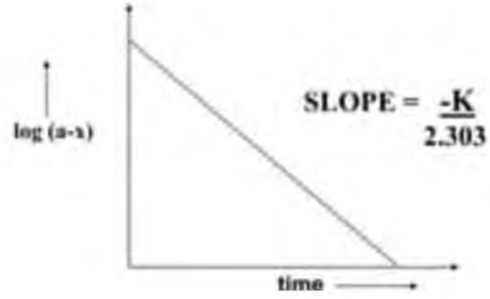
$$\log(a\text{-}x) = \frac{-K_1}{2.303}t + \log a \text{.........} \quad (v)$$

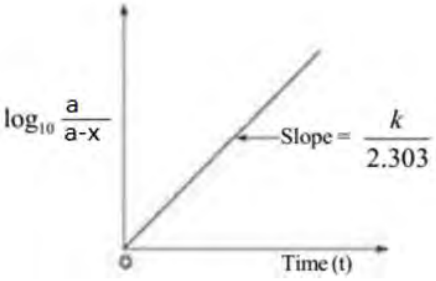
Equation (v) is in the form of y = mx + c

$$\log(a\text{-}x) = \frac{-K_1}{2.303}t + \log a.$$

$$y = mx + c$$

Now, plotting a graph between log(a-x) against t, we obtained a straight line with the slope $K_1/2.303$. Similarly, a graph of log a/(a-x) against 't' gives a straight line passing through the origin.





Characteristics of 1st order reaction

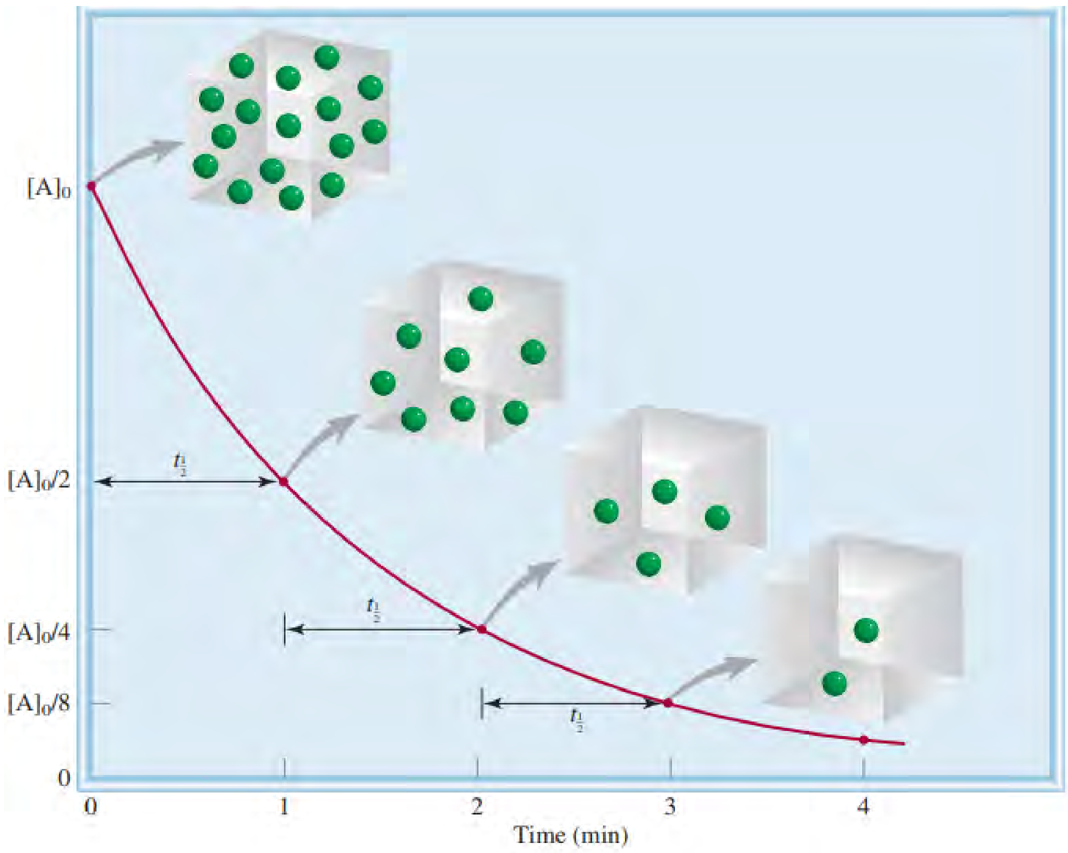
a. The unit of the rate constant of a first-order reaction is $\sec^{-1}$ or time^{-1}
b. The units of rate constant do not depend on the units of concentration expressed.
c. The rate constant remains unchanged throughout the reaction.
d. The time required to complete a definite fraction of the reaction is independent of the initial concentration.

3.7 Half-life of zero and first order reactions

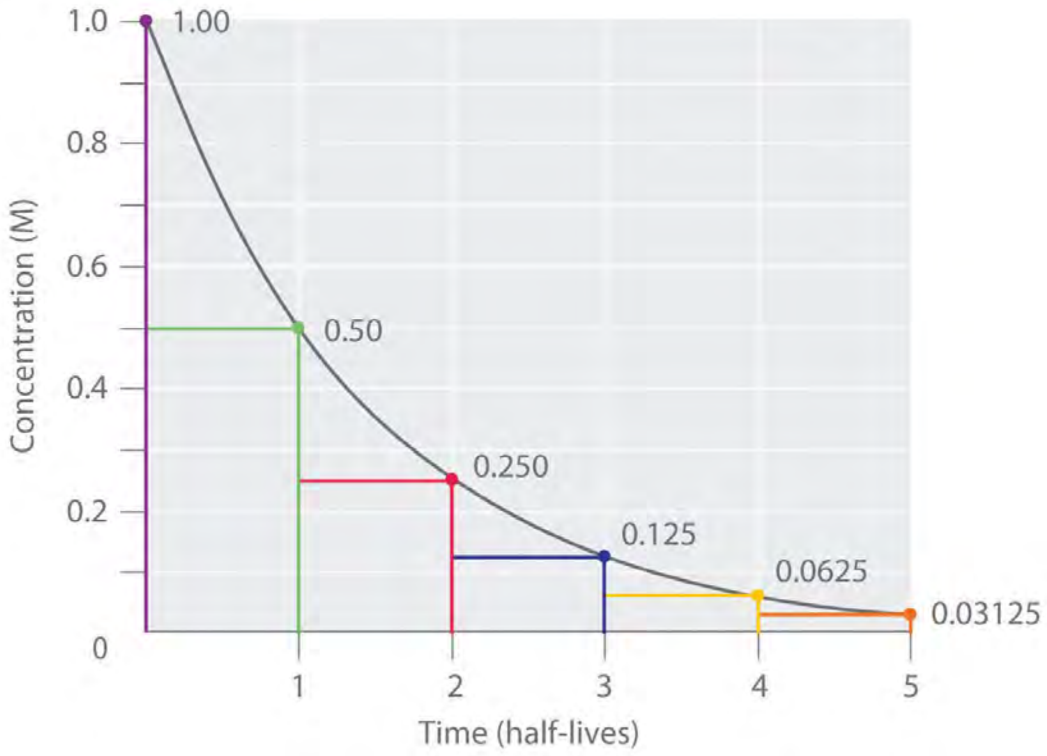
Activity:

Observe the graph showing the change in no. of particles with the progress of time and fill the table given.

	Zero time	1 min	2 min	3 min	4 min
Number of particles					



a. Half-Life of a Zero Order Reaction



A chemical reaction’s half-life can be defined as the amount of time required for half of the reactants to be depleted. It is represented by the symbol ‘$t_{1/2}$‘and is measured in seconds.

The integrated rate equation for zero order reaction is

$x = K_0 t$

During half-life, $t = t_{1/2}$ and $x = a/2$ [where a is the initial concentration of reactant]
Now,

$$K_0 = x/t$$

$$K_o = \frac{a/2}{t_{1/2}}$$

$$t_{1/2} = \frac{a}{2K_o}$$

$$\therefore t_{1/2} \propto a$$

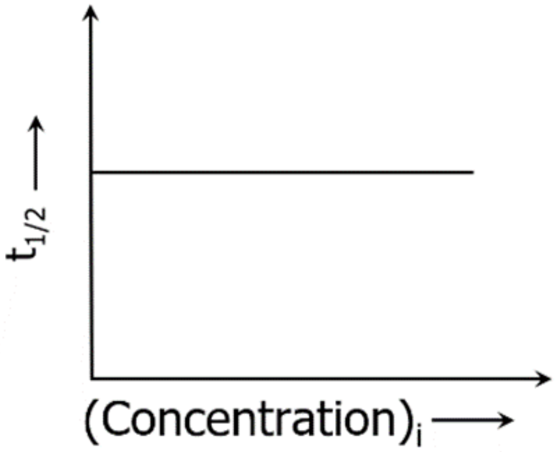
where, k_0 stands for the zero-order rate constant

The above equation clearly shows that the half-life of the reaction is dependent on both the rate constant and the initial concentration of the reactant.

c. Half-Life of a 1st Order Reaction

The integrated rate equation for 1st order reaction is

$$K_1 = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{.............} \quad \text{(i)}$$



At half-life, $t = t_{1/2}$ and $x = a/2$. Substituting these values in above equation,

$$k = \frac{2.303}{t_{1/2}} \log\left(\frac{a}{a-a/2}\right)$$

$$k = \frac{2.303}{t_{1/2}} \log\left(\frac{2a}{a}\right)$$

$$k = \frac{2.303}{t_{1/2}} \log(2)$$

$$k = \frac{0.693}{t_{1/2}}$$

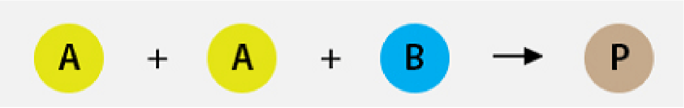
$$\boxed{t_{1/2} = \frac{0.693}{k}}$$

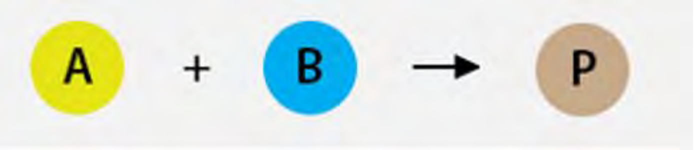
It means half-life of first order reaction is independent of the initial concentration of reactants.

Molecularity of Reaction

Activity:

Identify the number of species involved in each of the reaction given below





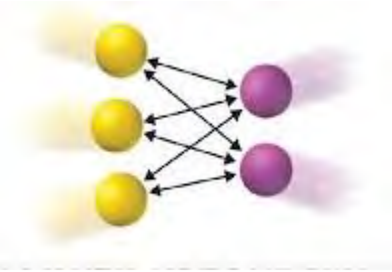


Fig : Collision among the molecules during the chemical reaction

The reaction of NO and O3 to form NO2 and O2 appears to occur as a result of a single collision involving suitably oriented and sufficiently energetic NO and O3 molecules:

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

Such reaction that occur in a single step and is called **elementary reactions**. The number of molecules that participate as reactants in an elementary reaction defines the **molecularity of the reaction**. If a single molecule is involved, the reaction is unimolecular.

The reaction between NO and O_3 is bimolecular. Elementary reactions involving the simultaneous collision of three molecules are termolecular.

Molecularity of a complete reaction has no significance and overall kinetics of the reaction depends upon the rate determining step. Slowest step is the rate determining step.

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

It is a theoretical concept based on the reaction mechanism and helps classify reactions according to the number of species colliding and reacting in a single step.

This was proposed by Van't Hoff. Example:

$NH_4NO_2 \rightarrow N_2 + 2H_2O$ (Unimolecular)

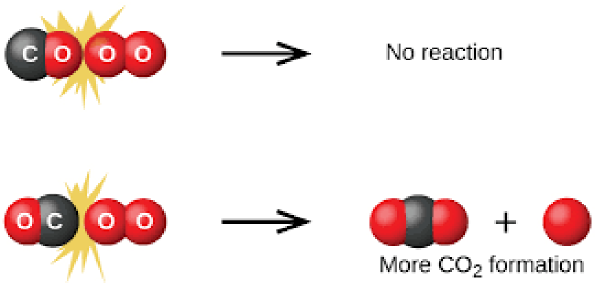
$NO + O_3 \rightarrow NO_2 + O_2$ (Bimolecular)

$2NO + O \rightarrow 2NO$ (Trimolecular)

Molecularity of a reaction can't be Zero, negative or fractional. Molecularity of a reaction is derived from the mechanism of the given reaction. Molecularity cannot be greater than three because the probability of simultaneous collisions involving more than three molecules is extremely low in practical conditions.

Molecularity is the minimum number of reacting particles (Molecules, atoms or ions) that collide in a rate determining step to form product or products.

3.8 Collision theory, concept of activation energy and activated complex



The Collison between CO and O2 molecules is shown above. What is the difference between these collisions?

Max Trautz and William Lewis created the Collision Theory of Chemical Reactions in 1916-1918, which was based on the kinetic theory of gases.

According to the Collision Theory of Chemical Reactions, “The molecules of reactants are assumed to be hard spheres, and the reactions are assumed to occur only when these spheres (molecules) collide with each other. It means the reacting particles (atoms, ions, or molecules) must collide with each other for the chemical reaction to occur. Not all collisions lead to a reaction. For a collision to result in a reaction,

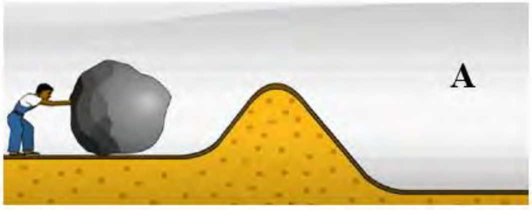
1. The colliding particles must have the correct mutual orientations.
2. The reacting particles must have sufficient kinetic energy to initiate the reaction

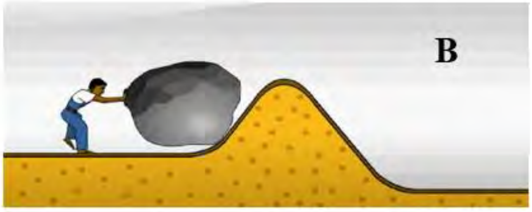
The rate of a reaction depends on the frequency of effective collisions. Factors such as temperature, concentration, surface area, and the presence of a catalyst influence the number of effective collisions. According to the collision theory, the energy needed to break bonds comes from the kinetic energy of the colliding molecules. During a collision between molecules, kinetic energy is converted to potential energy

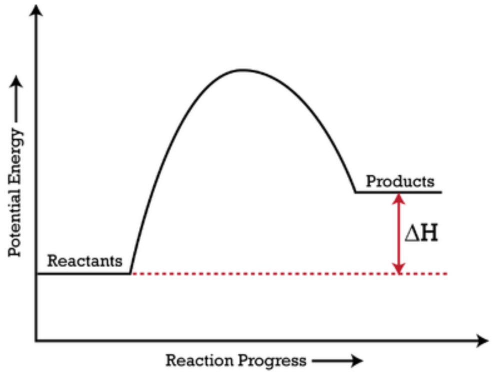
Activation energy

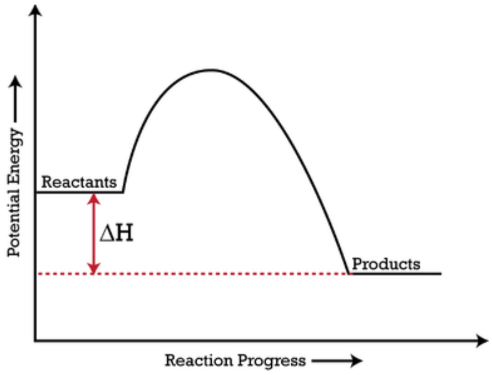
Activity:

Which figure needs more energy to roll the stone and why?









To begin a chemical reaction, chemical bonds in the reactants must be broken, which takes energy. The energy required to initiate the reaction is referred to as activation energy. When the Activation Energy is low enough, the reaction can begin at ambient temperature without being heated. When the Activation Energy gap is large enough, then the reaction occurs at elevated temperature i.e., external energy is provided to break the barrier of Activation Energy. When the activation energy is high, the reaction moves more slowly because fewer reactants have enough energy at any given time to break through the energy barrier. If the activation energy is high enough, a process won’t happen at all unless energy is added. For example, burning wood gives off a lot of energy, but a table made of wood doesn’t quickly catch fire. For wood to burn, it needs energy to start, which can come from a lighter. It represents the energy barrier that must be overcome for the reactants to transform into products.

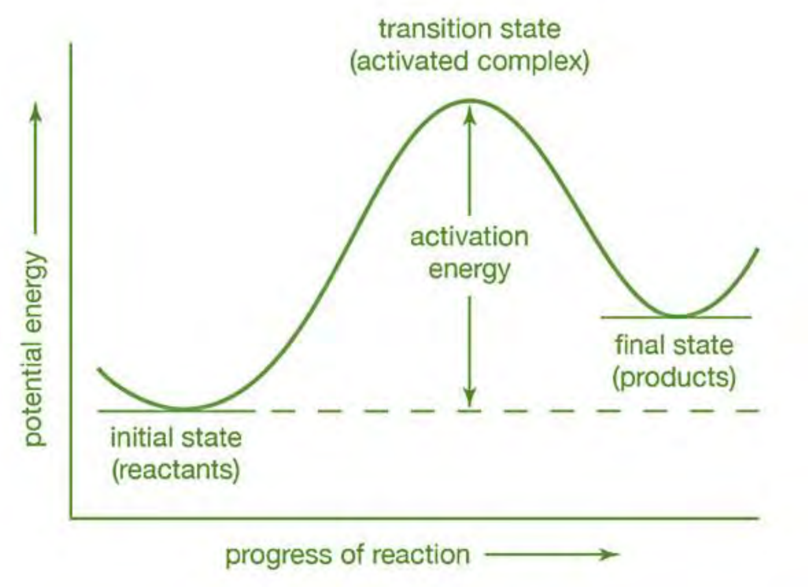
Reactions with higher activation energies proceed more slowly at a given temperature compared to reactions with lower activation energies. Increasing the temperature increases the kinetic energy of particles, making it more likely that they will collide with enough energy to overcome the activation energy. The Arrhenius equation shows how the rate of a process, the activation energy, and the temperature are related.

$$\mathbf{k = Ae^{-Ea/(RT)}}$$

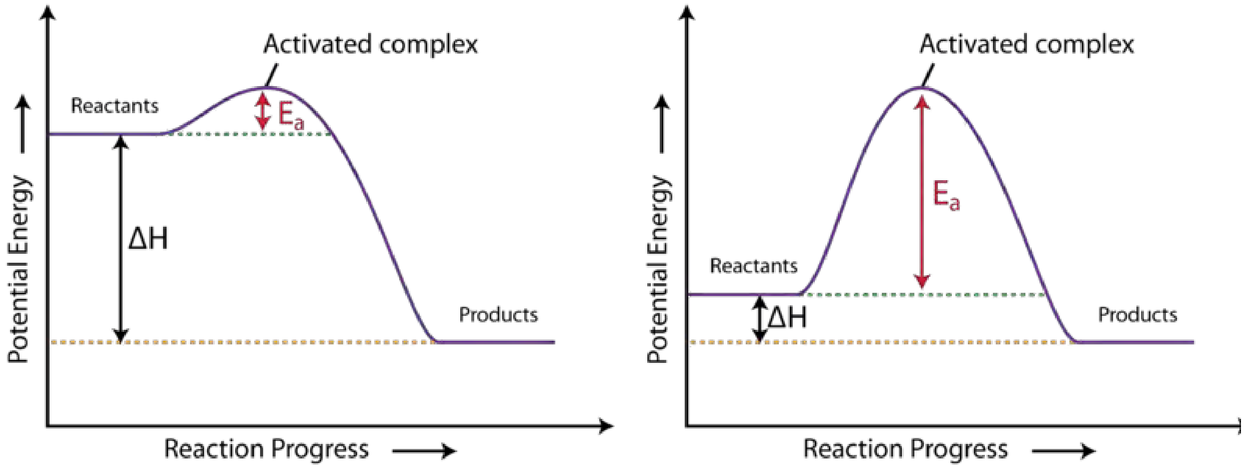
Here, **k** is the reaction rate coefficient, **A** is the frequency factor for the reaction, **e** is the irrational number (about 2.718), **Ea** is the activation energy**, R** is the universal gas constant, and T is the exact temperature (in Kelvin).

This derives the formula for activation energy.

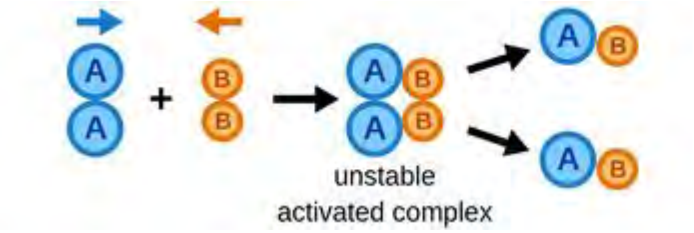
The activation energy is the minimum energy that colliding particles need for a reaction to occur.



Activated complex



Observe the graph given above and identify the diagram in which reactants change in to product easily and why?

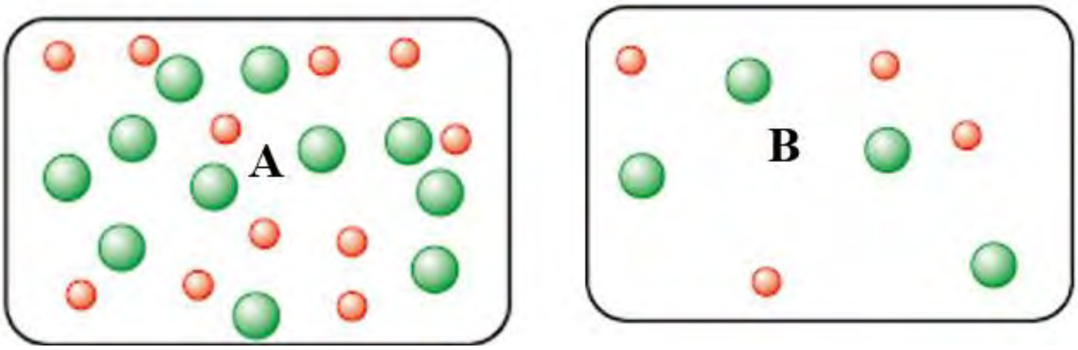


The activated complex is a temporary, unstable arrangement of atoms that forms at the peak of the energy barrier during a chemical reaction. It represents the state between the breaking of old bonds and the formation of new ones. It is highly energetic and short-lived. It can either decompose to form products or revert to reactants. On an energy diagram, the activated complex corresponds to the peak of the curve, representing the highest energy point during the reaction.

3.9 Factors affecting rate of reactions: Effect of concentration, temperature (Arrhenius Equation) and effect of catalyst (energy profile diagram)

Do you know why lizard comes out to bask in the sun frequently?

When a lizard comes out to bask in the sun, its body temperature increases, which in turn affects the rate of its metabolic activities such as digestion, movement, and respiration. It allows the lizard to move faster and escape predators.



Which of the container has more chances of collisions and why?

a. Nature of Reactants

Reactions occur faster when reactants are in the gaseous phase than in the liquid and solid phase. In gaseous phase, the kinetic energy of reacting species is more causing more collision than in the liquid and solid phases. Likewise, Simple molecules react faster than complex ones because fewer bonds need to rearrange.

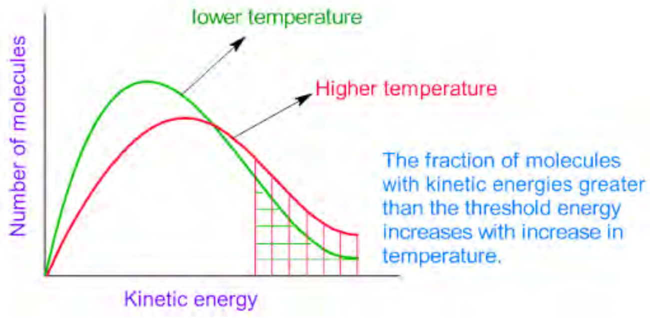
b. Concentration:

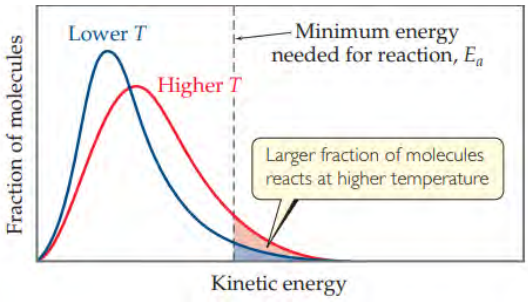
We know that concentrated HCl reacts faster than the dilute HCl. When concentration increases the frequency of collision among the reacting species increases causing higher rate of reaction.

c. Effect of temperature

Why do we keep food in refrigerator?

When food is refrigerated, the rate at which it spoils decreases significantly. When temperature increases, the speed of the particles increases which causes more collision and increase the rate of reaction. It means the number of particles with high speed overcome the activation energy barrier and so possibly initiate reaction. Experimentally it has been found that rate of reaction becomes doubles for every 10^0C rise in temperature. But in the case of gas where the chances of collision is more, the rate of reaction may increases 3 to 4 times. The graph in the figure below shows the Maxwell– Boltzmann distribution for the molecular speeds of nitrogen gas at three different temperatures. Recall that the area under all three curves is constant, as the total number of particles in the sample has not changed, and that the higher the temperature, the greater the spread of speeds of particles.





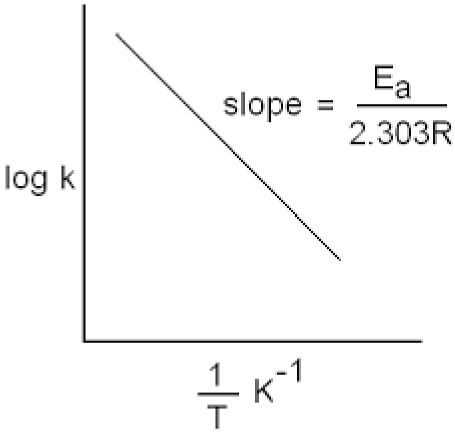
The Arrhenius equation describes the relationship between reaction rate, activation energy, and temperature.

We know the formula for rate constant is given by,

$$\mathbf{k = Ae^{-Ea./RT}}$$

Taking log on both sides we get,

$\ln k = -E_aRT + \ln A$
$2.303x \log k = -E_aRT + 2.303x \log A$
$\text{Log } k = -E_{a/2.303}RT + \log A$



For initial temperature T_1 and rate of constant k_1, the equation is written as,

$\ln k_1 = -E_a/RT_1 + \ln A$ …….. (1)

For the final temperature T_2 and rate of constant k_2, the equation is written as,

$\ln k_2 = -E_a/RT_2 + \ln A$ …….. (2)

Subtracting (2) from (1) we get,

$\ln k_2 - \ln k_1 = -E_a/RT_2 + \ln A - (-E_a/RT_1 + \ln A)$

$\ln (k_2/k_1) = E_aR (1/T_1 - 1/T_2)$

$2.303 \log (k_2/k_1) = E_aR (1/T_1 - 1/T_2)$

$\mathbf{E_a = 2.303\ R\ (\log k_2/k_1)\ [T_1T_2 / (T_2 - T_1)]}$

d. Effect of catalyst in the rate of reaction

Activity:

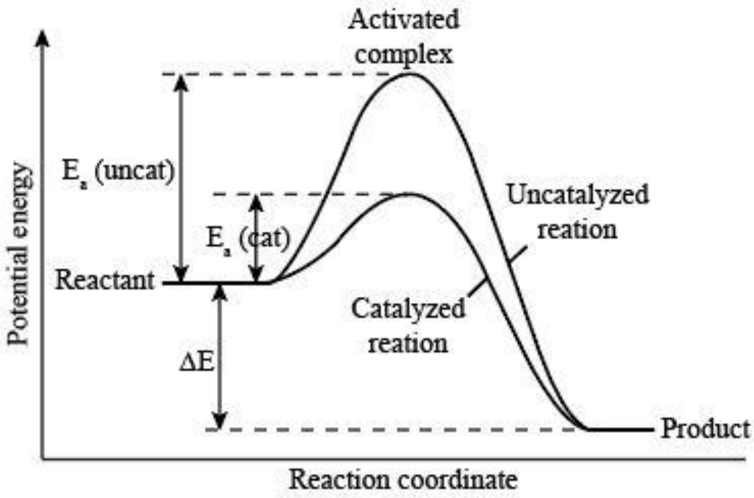
Name the catalyst in the given reactions.

$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2$ $\quad$ $2NO \xrightarrow{Pt} O_2 + N_2$

Figure: fermentation of alcohol.

The yeast in **marcha,** mainly Saccharomyces cerevisiae, produces **zymase**, a complex of enzymes. Zymase catalyzes the conversion of sugars (glucose, maltose) and helps in the fermentation of alcohol.

We know that catalysts participate in the reaction but are not consumed in the process. They can be used repeatedly to accelerate multiple reaction cycles. How do these catalyst increases the rate of reaction? Catalyst provides an alternate path with lower activation energy so that reaction proceeds faster. This means that more reactant molecules have sufficient energy to overcome the energy barrier and form products. By lowering the activation energy, catalysts increase the probability that collisions between reactant molecules will result in a reaction.



3.10 Catalysis and types of catalysis: homogeneous, heterogeneous and enzyme catalysis

Activity: Study the given chemical reactions with catalyst.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

$$\underset{(aq)}{2H_2O_2} \xrightarrow[(aq)]{KI} \underset{(l)}{2H_2O} + \underset{(g)}{O_2}$$

a. Identify the catalyst in the above reaction.
b. What is the difference between these catalysts in terms of their state with the reactants?

We have just discussed the role of catalysts in chemical reactions. The use of a catalyst varies depending on the nature of the chemical reaction. Catalysts may be solid, liquid, or even gaseous. The catalyst and the reactants involved in a reaction may exist in the same phase or in different phases.

A **catalytic converter(**shown in the figure right**)** is a key component of a vehicle's exhaust system. Catalytic Converters used in car exhaust converts toxic gases (hydrocarbon, carbon monoxide and nitrogen oxides) into less harmful gases (CO_2, H_2O and N_2) before they're released into the atmosphere. Inside the catalytic converter, exhaust gases pass over a honeycomb-like structure coated with precious metals like **platinum, palladium, and rhodium.** These metals act as **heterogenous catalysts** to trigger chemical reactions

If the catalyst is in the same phase as the reactants in a reaction mixture, it is referred to as a **homogeneous catalyst**. On the other hand, if the catalyst is in a different phase from the reactants, it is called a **heterogeneous catalyst**. These processes are known as **homogeneous catalysis** and **heterogeneous catalysis**, respectively.

For example, the esterification of acetic acid with methanol in the presence of an acid is an example of homogeneous catalysis, as all the reactants and the catalyst are in the aqueous phase.

$$CH_3COOH + CH_3OH \xrightarrow{H^+} CH_3COOCH_3 + H_2O$$

A heterogeneous catalyst is one that exists in a phase different from the phase of the reactant molecules, usually as a solid in contact with either gaseous reactants or with reactants in a liquid solution. Many industrially important reactions are catalyzed by the surfaces of solids. For example, hydrocarbon molecules are rearranged to form gasoline with the aid of what are called “cracking” catalysts.

Remember: A substance that slows down or stops a reaction in known as an inhibitor

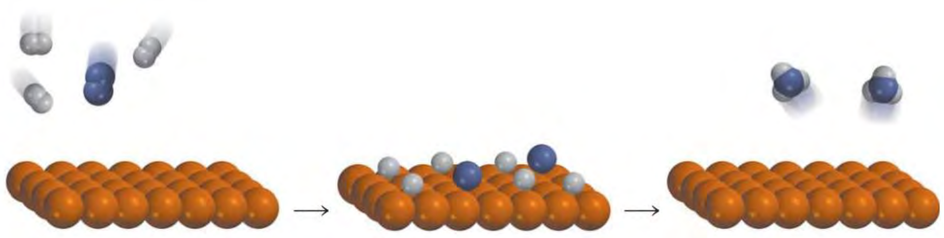


Figure: reaction of H_2 and N_2 in the surface of iron. Iron acts as a heterogenous catalyst

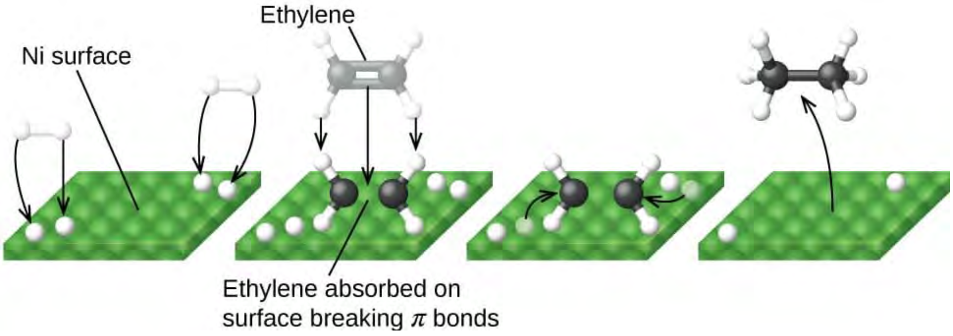


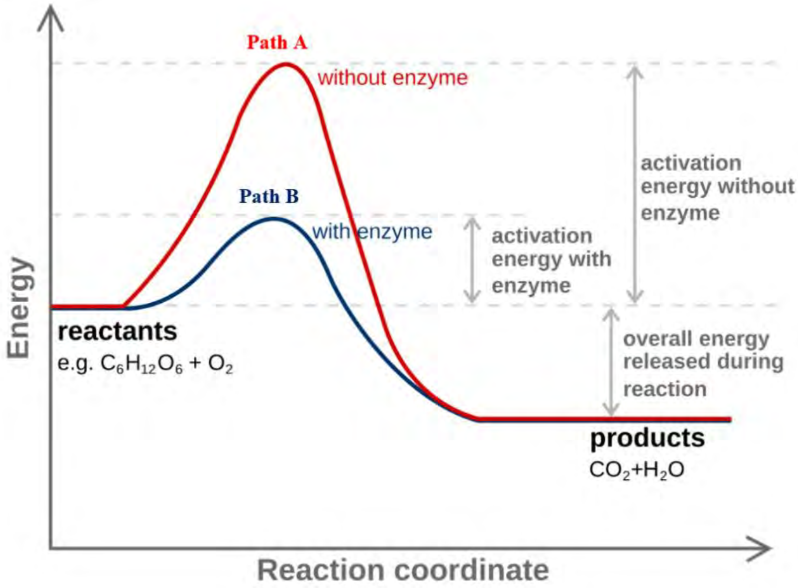
Figure: Hydrogenation of ethylene on the surface of nickel (heterogenous catalyst)

Enzyme catalysis

Activity:

Use the energy profile diagram for the oxidation of glucose given below and discuss to answer the given questions.

a. Write the balanced chemical equation for the oxidation of glucose.
b. Identify the path (A or B) that is faster and give reason behind.



We know that **amylase** an enzyme present in the saliva helps to break large starch molecules. It means it helps in the digestion by catalyzing the hydrolysis of starch into sugar. This is the example of enzyme catalysis. The word “enzyme” comes originally from the Greek term *“enzymos*” meaning in yeast. Enzymes are essential ingredient in bread, wine, yogurt, and beer There are about 3000 different types of enzymes in the living cell. Each of them has unique role in specific reactions. They increase the rate of reaction up to 1000 times. Enzyme catalysis is usually **homogeneous** because the substrate and enzyme are present in aqueous solution.

Enzyme catalyst is referring to the process by which enzymes accelerate chemical reactions.

Properties of Enzyme Catalysis

a. Enzymes are highly specific to their substrates (the molecules they act upon). This specificity is often compared to a "lock and key" or an "induced fit" model.
b. Enzymes provide an alternative reaction pathway with a lower activation energy, making the reaction faster.
c. Even small amounts of enzymes can catalyze reactions involving large amounts of substrate, and they remain unchanged at the end of the reaction.
d. Enzymatic activity is regulated by various factors, including pH, temperature, inhibitors, activators, and feedback mechanisms.

Common Enzyme Catalysts

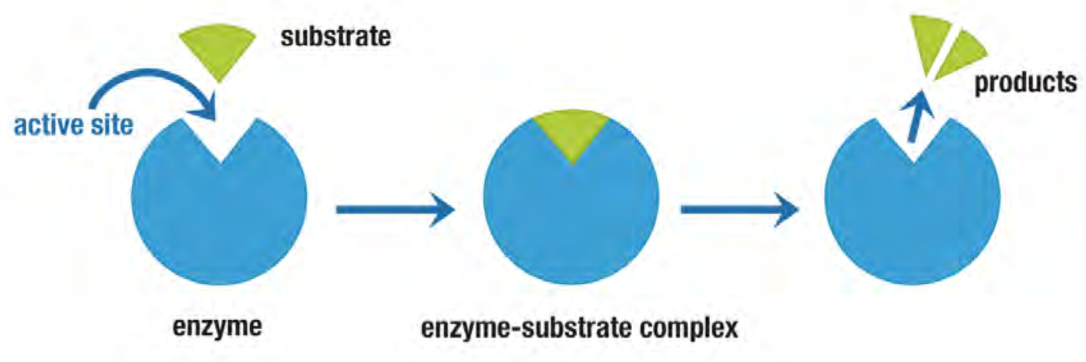
Amylase – Found in saliva; breaks down starch into sugars during digestion.

Protease – Used in meat tenderizers and laundry detergents to break down proteins.

Lactase – Helps lactose-intolerant people digest lactose in dairy products.

Zymase – In yeast; catalyzes alcohol fermentation

Mechanism of enzyme catalysis



An enzyme is typically a large protein molecule that contains one or more **active sites** where interactions with **substrates** take place. These sites present in the enzymes are specific to particular substrate molecule as key fit to lock. When substrate binds to the active site of the enzyme, an enzyme substrate complex is formed. Then the complex change into product leaving the enzyme ready to catalyze another reaction.

Project work

1.

a. Take a beaker and add 100 mL of dilute sulfuric acid.
b. Add a 2 g piece of marble to the beaker and observe the reaction.
c. Record the time taken for the gas evolution to stop.
d. Take another beaker with 100 mL of the same dilute acid.
e. Crush 2 g of marble into a fine powder and add it to the acid.
f. Note the time taken for the gas evolution to cease.
g. Repeat the experiment using concentrated sulfuric acid instead of dilute acid.
h. Observe and record the differences in reaction rate and gas evolution.
i. Document all findings in the given table.

Nature of marble	**Type of acid used**	**Time for complete reaction**
Piece	Dilute	
Piece	Concentrated	
Powder	Dilute	
Powder	Concentrated	

2. Take a chart paper and complete the given table as mentioned below.

Order of reaction	Integrated rate equation	Unit of K	Rate vs time plot	Concentration vs time plot	Half life	Half-life vs initial concentration plot
Zero order						
1st order						
2nd order						

Exercise

A. Multiple choice questions

1. **Which of the following statements is correct about the rate of reaction?**

   a. The rate of a reaction decreases with passage of time as the concentration of reactants decreases.

   b. The rate of a reaction is same at any time during the reaction.

   c. The rate of a reaction is independent of temperature change.

   d. The rate of a reaction decreases with increase in concentration of reactant(s).

2. **Rate law for the reaction $A + 2B \rightarrow C$ is found to be rate = k[A][B]. The concentration of reactant B is doubled, keeping the concentration of A constant, what will be the value of rate of the reaction?**

   a. same

   b. doubled

   c. quadrupled

   d. halved

3. According to collision theory: which of the given statements is true?
   a. all collisions are sufficiently violent
   b. all collisions are responsible for product formation
   c. all collisions are effective
   d. only a fraction of collisions is effective which have enough energy to form products
4. According to the collision theory of reaction rates, which of the following causes the increased rate with temperature?
   a) greater number of collisions

   b) higher velocity of reacting molecules

   c) greater number of molecules having the activation energy

   d) decrease in the activation energy

5. The rate of the first order reaction, A product is 7.5 X 10 -4 mol L -1 s -1 , when the concentration of A is 0.2 mol L -1 . what is the rate constant of the reaction ?

   a) 2.5×10^{-5} s^{-1}

   b) 8.0×10^{-4} s^{-1}

c) $6.0 \times 10^{-4}\ s^{-1}$

d) $3.75 \times 10^{-3}\ s^{-1}$

6. For the reaction, $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, the reaction rate is: rate= $K[H_2][Br_2]^{1/2}$

Which one of the following statements is true for the reaction?

a) The reaction is of second order

b) The molecularity of the reaction is 3/2

c) The unit of k is sec -1

d) The molecularity of the reaction is two

7. **Half-life period for a first order reaction is 20 min. How much time is required to change the concentration of the reactant form 0.08 M to 0.01 M?**

a) 20 min

b) 60 min

c) 40 min

d) 50 min

8. **What is the primary difference between average rate and instantaneous rate of a reaction?**
a) Average rate is time-independent, while instantaneous rate is time-dependent
b) Average rate is determined over a time interval, while instantaneous rate is determined at a specific time
c) Average rate applies only to fast reactions, while instantaneous rate applies only to slow reactions
d) There is no significant difference between the two

9. **Given the reaction** $A \rightarrow B$, **if the concentration of A decreases from 0.8 M to 0.6 M in 20 seconds, what is the average rate of the reaction?**
a) 0.01 M/s
b) 0.02 M/s
c) 0.04 M/s
d) 0.10 M/s

10. **Which of the following is true about the rate constant** (k)**in a rate law?**
a) It changes with the concentration of reactants
b) It depends on the order of the reaction
c) It is constant at a given temperature
d) It varies with the catalyst used but not with temperature

11. **Molecularity is the no. of species involved in the rate determining collision .Which of the following reactions can have a molecularity greater than 3?**
a) Elementary reaction
b) Complex reaction

c) Zero-order reaction
d) Pseudo-first-order reaction

12. **For the reaction** $2A+B \rightarrow C+D$, **the experimentally determined rate law is** $R = k[A]^2$**. What is the identity of this reaction?**
a) Second-order and bimolecular
b) Second-order and trimolecular
c) Second-order overall but unimolecular in B
d) First-order in A and B

13. **Which of the following plots corresponds to a zero-order reaction?**
a) A straight line with a negative slope for [A]vs. time
b) A straight line for ln[A] vs. time
c) A curved line for [A] vs. time
d) A straight line for 1/A]1 vs. time

14. **Half life gives the idea about the rate of reaction. Which of the following affect the half-life of a first-order reaction ?**
a) Initial concentration of the reactant
b) Rate constant only
c) Temperature and pressure
d) Both a and b

15. **According to collision theory, which of the following factors does NOT directly affect reaction rates?**
a) Number of collisions per second
b) Activation energy
c) Orientation of colliding molecules
d) Molecular weight of the reactants

16. **What is the role of an activated complex in a chemical reaction?**
a) It is a stable intermediate
b) It is a short-lived, high-energy species that forms before products
c) It is a low-energy state that slows the reaction
d) It is the final product

17. **Which of the following cane be calculated using Arrhenius equation ?**
a) Order of reaction
b) Activation energy
c) Half-life
d) Molecularity

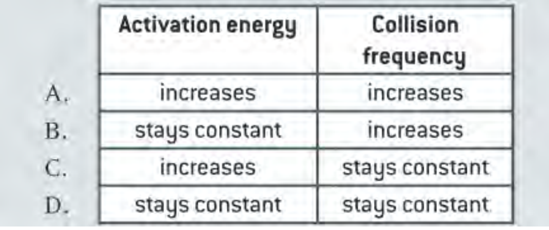
18. **Catalyst alters the rate of chemical reaction so are useful in many industrial and chemical processes. How does a catalyst affects the rate of a chemical reaction ?**

a) Lowering the activation energy
b) Increasing the concentration of reactants
c) Shifting the equilibrium constant
d) Increasing the temperature

19. **Which of the following factors increases the rate of reaction but does not alter the equilibrium constant?**
a) Catalyst
b) Pressure
c) Temperature
d) Reactant concentration

20. **Catalysis may be homogeneous or heterogeneous .Which of the following is an example of heterogeneous catalysis?**
   a) Enzyme action on glucose
   b) Decomposition of hydrogen peroxide by manganese dioxide
   c) Acid-catalyzed ester hydrolysis
   d) Ozone depletion by chlorine radicals
21. **Enzyme catalysis involves the role of biological catalyst in the living body. How does it differs and unique from other chemical catalyst ?**
   a) It works only at high temperatures
   b) It is highly specific and efficient
   c) It increases activation energy
   d) It works only in gaseous reactions
22. **Substrate concentration affect the rate of rate in enzyme catalysis .Which of the following cause the reaction rate reaches a maximum at high substrate concentration ?**
   a) All enzyme molecules are saturated with substrate
   b) Activation energy becomes zero
   c) The temperature becomes constant
   d) Enzymes are consumed
23. **If the rate of a reaction doubles when the temperature is increased from 300 K to 310 K, what is the activation energy? (Assume** R=8.314 J/mol K)
   a) 57.9 kJ/mol
   b) 48.2 kJ/mol
   c) 34.7 kJ/mol
   d) 23.5 kJ/mol

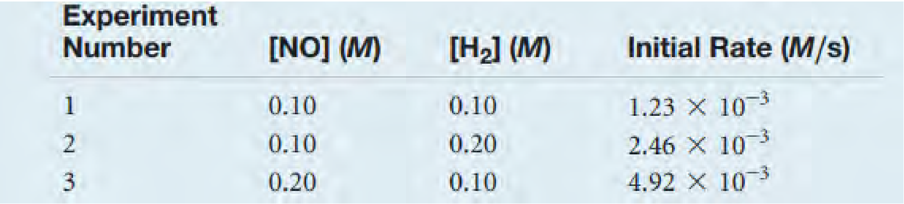
24. Hydrochloric acid is reacted with large pieces of calcium carbonate; the reaction is then repeated using calcium carbonate powder. How does this change affect the activation energy and the collision frequency?



	Activation energy	Collision frequency
A.	increases	increases
B.	stays constant	increases
C.	increases	stays constant
D.	stays constant	stays constant

25. The following data were measured for the reaction of nitric oxide with hydrogen:

$$2\,NO(g) + 2\,H_2(g) \rightarrow N_2(g) + 2\,H_2O(g)$$



Experiment Number	[NO] (M)	[H_2] (M)	Initial Rate (M/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

What is the overall order of the reaction

   a. 0
   b. 1
   c. 2
   d. 3

B. Short answer questions

---

1. Define the following terms
    e. Rate of reaction and rate constant
    f. Activation energy and activated complex

2. Differentiate the following
    a. Average and instantons rate
    b. Order and molecularity
    c. 1st order and 2nd order reaction
    d. Homogeneous and heterogeneous catalysis

3. What is meant by the rate of a chemical reaction? What are the units of the rate of a reaction? Can you suggest two reactions that are very slow (take days or longer to complete) and two reactions that are very fast (reactions that are over in minutes or seconds
4. Distinguish between average rate and instantaneous rate. Which of the two rates gives us precious measurement and why?
5. Define the meaning of initial rate. What are the advantages of measuring the initial rate of a reaction?
6. What do you mean by rate law? Write the rate law expressions for the following reactions in terms of the disappearance of the reactants and the appearance of products:
    (a) $H_2(g) + I_2(g) \rightarrow 2HI(g)$
    (b) $N_2 + 3H_2 \rightarrow 2NH_3$

7. Define rate constant (k) .State the units of k corresponding to each of the following rate equations:
    a rate = $k[NO]^2$
    b rate = $k[NH_3]^0$
    c rate = $k[BrO_3^-][Br^-][H^+]^2$

8. Suppose that nitric oxide (NO) is reacting with oxygen at the rate of 0.066 mol per liter /s to form NO_2 as given:
    $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
    a. write the rate law expression of this reaction
    b. calculate the rate of formation of NO_2
9. The rate constant for the decomposition of dinitrogen pentoxide, N_2O_5, at 45 °C dissolved in chloroform, $CHCl_3$, is 6.2 10^{-4} min^{-1}.
    $2N_2O_5 \rightarrow 4NO_2 + O_2$
    a. What is the order of this reaction and how do you know it?
    b. What is the molecularity of this reaction?
    c. What is the rate of the reaction when $[N_2O_5] = 0.40\ M$?

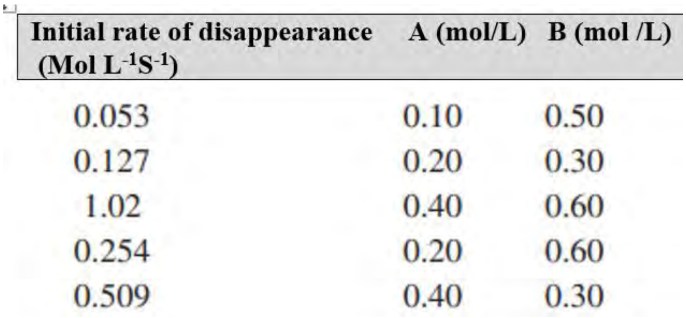
10. For the reaction Q→W+X,Q→W+X, the following data were obtained at 30 °C:

$[Q]_{\text{initial}}$ (M)	0.170	0.212	0.357
Rate (mol/L/s)	6.68×10^{-3}	1.04×10^{-2}	2.94×10^{-2}

   a. What is the order of the reaction with respect to [Q], and what is the rate equation?
   b. What is the value of rate constant?
   c. Write the rate law equation.

11. Explain what is meant by the rate law of a reaction. What are the units for the rate constants of zeroorder, first-order, and second-order reactions?

12. For the given reaction
   A +B → C
   a. Calculate the order of reaction with respect to A and B
   b. Calculate the rate of reaction when A=0.5 mol/L and B= 0.3 mol/L



Initial rate of disappearance (Mol $L^{-1}S^{-1}$)	A (mol/L)	B (mol /L)
0.053	0.10	0.50
0.127	0.20	0.30
1.02	0.40	0.60
0.254	0.20	0.60
0.509	0.40	0.30

13. For a first-order reaction, how long will it take for the concentration of reactant to fall to one-eighth its original value? Express your answer in terms of the half-life (t1/2) and in terms of the rate constant k

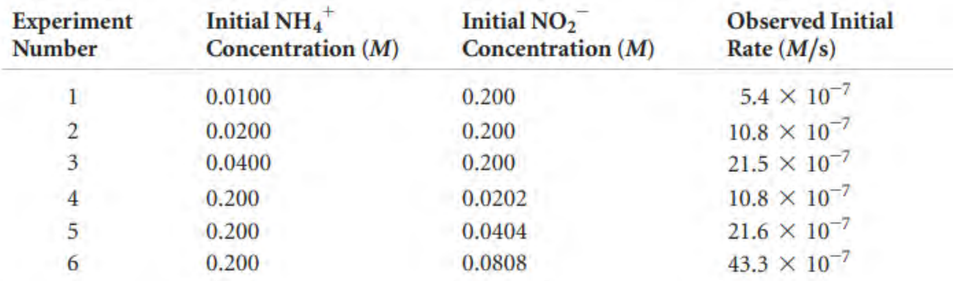
14. Given the same reactant concentrations, the reaction CO(g) + Cl2(g) → COCl2(g) at 250°C is 1.50 3 103 times as fast as the same reaction at 150°C. Calculate the activation energy for this reaction. Assume that the frequency factor is constant. 13.39 For the reacti

15. **Half-life period for a first order reaction is 20 min. How much time is required to change the concentration of the reactant form 0.08 M to 0.01 M?**

16. Distinguish between homogeneous catalysis and heterogeneous catalysis. Describe three important industrial processes that utilize heterogeneous catalysis.

17. When the concentration of A in the reaction A → B was changed from 1.20 M to 0.60 M, the half-life increased from 2.0 min to 4.0 min at 25°C. Calculate the order of the reaction and the rate constant.

18.
   a. Compare the initial concentration of NH_4^+ and initial observed rate in experiment number 1 and 2 and make a relation with concentration and rate of reaction.
   b. Find the order of reaction with respect to each reactant and determine the value of rate constant.



Experiment Number	Initial NH_4^+ Concentration (*M*)	Initial NO_2^- Concentration (*M*)	Observed Initial Rate (*M*/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

19. Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation:

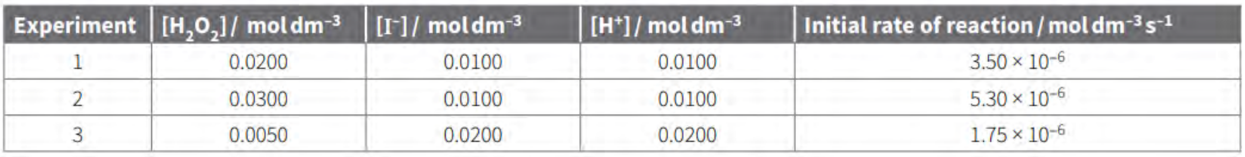
$H_2(g)+2NO(g) \rightarrow N_2O(g)+H_2O(g)$

Determine the rate equation, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (*M*)	0.30	0.60	0.60
$[H_2]$ (*M*)	0.35	0.35	0.70
Rate (mol/L/s)	835×10^{-3}	134×10^{-2}	2.268×10^{-2}

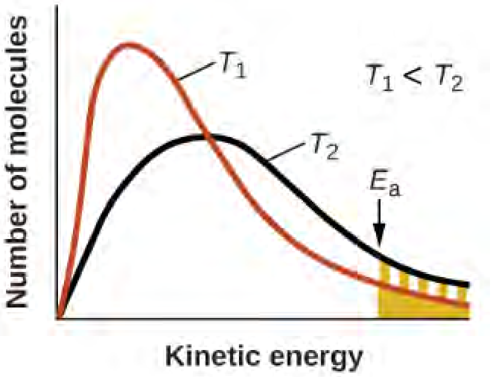
20. How much and in what direction will each of the following affect the rate of the reaction: $CO(g)+NO2(g) \rightarrow CO2(g)+NO(g)$ if the rate law for the reaction is rate=$k[NO_2]^2$?
    a. Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
    b. Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

21. Using the given information in the table below
    a. Find out the order of reaction with respect to each reactant
    b. Write the rate law equation
    c. Calculate the value of K



Experiment	$[H_2O_2]$/ mol dm^{-3}	$[I^-]$/ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.0200	0.0100	0.0100	3.50×10^{-6}
2	0.0300	0.0100	0.0100	5.30×10^{-6}
3	0.0050	0.0200	0.0200	1.75×10^{-6}

22. Maxwell's distribution curve at two different temperature is given to explain the effect o temperature on the rate of reaction



g. Name the variables in the x and y -axis

h. Is there any change in the activation energy at higher temperature?

i. Using the graph how can you explain the effect of temperature at higher temperature?

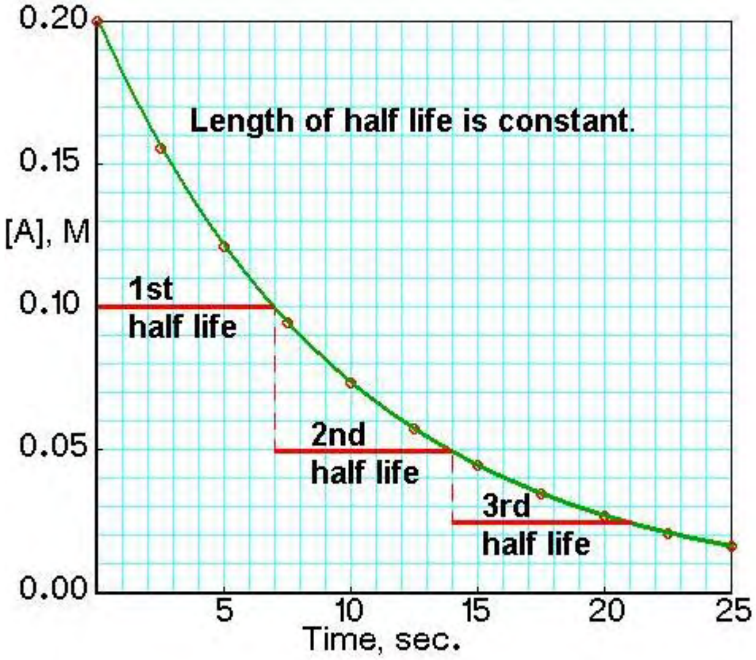
C. Long answer questions

1. Nitrogen (II) oxide reacts with chlorine according to the equation: $2NO(g)+Cl_2(g)\rightarrow 2NOCl(g)$
   The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L^1)	**[Cl$_2$] (mol/L)**	**Rate (mol/L/h)**
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

   a. What is the rate equation that describes the rate's dependence on the concentrations of NO and Cl_2?
   b. What are the orders with respect to each reactant?
   c. What is the value of rate constant?
   d. Find the rate of reaction when the reactant concentration are 2.0mol/L each .

2. The relationship between the concentration of reactants with time for certain reaction is shown in the plot given.



   a. Define the term half-life? Why is important to know the half liefe of a reaction or process?
   b. Identify the order of reaction given using the information in the plot and give reason for your choice.
   c. Calculate the rate of reaction for the change in concentration from 0.15 mol per liter to 0.05 mol per liter.
   d. What is the rate constant of the given reaction assuming it as a first order reaction .
   e. Predict the time for the completion of reaction .

3. The Haber's process of formation of ammonia is carried out in the presence of iron catalyst

$$N_2 + 3H_2 \underset{\text{Endothermic}}{\overset{\text{Exothermic}}{\rightleftharpoons}} 2NH_3$$

a. Define the term catalyst. How does catalyst alters the rate of reaction ?
b. What type of catalysis is this, define this catalysis.
c. Give reason behind low temperature and high pressure required to increase the yield of ammonia.
d. Is there any effect of catalyst in the position of equilibrium? why?

4. The initial rate of a reaction was measured for several different starting concentrations of A and B, and the results are as follows: $A + B \rightarrow C$

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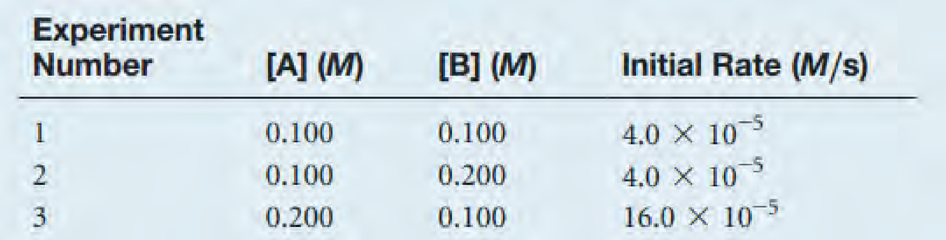


Experiment Number	[A] (*M*)	[B] (*M*)	Initial Rate (*M*/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

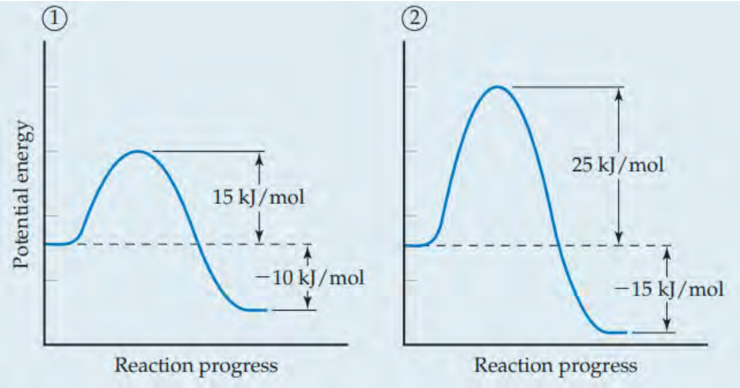
Using these data, determine
(a) the rate law for the reaction,
(b) the rate constant,
(c) the rate of the reaction when [A]= 0.5M and [B]= 0.05M

5. A hypothetical reaction is zero order with respect to X and 2nd order with respect to Y

$$X + Y \rightarrow XY$$

a. Write the rate law equation for this reaction
b. Determine the overall order of the reaction,
c. If the rate constant of this reaction is $2.0x\ 10^{-2}$ L mol^{-1} s^{-1} , determine the initial rate of disappearance of X when the concentration of X is 0.30 M and that of Y is 0.40 M

6. Energy profile diagram is given.



a. What do you mean by energy profile diagram?
b. Identify the figure whether it is endothermic or exothermic and why ?
c. What is the value of activation energy in each diagram?
d. Which one proceeds faster and why?
e. Which of the process (1 or 2) gives the more stable product and why?

Unit 4

Chemical thermodynamics

Activity:

a. Take two beakers and pour 50 mL of cold water into each. Measure and record their initial temperatures.

b. Heat the water in one of the beakers until it reaches about (40-50) °C. Measure and record the temperature.

c. Pour both samples of water (cold and warm) into a single beaker and mix them well. Measure and record the final temperature of the mixture.

	Cold water	Hot water	Mixture
Temperature/°C			

Conclusion :

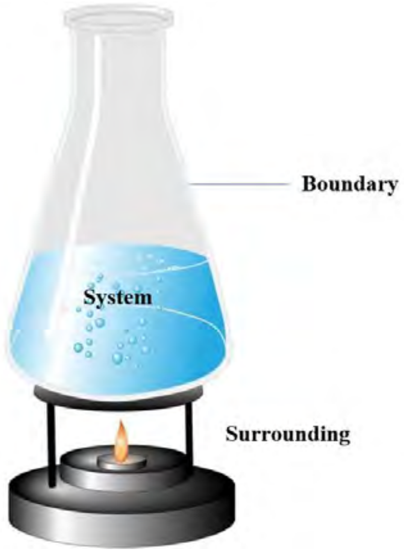


Fig: system gets energy from the surrounding

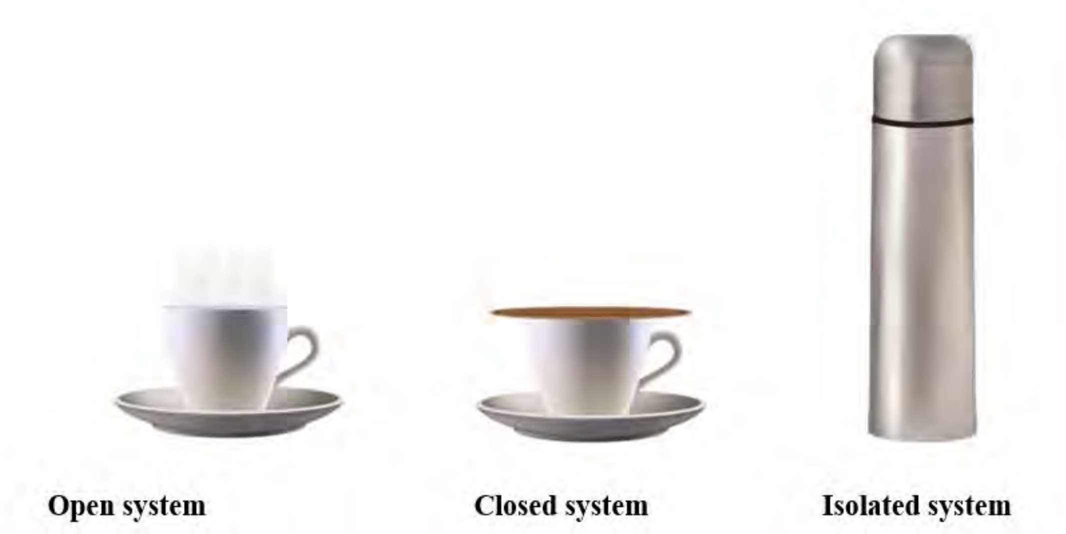
4.1 Introduction

When you keep a glass of hot water on the table, it becomes cool after some time. Why?

The hot water loses its heat to the surroundings, and the surroundings absorb the heat. You can warm the water again so that it takes heat from the surroundings and becomes hot. This exchange of heat energy between the water and its surroundings is thermodynamics.

A **system** is the part of the universe we are studying. The **surroundings** include everything outside the system. The **boundary** is an imaginary line that separates the system from its surroundings.

There are different types of systems:



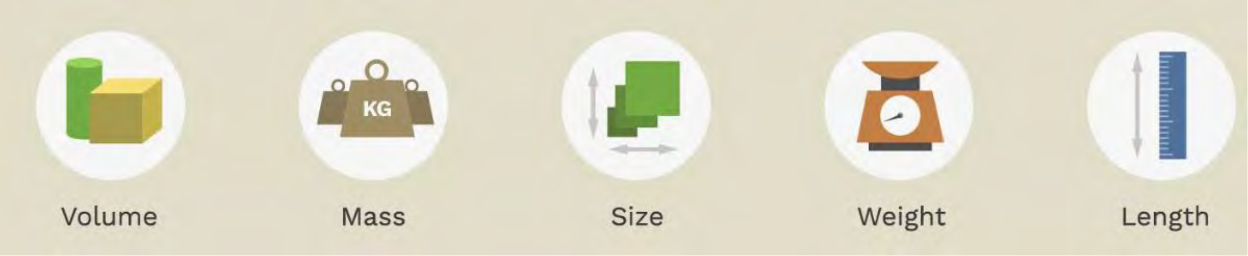
1. **Open System**: In this system, both matter and energy can move between the system and its surroundings. An example is an open cup of tea, where you can add more tea (matter) or heat it again (energy).
2. **Closed System**: In this system, only energy can move in and out, but matter cannot. For example, if you close a container, it can still gain or lose heat, but you cannot add or remove matter unless you open it.
3. **Isolated system:** In this system**,** neither matter nor energy can move in and out of the system. For example, the hot water stored in the thermos flask remain hot unless you open it**.**

Thermodynamics is the study of energy and how it is interconverted between system and surrounding.

4.1.1 properties of system

Activity :

Observe the differnet properties of the system given.Discuss in pair and identify which of the properties depend upon number of particles (or amount) and which do not and fill the table as given.



Properties	Depend up on amount/number	Does not depend upon amount /number
Volume	✓	✗

If you have a glass of water, you can measure its mass, volume, temperature, density, heat, and other properties. These properties define the system under specific conditions.

Some properties remain the same regardless of the amount of substance, such as temperature. For example, the temperature of water in a bucket is the same as that of the water in a glass. These are called **intensive properties**. Other properties, like heat, entropy, or internal energy, change with the size or amount of matter. These are known as **extensive properties.**

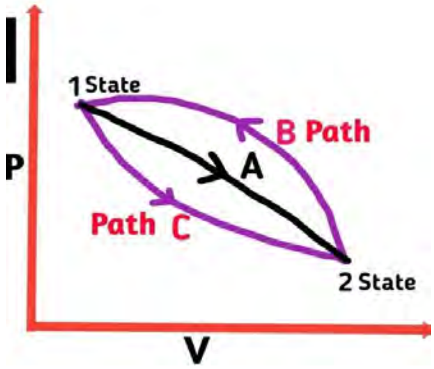
Figure: Ice cube of different mass have same temperature, specific heat capacity and refractive index but have different volume, enthalpy, entropy and internal energy

Intensive properties remain the same regardless of the amount of substance where as extensive properties change with the size or amount of matter.

4.1.2 State function and path function

If water is heated from 25°C to 100°C, change in temperature (75°C) is same whether you heat it slowly or quickly. But work done is different if the process occurs slow or fast. It means, in thermodynamics, properties of a system are classified as **state functions** and **path functions** based on their dependence on the process or path taken.

Properties of the system like Pressure (P) Temperature (T), Volume (V), Internal Energy (U), Enthalpy (H), Entropy (S) or Gibbs Free Energy (G) depends upon initial and final state not on the path followed. They are called **state functions**. For these functions we can measure the change so we write ΔP, ΔV, ΔH or ΔE.



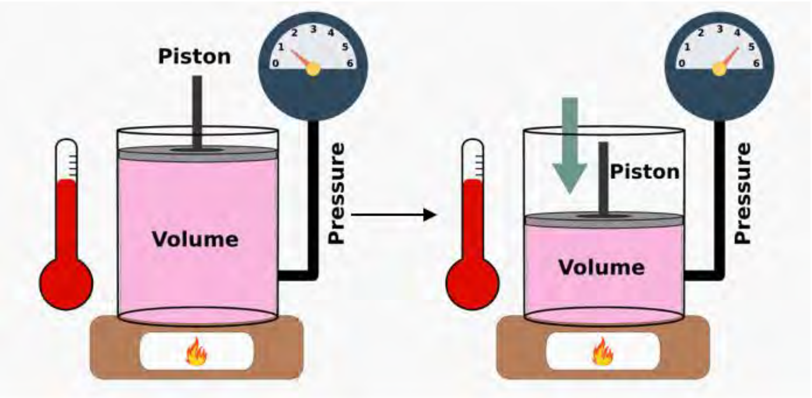
Work done (W) or heat(Q) for the path **A** in the figure is different from the path **B** and **C**. So, these functions are called **path functions**. **Example:** The amount of work done in compressing a gas depends on whether the process is slow, fast, isothermal, or adiabatic.

A state function is a property that depends only on the initial and final states of the system, not on the path taken to reach that state.

A path function is a property that depends on the specific path or process taken to go from one state to another.

4.1.3 Thermodynamic processes

Activity: Identify the properties (temperature ,pressure ,pressure) of the gas kept in cylinder(system) that remain constant and those that change in the given figure moving from left to right .



When a system changes from one state to another, there is a change in the properties of system like volume, pressure, temperature etc. There are different types of thermodynamic process which describes these changes.

a. Isothermal Process ($\Delta T = 0$)

In this process, temperature remains constant. Heat exchange occurs to maintain constant temperature. Example: Slow expansion/compression of gas in a heat bath.

b. Adiabatic Process ($Q = 0$)

In this process there is no heat exchange with surroundings. So that work done changes internal energy of the system. Example: Rapid compression/expansion of a gas in an insulated container.

c. Isobaric Process ($\Delta P = 0$)

In this process, pressure remains constant. Heat absorbed or released changes volume and temperature. Example: Boiling water at atmospheric pressure.

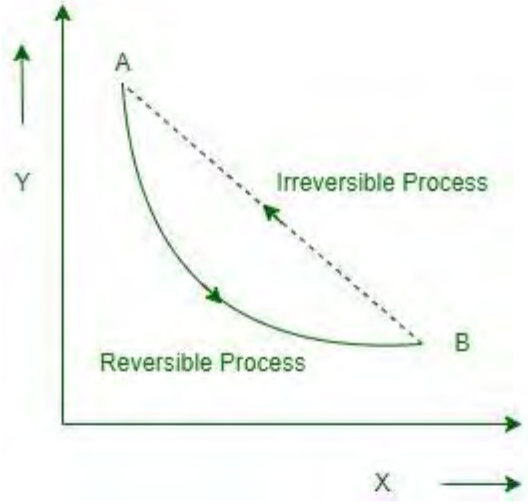
d. Isochoric Process ($\Delta V = 0$)

In this process, volume remains constant. So, there is no work is done ($w = p\Delta V$). Heat transfer changes temperature and pressure of the system. Example: Heating a gas in a closed rigid container.

e. Cyclic Process

The system returns to its initial state after a cycle. Such process is useful in heat engines and refrigerators. The change in internal energy(ΔE) is zero.

f. Reversible and Irreversible Processes

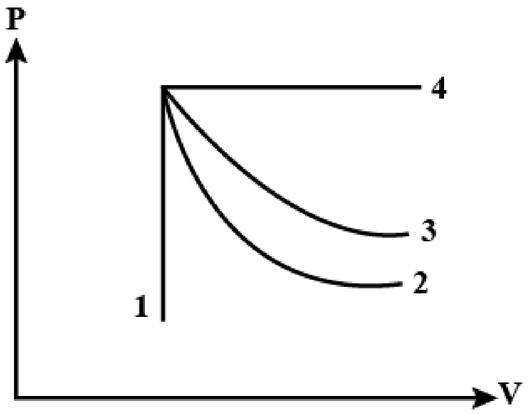


A **reversible process** is an idealized thermodynamic process that can be reversed without leaving any change in the system or surroundings. It proceeds infinitely slowly, so that the system is in **thermodynamic equilibrium** at every stage. Work done in a reversible process is maximum for an expansion process and minimum for a compression process.

An **irreversible process** is a real-world thermodynamic process that cannot be exactly reversed. It results in an increase in entropy and involves losses due to dissipative factors. Work output is always less than the maximum possible work due to energy losses. **Example:** rapid compression or expansion of a gas.

Try yourself:

Identify the process (1-4) in the given diagram whether it is isothermal. Isobaric, isochoric or adiabatic.

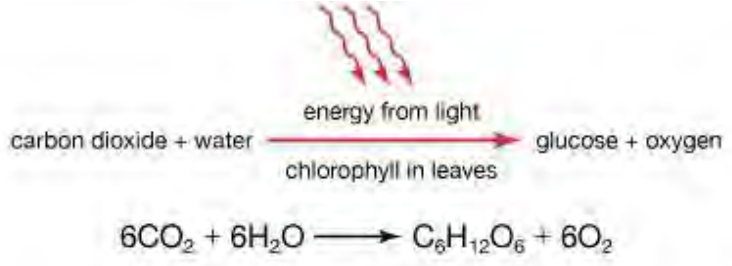


4.2 Energy in a chemical reaction

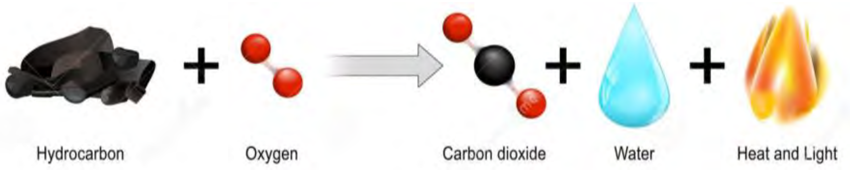
Activity:

Two examples of chemical reactions (photosynthesis and combustion) are given.

Identify the process in which energy is absorbed and in which energy is released



Photosynthesis reaction



Combustion reaction

As we already discussed about the change in energy between the system and surrounding so that there is a conservation of energy. In the chemical reaction also either there is a gain or loss of energy between the system and surrounding .The reactants ,products or the solvent used acts as a system in the chemical reaction .Likewise the the appratus , any measuring devices or the laboratory acts as a surrounding.While changing the reactants to the products chemical bonds in the reactants are broken whereas new bonds are formed in the product. So bond breaking is an **endothermic process** and bond formation is an **exotheric process.** For example, energy is absorbed from the surroundings in the photosynthesis and energy is released to the surroundings in combustion reaction.

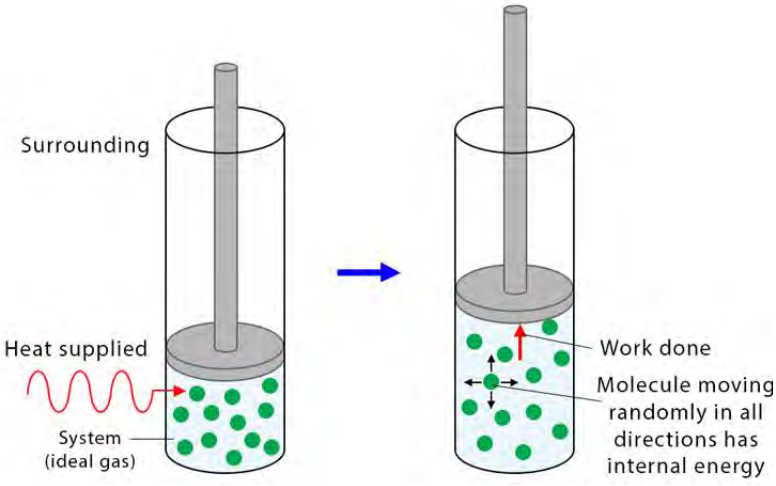
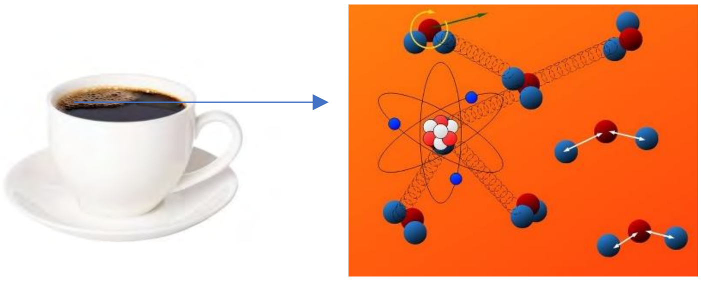


Figure: energy is absorbed by the system and does some work

4.3 Internal energy (E or U)



The hot coffee has high internal energy due to its high temperature. As it cools, heat is transferred to the surroundings, and internal energy decreases. Likewise, Battery produces electrical energy by the conversion of chemical energy. Chemical energy inside the battery is produced due to the different types of energy (kinetic, potential etc.) of the molecules present in it. Kinetic energy is due to translational, vibrational, and rotational motion of the particles whereas potential energy is due to intermolecular forces among these particles.

The sum of all form of energy of a system (internal energy, kinetic energy, potential energy, and other forms of energy) is considered as internal energy. It is denoted by **E** or **U**

E = Kinetic energy +potential energy + rotational energy+ vibrational energy + translational energy etc.

Since, the change in internal energy depends on the initial and final states and not on the path followed, it is a state function, not a path function. The change in internal energy can be written as

$$\Delta E = E_{final} - E_{initial}$$

Where,

E_{final} : Internal energy of the final state

$E_{initial}$: Internal energy of the initial state

In an **isolated system**, internal energy remains constant since no heat or work is exchanged with the surroundings.

Internal energy is the total energy contained within a system due to the motion and interactions of its particles

Internal energy depends upon the number of particles present, block of 100 kg iron has more internal energy than that of 50 kg iron. When heat is added to the substance, the particles start to vibrate and move more vigorously so internal energy increases.

4.4 First law of thermodynamics

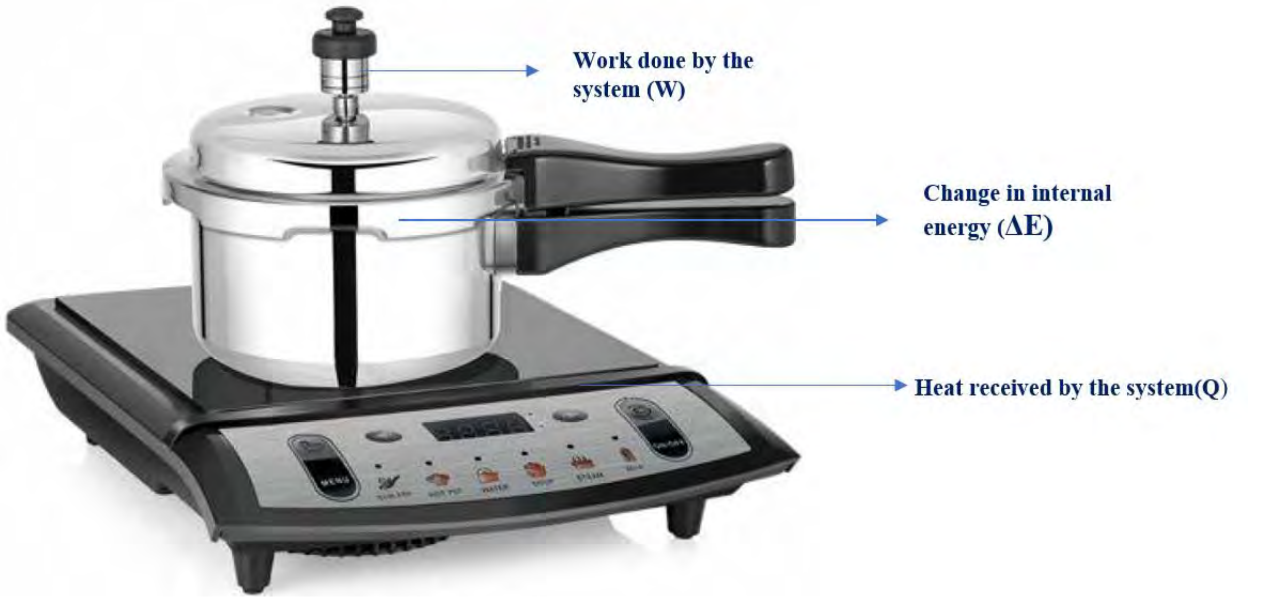


Fig: heat received is used to increase the internal energy and work done

The food that we eat contains chemical energy. Our body converts this energy into **mechanical work and heat**. Devices like microwaves or heaters transform electrical energy into **heat or work**. Likewise, car engines convert heat energy into mechanical work. It means there is a conversion of energy from one form to another.

The first law of thermodynamics is based on the principle of **conservation of energy** and it states that **whenever heat is added to a system, the heat will transform to some other form of energy in the same amount**.

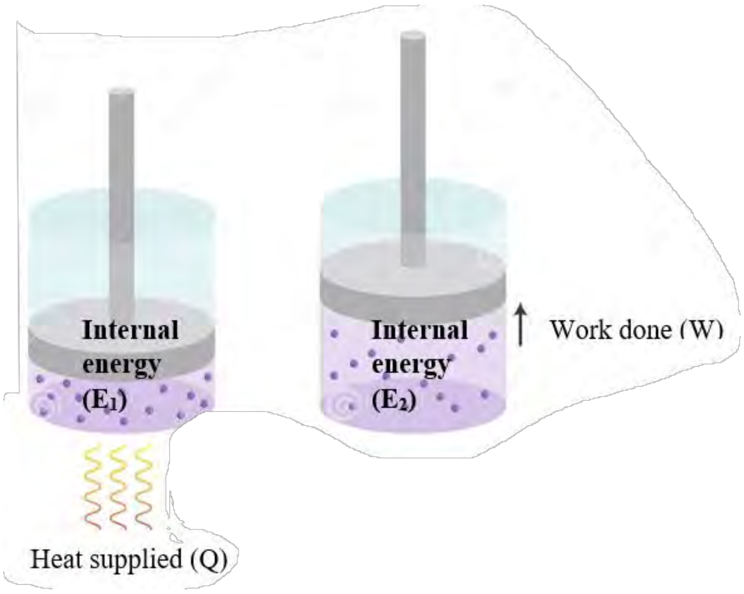
Mathematical formulation of the first law of thermodynamics

Let us consider a system having internal energy **E**. If **Q** amount of heat is added to the system, its internal energy increases due to the increased kinetic energy of the particles, The increased energy does some work '**w**'

Therefore, the change in internal energy **(ΔE) =Q-W**

Or

Heat added to a system = increase in internal energy of the system + external work done by the system.



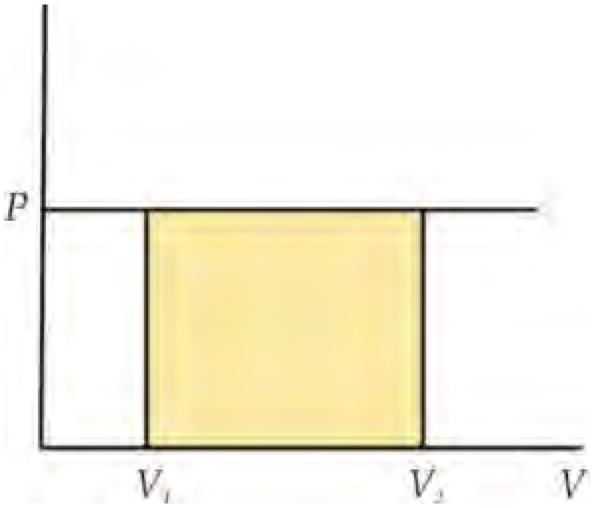


Figure : work done(W) = P×change in volume(ΔV)

Sign convention

Q = +ve when heat is absorbed and -ve when released
W = +ve when work is done on system and -ve when work is done by the system.

The work done on the surroundings by the reversible expansion of the system against the piston can be calculated as:

$$w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1}$$

Special cases of first law of thermodynamics

- **Isolated System**
  In isolated system (e.g. thermos flask) where no heat or work is exchanged with surroundings. Therefore, Internal energy remains constant ($\Delta E=0$).
  The above relationship is written as
  Q=W

a. **Isothermal Process**
   In isothermal process (For Example: Expansion or compression of an ideal gas in a cylinder with a movable piston) ,temperature remains constant($\Delta T=0$).Therefore change in internal energy ($\Delta E=0$) .
   Q=W
   It means all heat added is converted into work.

b. **Adiabatic Process**
   In adiabatic process (Example: Rapid compression of gas in an engine cylinder) there is no exchange of heat ($\Delta Q=0$). The First Law reduces to
   $\Delta E=-W$. It means work done by the system decreases internal energy.

c. **Isochoric Process**
   In isochoric process (example, heating a gas in a rigid, sealed container.) volume remains constant($\Delta V=0$)
   The First Law simplifies to $\Delta E=Q + W$
   $\Delta E=Q + P\,\Delta V$
   Or, $\Delta E=Q$
   It means all heat added increases internal energy.

d. **Isobaric Process**

   In isobaric process (example Boiling water at atmospheric pressure) pressure remains constant **$\Delta P=0$**

   So, there is no work done

   Heat added to the system is partly used to change internal energy and partly to do work.

Try yourself

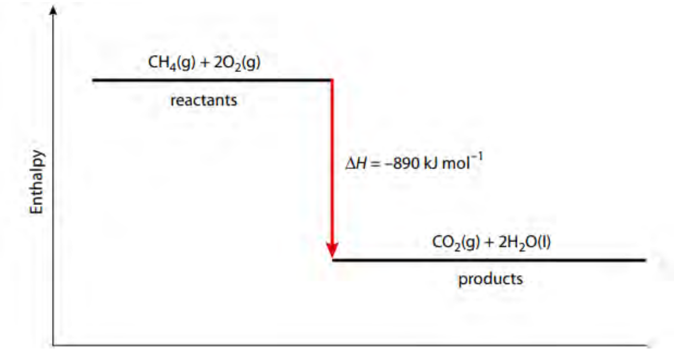
A gas in a piston absorbs **600 J** of heat and does **200 J** of work by expanding. Calculate the change in internal energy.

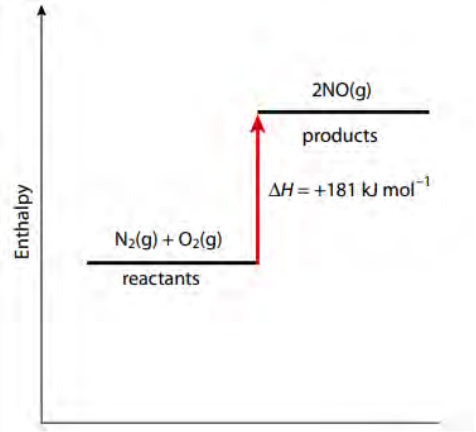
Remember: When two systems A and B each in thermal equilibrium with a third system C, then A and B are also in thermal equilibrium with each other at same temperature. This is called **zeroth law of thermodynamics**

4.5 Enthalpy and enthalpy changes: Endothermic and exothermic processes

Activity:

Use the given figure to answer the questions





a. Write the balanced chemical equation for each of the given reaction.

b. What is the difference between these two processes in terms of enthalpy (energy)?

If you touch ice, it feels cold because it takes heat from your hand. Ice absorbs energy from the environment, this energy increases the kinetic energy of the water molecules, allowing them to move more freely and transform into the liquid state. The total heat content in the ice or water is said to be its **enthalpy**. The enthalpy of water is greater than that of ice, therefore the change in enthalpy **(ΔH) is positive** and the process is called **endothermic process**.

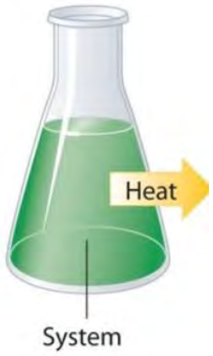
fig: melting of ice is an endothermic process

fig: burning of firewood is an exothermic process

In the same way burning of firewood releases heat to the surrounding so the change in enthalpy **(ΔH) is negative**. This process is called **exothermic process.**

Enthalpy is a thermodynamic property that represents the total heat content of a system

Enthalpy Change (ΔH)



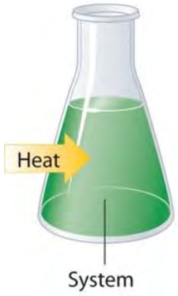
Enthalpy change refers to the heat absorbed or released during a process at constant pressure. It is calculated as:

$\mathbf{\Delta H = H_{final} - H_{initial}}$

for a chemical reaction:

change in enthalpy (ΔH) $= H_{products} - H_{reactants}$

If $\Delta H < 0$ (negative) → The reaction is **exothermic** (releases heat).



If $\Delta H > 0$ (positive) → The reaction is **endothermic** (absorbs heat).

Reversing a reaction or a process changes the sign of Δ***H***.

$\text{heat} + H_2O(s) \rightarrow H_2O(l) \quad \Delta H > 0$

$H_2O(l) \rightarrow H_2O(s) + \text{heat} \quad \Delta H < 0$

Mathematically enthalpy is defined as the internal energy plus the product of the pressure and volume of the system:

$$\mathbf{H = E + PV}$$

Where, H = Enthalpy

E = Internal energy of the system
P = Pressure
V = Volume

change in enthalpy (ΔH) $= H_{products} - H_{reactants}$

$$\mathbf{\Delta H = \Delta E + p\Delta V} \text{ [at constant pressure] ……. } \mathbf{(1)}$$

From first law of thermodynamics

$\Delta E = q + w$

Equation (1) becomes

$\Delta H = q + w + p\Delta V$

If work done by the system at constant pressure = $-p\Delta V$

$\Delta H = q_p$

Thus, the change in enthalpy equals the heat gained or lost at constant pressure

The change in enthalpy at standard conditions (1 atmospheric pressure, 25 ^{0}C temperature and 1 mol /L concentration) is called standard enthalpy change (ΔH^0)

4.6 Enthalpy of reaction

a. Standard Enthalpy change of solution (ΔHsol)

Have you ever used instant cold pack in first aid to reduce swelling and pain? Do you know chemistry behind it?

Inside the pack, there are two compartments: containing water (in the inner bag) and solid salt (ammonium nitrate). When squeezed, the inner water bag breaks, allowing the salt to dissolve in water. The **dissolution process** absorbs heat from the surroundings, making the pack feel **cold**.

The dissolution of ammonium nitrate can be written as

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq) \quad \Delta H^\circ_{\text{sol}} = +25.7\ \text{kJ/mol}$$

It means 25.7kJ of energy is absorbed by 1 mole of solid ammonium nitrate to form a solution. 25.7kJ is called **enthalpy of solution** of ammonium nitrate.

Standard Enthalpy change of solution (ΔH ^{0}sol) is the enthalpy change when one mole of solute is dissolved in excess solvent to form a solution of 'infinite dilution' under standard conditions.

Try yourself

Using the enthalpy of solution given answer the question

Salt	ΔHsol° (kJ/mol)
Ammonium Nitrate (NH_4NO_3)	+25.7
Urea ($CO(NH_2)_2$)	+13.9
Ammonium Chloride (NH_4Cl)	+14.7

a. which salt absorbs more heat to form a solution?
b. Why is ammonium nitrate preferred in the cold pack?

b. Standard Enthalpy of reaction ($\Delta H°r_{xn}$)

Observe the enthalpy change of the given two reactions

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)} \quad \Delta H_2 = +180\ kJ$$

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)} \quad \Delta H_3 = -112\ kJ$$

The first reaction shows 180kJ of energy is required to proceed this reaction whereas -112kJ of energy is released in the second reaction. These values (ΔH_1 and ΔH_2) are **enthalpy of these reactions.** The **Standard Enthalpy of Reaction ($\Delta H°r_{xn}$)** is the enthalpy change when a reaction occurs under standard conditions (298 K &1 atm).

Enthalpy of Reaction ($\Delta H°r_{xn}$) is calculated using the standard enthalpies of formation ($\Delta H°f$) of the reactants and products

$$\Delta H^\circ_{rxn} = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})$$

For a general chemical reaction

$$aA + bB \longrightarrow cC + dD$$

$$\Delta H^\circ_{rxn} = [c\Delta H^\circ_f(C) + d\Delta H^\circ_f(D)] - [a\Delta H^\circ_f(A) + b\Delta H^\circ_f(B)]$$

c. Standard Enthalpy of Formation ($\Delta H_f°$)

Let us consider a reaction for the formation of water, the enthalpy change of this reaction is given as

$H_2(g)+1/2O_2(g)\rightarrow H_2O(l) \quad \Delta H=-285.8$ kJ/mol

This means 285.8 kJ of energy is released when 1 mole of liquid water is formed from H_2 and O_2 in their standa states. This value (−285.8 kJ) is standard enthalpy of formation of water. Negative sign indicates process is exothermic and energy is released.

Likewise, standard enthalpy of formation of carbon dioxide is given as

$C(graphite)+O_2(g)\rightarrow CO_2(g)\ \Delta Hf° = -393.5$ kJ/mol

Standard Enthalpy of Formation ($\Delta H_f°$) determines the relative stability of the compound. More negative the va indicates more energy is released while forming the compound and the compound is more stable compared to negative value. For example the standard enthalpy of formation of CO_2 is more negative than CO, so CO_2 is m stable than CO .

$C(s, graphite)+1/2O_2(g)\rightarrow CO(g) \quad \Delta H_f° = -110.5$ kJ/mol
$C(s, graphite)+O_{2(}g)\rightarrow CO_2(g) \quad \Delta H_f° = -393.5$ kJ/mol

$\Delta H_f°$ of an element in its standard state is **zero** (e.g., $O_2(g)$, $N_2(g)$, C(graphite), etc.) When an element is in its standard state, it is in its most stable form, meaning it does not need to undergo any change to exist in these conditions. Therefore, there is no energy absorbed or released, and the enthalpy change is zero

Try yourself

Compound	Enthalpy of formation (kJ/mol)
Hydrogen (H_2)	0
Methane (CH_4)	-74.6
Ethane (C_2H_6)	-84
Ethylene(C_2H_4)	52.5
Carbon dioxide (CO_2)	-393.5
Water (l)	-286

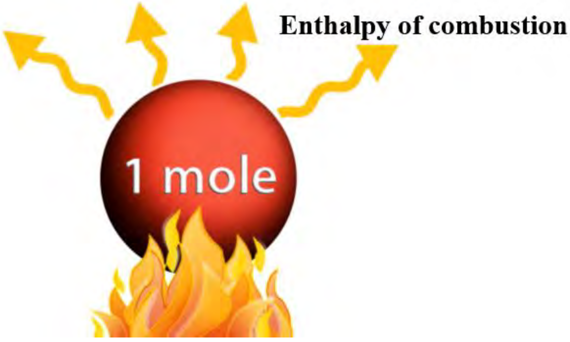
Which of the substance given above is highly stable and why?

Standard Enthalpy of Formation ($\Delta H_f°$) is the change in enthalpy when one mole of **a compound is formed from its elements in their standard states under standard conditions** (**1 atm pressure and 298.15 K temperature**)

d. Standard Enthalpy of Combustion ($\Delta H_c°$)

We know that when hydrocarbon like methane is burnt with oxygen, carbon dioxide and water is formed along with energy. This reaction can be written as,

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H_c^\circ = -890.3\ \text{kJ/mol}$$



It means 890.3 kJ of energy is released when 1 mole of methane burns completely. This enthalpy change (**-890.3 kJ)** is **enthalpy of combustion** of methane**.** Likewise, the enthalpy of combustion of ethanol is given as,

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H_c^\circ = -1367\ \text{kJ/mol}$$

So that ethanol is used as a biofuel.

It is **always negative** because combustion is an **exothermic** process (releases heat). Hydrocarbons with more carbon atoms release more energy because they have more C-H bonds. Unsaturated compounds release less energy compared to saturated hydrocarbons.

The Standard Enthalpy of Combustion (ΔHc°) is the enthalpy change when one mole **of a substance completely burns in oxygen under standard conditions.**

Calorific value

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H_c^\circ = -890.3\ \mathrm{kJ/mol}$$

The above equation indicates -890.3kJ of energy is released when 1 mole of methane is burnt completely. What is the energy released when 1g of methane is burnt completely?
We can calculate it simply
1 mole of methane = -890.3kJ
16 g of methane = -890.3kJ
1 g of methane = - 222.5kJ

This value is the calorific value of methane. Higher the calorific value of food or fuel indicates its higher quality. This value is important in choosing the most efficient fuel for engines and power plants.

Remember:

a. Fossil fuels (petrol, diesel, coal) have high calorific values, making them efficient but polluting.
b. Biofuels (ethanol, wood) have lower calorific values but are renewable.

Calorific value is the amount of energy released when 1 g or 1 kg of a substance is completely burned in oxygen. It is usually expressed in: kJ/g or kJ /kg

Try yourself:

Using the table given, answer the given questions

Fuel	Calorific Value (kJ/kg)
Hydrogen (H_2)	142,000
Methane (CH_4)	55,500
LPG (Liquefied Petroleum Gas)	46,000
Petrol (Gasoline)	47,300
Diesel	45,500
Kerosene	46,000

a. Which of the fuel is most efficient fuel and why?
b. What is the enthalpy of combustion of hydrogen?

4.7 Laws of thermochemistry

Germain Henri Hess (1802–1850) was a Russian chemist and physician of Swiss origin, best known for his work in thermochemistry. Hess formulated Hess's Law in 1840, which states that the total enthalpy change in a chemical reaction is independent of the reaction pathway, a fundamental principle in thermodynamics. He also conducted important research on sulfur and platinum compounds. Hess's contributions laid the groundwork for later developments in chemical thermodynamics**.**

a. Laplace Law (First law of thermochemistry)

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), \quad \Delta H = -285.8\ \mathrm{kJ/mol}$$

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g), \quad \Delta H = +285.8\ \mathrm{kJ/mol}$$

The above example illustrates that **heat of formation** of water and **heat of decomposition** of water are equal in value but the sign is different. It means formation of water releases energy (exothermic) and same amount of energy is absorbed to decompose water (endothermic). This was given in the form of law by Lavoisier and Laplace in 1780. Lavoisier and Laplace law also called **first law of thermochemistry** states that "

The heat required to decompose a compound into its elements is equal in magnitude but opposite in sign to the heat evolved when the compound is formed from its elements.

$$S(s) + O_2(g) \rightarrow SO_2(g)\ \Delta H = -296.9\ \mathrm{kJ}$$

$$SO_2(g) \rightarrow S(s) + O_2(g)\ \Delta H = +296.9\ \mathrm{kJ}$$

a. Hess's law (second law of thermochemistry)

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H_1 = -110.5\ \mathrm{kJ}$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H_2 = -283.0\ \mathrm{kJ}$$

What will be the heat of formation of carbon dioxide?

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

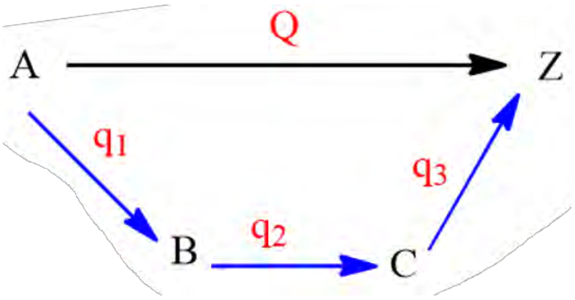
Using second law of thermochemistry (Hess's law) the heat of formation of carbon dioxide can be calculated as

$$\Delta H_{\mathrm{overall}} = \Delta H_1 + \Delta H_2$$

$$\Delta H_{\mathrm{overall}} = (-110.5) + (-283.0) = -393.5\ \mathrm{kJ}$$

If a reaction occurs in multiple steps, the enthalpy change of the overall reaction is the sum of the enthalpy changes of the individual steps:

$\Delta H_{\mathrm{overall}} = \sum \Delta H_{\mathrm{steps}}$



$Q = q_1 + q_2 + q_3$

The total enthalpy change of a reaction is the same, regardless of the number of steps in which the reaction occurs, as long as the initial and final conditions remain the same

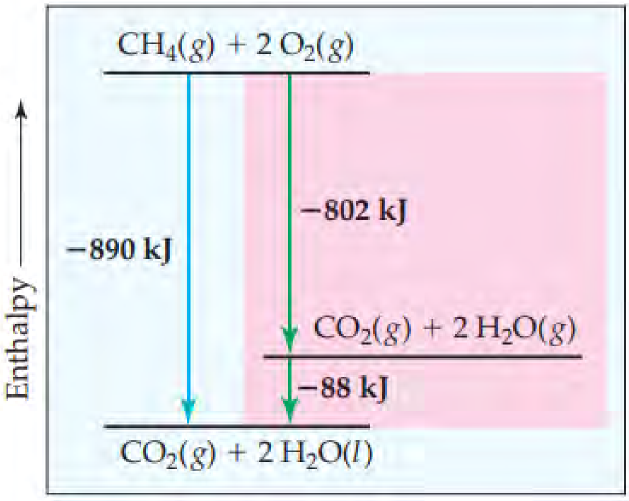
For example , the enthalpy change of two differnet process are given

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad \Delta H = -802\ \mathrm{kJ}$$

$$2\,H_2O(g) \longrightarrow 2\,H_2O(l) \qquad \Delta H = -\ 88\ \mathrm{kJ}$$

You can add these two steps to get the enthalpy change of the given reaction as shown in the figure below:

$$CH_4(g) + 2\,O_2(g) + 2\,H_2O(g) \longrightarrow CO_2(g) + 2\,H_2O(l) + 2\,H_2O(g)$$



Hess's law is useful and is the only way of calculating such non-measurable enthalpy changes in physical and chemical changes.

For example, measuring the enthalpy of formation of benzene, from carbon and hydrogen is not possible, because carbon and hydrogen may combine to form not only benzene, but also other types of hydrocarbons in the given conditions. But this can be calculated from Hess's law using the combustion data of carbon, hydrogen and benzene.

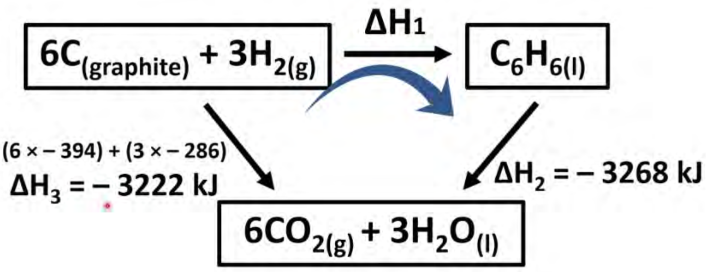
$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l);\ \Delta H=-286kJ$

$C(s)+O_2(g)\rightarrow CO_2(g);\ \Delta H=-394kJ$

$C_6H_6(l)+\frac{15}{2}O_2(g)\rightarrow 6CO_2(g)+3H_2O(l)\quad \Delta H=-3268kJ$

$6C + 3H_2 \rightarrow C_6H_6 \qquad \Delta H = ?$

These reactions can be arranged in the form cycle called **enthalpy cycle** or **Hess's cycle** as:



Using Hess's law, $\Delta H_1 + \Delta H_2 = \Delta H_3$

$$\text{or},\ \Delta H_1 - 3268 = -3222$$

$$\text{therefore},\ \Delta H_1 = -3222 + 3268$$

$$= 46\ kJ$$

You can solve this problem directly using the combustion equation of benzene.

$C_6H_6(l)+152O_2(g)\rightarrow 6CO_2(g)+3H_2O(l)$ $\Delta H= -3268kJ$

$\Delta H = \sum H_{\text{Products}} - \sum H_{\text{reactants}}$

$\Delta H \; = 6x-394+3x(-286)$

$= 46k\ J$

Try yourself

From the data given find the heat of formation of methanol

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\Delta H = -726kJ$$

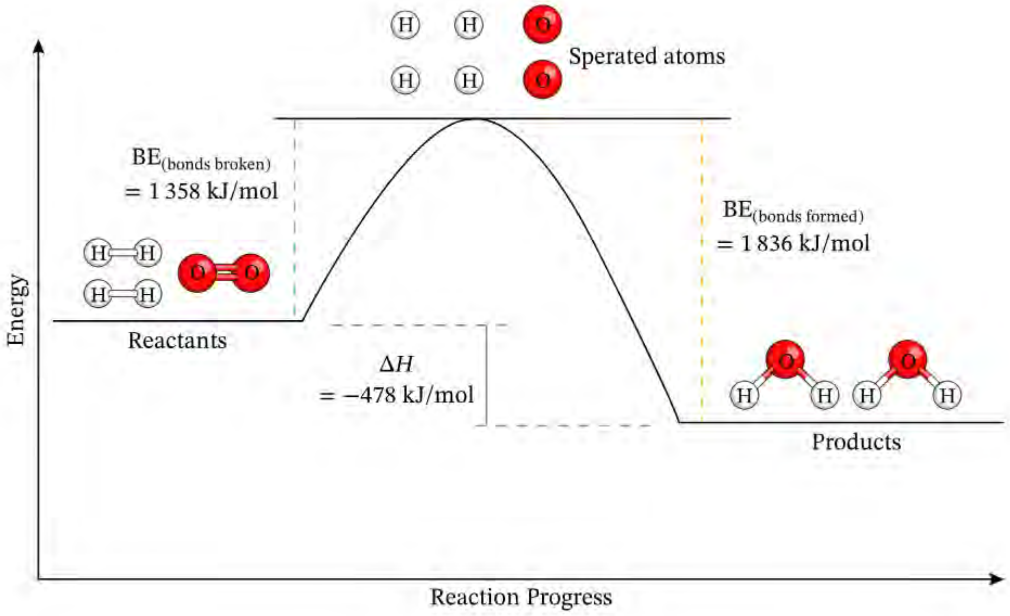
$$C(s) + O_2(g) \longrightarrow CO_2(g);\Delta H = -394kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\Delta H = -286kJ$$

4.7.1 Bond energy or bond enthalpy

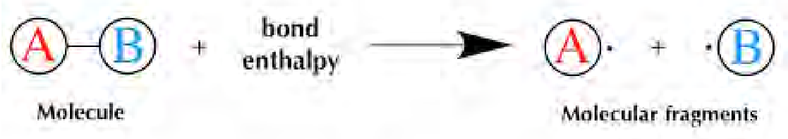
Activity:

Observe the energy profile diagram given and fill the table provided:



Number of H-H bon in the reactant	Number of O=O bond in the reactant	Number of O-H bond in the product	Change in enethalpy during the reaction

All the covalent bonds in a molecule are not equally strong.It's value depends upon the nature of bonded atom and its environment.For example it requires 612kJ of energy to break one mole of C=C bond but only 347kJ is required to break one mole of C-C bond.It means C=C is stronger than C-C. These values are called bond energy or bond enthalpy of that particular bond. It is measured in **kilojoules per mole (kJ/mol)**.



Bond enthalpy bond energy is the amount of energy required to break or form one mole of of bond.

Factors Affecting Bond Enthalpy

a. **Bond Order**

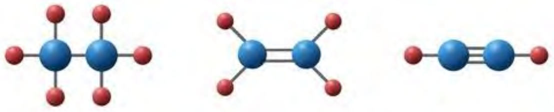
Higher bond order (single < double < triple) leads to stronger bonds and higher bond energy.

Example:

C-C (single) = 348 kJ/mol

C=C (double) = 612 kJ/mol

C≡C (triple) = 837 kJ/mol



b. **Bond Length**

Shorter bonds are stronger and require more energy to break.

Example:

F-F bond (longer) = 158 kJ/mol (weak bond)

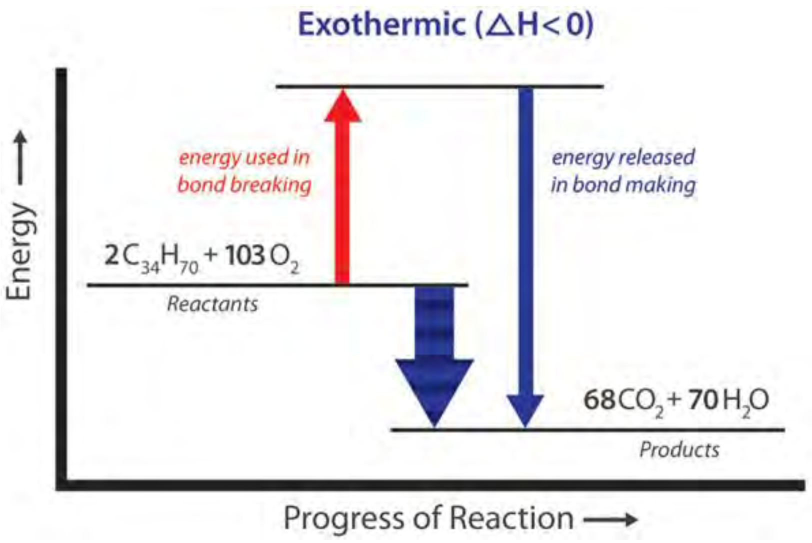
N≡N bond (shorter) = 945 kJ/mol (strong bond)

c. **Electronegativity**

More electronegative atoms form stronger bonds and has more bond energy.

Example: C-F bond (485 kJ/mol) is stronger than C-I bond (240 kJ/mol) due to higher electronegativity of fluorine

During the chemical reactions the bond in the reactants are broken so it requires energy (endothermic) whereas while forming the products ,energy is released (exothermic).The sum of all the bond energy gives the **enthalpy of that reaction**.



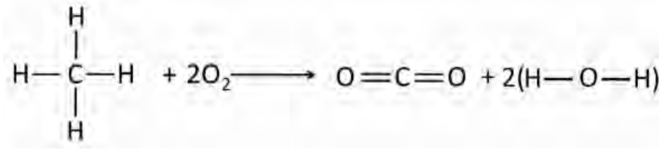
The above graph shows the combustion reaction of hydrocarbon to form carbondioxide and water. The total enthalpy change of this process is the sum of energy required to break all the bonds present in the reactants and the energy released in the formation of products.

The **enthalpy change** (ΔH) of a reaction can be estimated using bond enthalpies:

$$\Delta H = \sum \text{Bond enthalpies of bonds broken} - \sum \text{Bond enthalpies of bonds formed}$$

For Example in the combustion of Methane

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



There are four C-H bonds ,two O=O bonds in the reactants likewise two C=O bonds and four O-H bonds in the products.

$\Delta H = \sum \text{Bond enthalpies of bonds broken} - \sum \text{Bond enthalpies of bonds formed}$

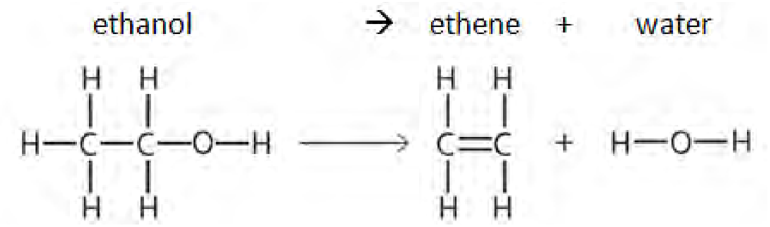
$= (4\times412+2\times498) - (2\times805+ 4\times463)$

$==-818$ kJ

Since Since ΔH is negative, the reaction is **exothermic**.

Try yourself:

Calculate the enthalpy of given reaction using the bond enthalpy value given in activity1:

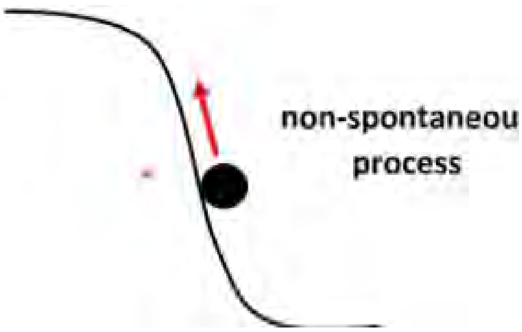


4.8 Entropy and spontaneity

Activity: observe the process shown and identify the process that is spontaneous and non-spontaneous and discuss the reason behind your selection.

4.8.1 Spontaneous and non-spontaneous process

When a ball is placed at the top of a hill, it naturally rolls down without any external force. However, to push the same ball back up, an external force is required. This demonstrates that some processes occur naturally, while others need external assistance. The rolling down of the ball represents a **spontaneous process**, whereas moving it back uphill is a **non-spontaneous process.**



Non spontaneous process in Nature:

a. Water freezing at room temperature
b. Electrolysis of water (splitting H_2O into H_2 and O_2)
c. Photosynthesis in plants (requires sunlight)
d. Pumping water uphill

Spontaneous processes in Nature:

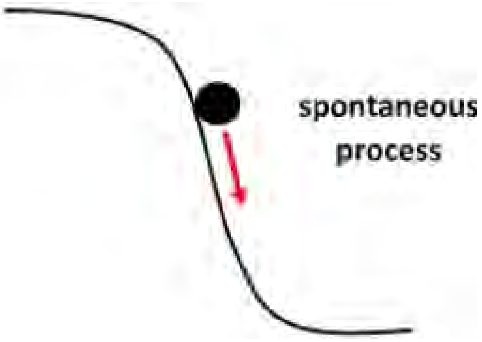
a. Water flowing downhill

b. Ice melting at room temperature

c. Rusting of iron

d. Diffusion of gases

e. Respiration in living organisms



In most of the spontaneous process the randomness or disorder of the system increases. For example, the water in the tank is more order than in the tap. So that it spontaneously goes down from the tap. Likewise, the mixing of two gases is random and disorder than the separation in to two different container. Such randomness or disorder is measured in terms of **entropy**.

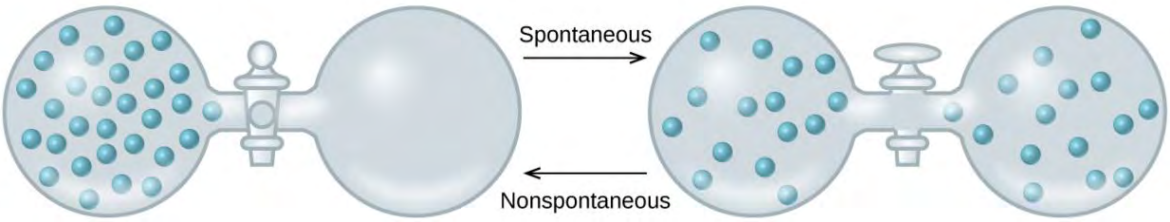
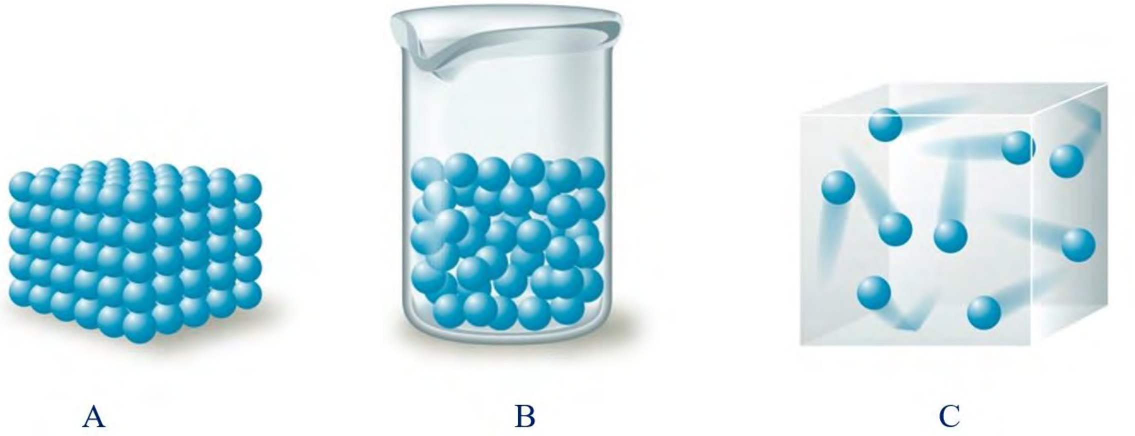


Fig : Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

4.8.2 Entropy

Activity:

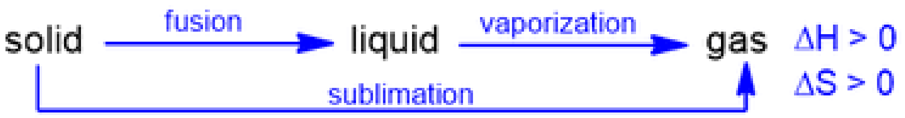
Which of the state in the figure of has highest disorder of the molecules and why?



You know Ice has fixed shape but water does not. It is because the molecules in ice are in fixed arrangement due to strong hydrogen bonding. When solids melt into liquids or liquids evaporate into gases, the particles are more random and more disordered because the molecules are far from each other. This property is termed as **entropy** in thermodynamics. A highly ordered system has low entropy, while a disordered system has high entropy.

Entropy is a measure of disorder or randomness in a system

Entorpy is denoted by 'S'. Like enthalpy and internal energy it is also state function which depends upon initial and final state of the system.So we can measure the change in entropy (ΔS) $= S_2 - S_1$



For the special case of an isothermal process, change is entropy (ΔS) is equal to the heat that would be transferred if the process were reversible, qrev, divided by the absolute temperature.

$$\Delta S = \frac{Q_{\text{rev}}}{T}$$

where:

ΔS = entropy change

Qrev_ = the heat absorbed or released in a reversible manner.

T = absolute temperature (in Kelvin)

Therefore unit of entropy includes the unit of heat and temperature i.e joule per kelvin or calorie per kelvin.

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} = 0$ the process is at equilibrium

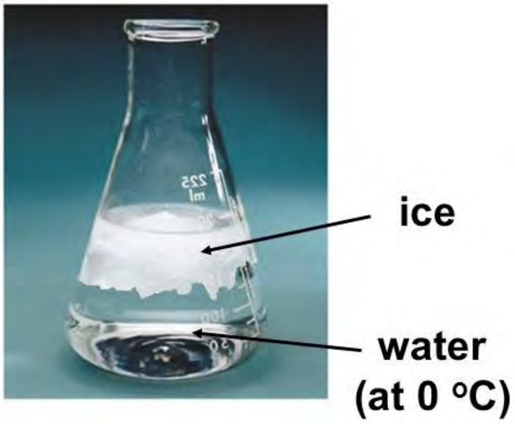
$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$ the process is spontaneous

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} < 0$ the process is non spontaneous

Different types of entrpy change

Like the change in enthalpy , change in entropy varies from process to process .

a. Entropy of fusion (ΔSf)



$$H_2O(s) \rightleftharpoons H_2O(l)$$

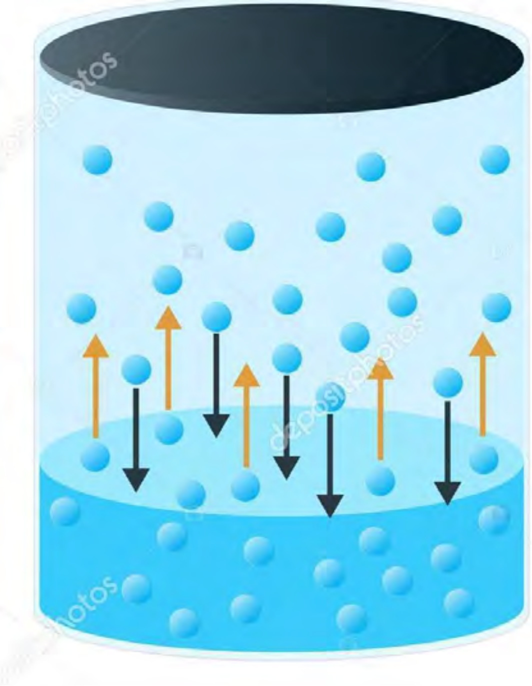
The entropy change involved when one mole of solid change into liquid at its melting point is called entropy of fusion.

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_m}$$

where, ΔH fusion = enthalpy of fusion or latent heat of fusion

Tm= melting point

b. Entropy of vaporization (ΔS_{vap})



Liquid ⇌ Vapour

The entropy change when one mole of liquid is changed into its vapour at boiling point is called entropy of vaporization .Mathematically

$$\Delta S_{vaporization} = \frac{\Delta H_{vaporization}}{T_b}$$

Where ,

where, ΔH vaporization = enthalpy of vaporization or latent heat of vaporization

Tb= boiling point

Likewise, entropy of sublimation (**ΔS_{sub})** is the entropy change involved when one mole of solid substance is directly converted into vapor below its melting point.

Entropy changes in a chemical reaction

Entropy (S) is a measure of disorder or randomness in a system. During a chemical reaction, the entropy of the system can increase or decrease, depending on the nature of the reactants and products.

The entropy change in a chemical reaction is given by:

$\Delta S_{reaction} = \sum S_{products} - \sum S_{reactants}$

For a general chemical reaction

$aA+bB \rightarrow cC+dD$

$\Delta S_{reaction}=\sum S_{products}-\sum S_{reactants}$

$\Delta S_{reaction}=(cS_C+dS_D)-(aS_A+bS_B)$

a. If phase change from solid to liquid to gas, **$\Delta S > 0$** → Entropy increases
b. If a reaction produces **more gaseous molecules**, **$\Delta S > 0$** → entropy increases.

Example: **N_2O_5 (s) → 2 NO_2 (g) + ½ O_2 (g)** ($\Delta S > 0$)

Test yourself

The enthalpy of fusion for H_2O (ΔH_{fusion}) is 6.01 kJ per mole . calculate the entropy change of melting 1 mol of ice at 273 K

4.9 Second law of thermodynamics

Consider a hot object (T_1 = 80°C) and a cold object (T_2 = 20°C) in thermal contact. From first Law of thermodynamics

Heat lost by the hot object = Heat gained by the cold object.

i.e $\Delta E_{hot}=-Q$ and $\Delta E_{cold}=+Q$

But this law does not specify whether heat should go from hot to cold or vice versa. It means First Law of Thermodynamics is crucial for understanding energy conservation but has some limitations:

a. It does not predict spontaneity or direction of processes.
b. It ignores entropy and irreversibility.
c. It does not set efficiency limits for real-world machines.
d. It cannot predict chemical reaction feasibility.

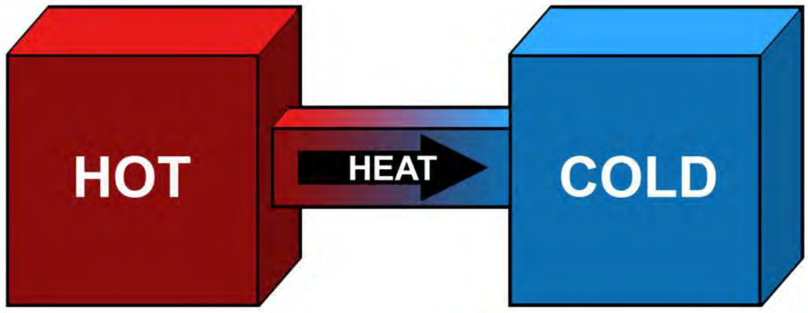


Fig : second law of thermodynamics explains the direction of heat flow

When heat **(Q)** flows from **hot to cold**, the entropy(randomness) of the cold object **increases** because it gains heat.The entropy of the hot object **decreases** because it loses heat.

However, the gain in entropy by the cold object is greater than the loss by the hot object, resulting in **net entropy increase**. Since entropy increases (**ΔSuniverse > 0**), the process is **spontaneous.**

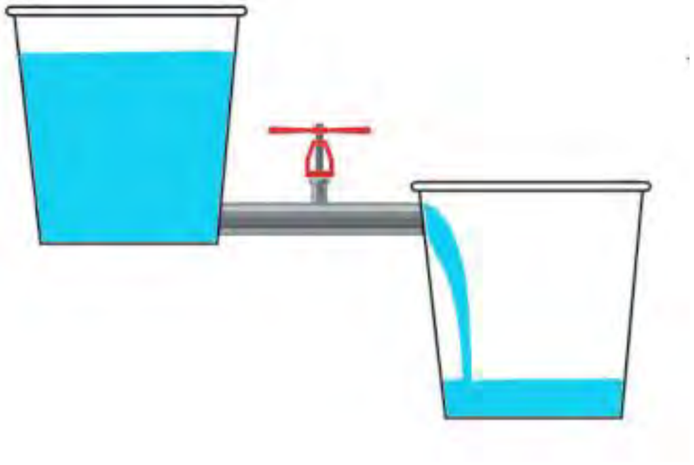


Figure: Water flows spontneously from higher level to lower level but the reverse is not spontaneous.

In general, processes that are spontaneous in one direction are nonspontaneous in the opposite direction.
The sum of the entropy of a system plus the entropy of the surroundings gives the entropy of the universe. Therefore, the total entropy change is referred as the entropy change of the universe, . We can therefore state the second law of thermodynamics in terms of two equations.

$$\textit{Reversible Process:}\ \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

$$\textit{Irreversible Process:}\ \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

The entropy (S) of a system is a measure of its disorder. The Second Law states that the total entropy of the universe always increases in a spontaneous process: ΔSuniverse=ΔSsystem+ΔSsurroundings>0

Applications of second law of thermodynamics

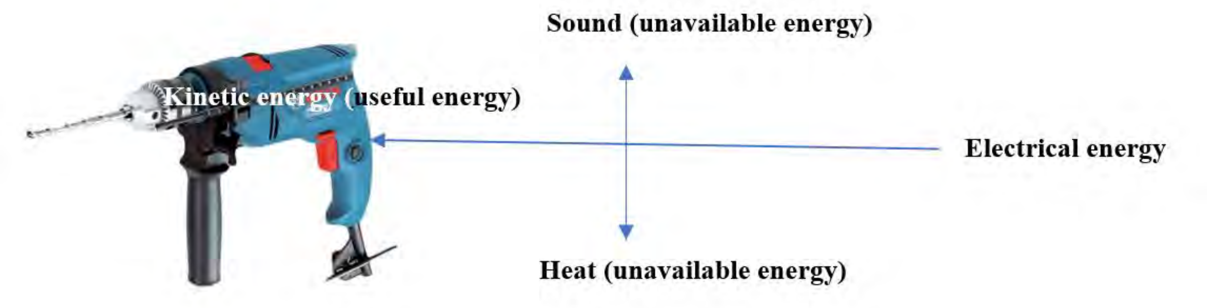
The Second Law of Thermodynamics is fundamental in various natural and technological processes. It explains why certain processes are irreversible and governs the efficiency of energy conversion.

a. The Second Law states that no engine(car engine ,Jet engine) can be 100% efficient because some energ is always lost as heat.
b. Refrigerators and Air Conditioners transfer heat from a cold area to a hot area using external work,
c. The Second Law explains the spontaneity of processes like melting of ice ,dissolution of sugar . These processes cannot be reversed naturally without external work.
d. Photosynthesis converts sunlight into chemical energy, reducing entropy locally in plants but increasing entropy in the surroundings.

4.10 Gibbs' free energy and prediction of spontaneity

J. Willard Gibbs (1839–1903) was a pioneering American mathematician, physicist, and chemist, best known for his foundational contributions to thermodynamics, statistical mechanics, and vector calculus. He developed the concept of **Gibbs free energy,** which is crucial in chemical thermodynamics.

You may have seen a drilling machine that uses electrical energy to operate. However, not all the electrical energy supplied to the machine is converted into mechanical energy for drilling. A portion of the energy is lost as heat and sound, which do not contribute to the drilling process and are considered **unavailable energy**.



According to the Second Law of Thermodynamics, the entropy of any natural process always increases. This means that not all the input energy is converted into useful work; some of it contributes to the overall disorder of the system and the surroundings. **The portion of energy that can be effectively converted into useful work is called available energy or free energy**, while the energy dissipated as heat and other inefficiencies is termed unavailable energy

Total energy = available energy (free energy) + unavailable energy

American mathematician J. Willard Gibbs developed mathematical function integrating both entropy and enthalpy called **Gibbs free energy(G) or only free energy.**

$G = H - TS$

Like all the other parameters enthalpimetry Gibb’s free energy is a state function. So we can measure the change in free energy (ΔG) .

$\Delta G = G_2 - G_1$

$= (H_2 - TS_1) - (H_1 - TS_1)$

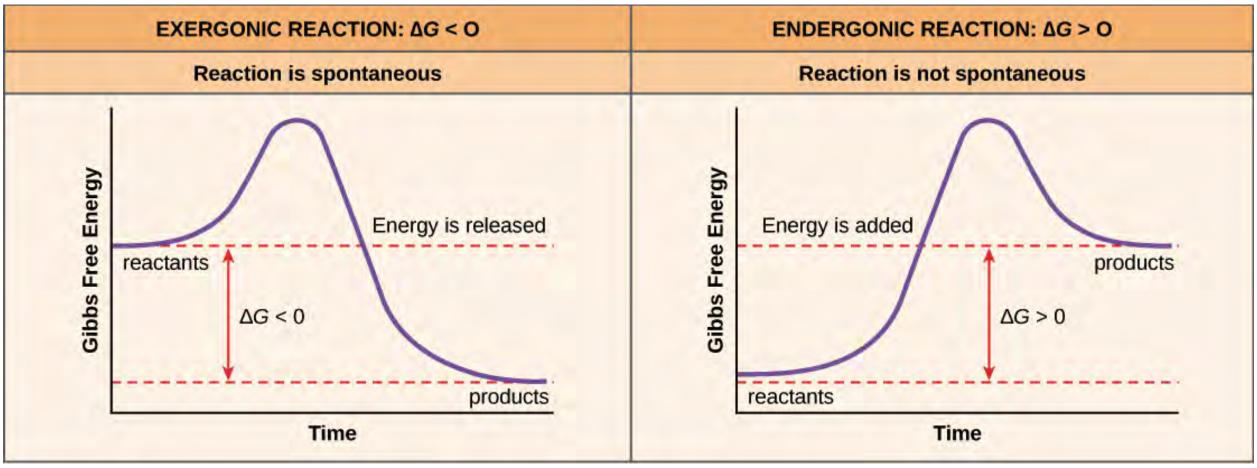
$= \Delta H - T\Delta S$

Under standard conditions this relationship can be written as

$\Delta G° = \Delta H° - T\Delta S°$

Where $\Delta G°$ is called standard change in free energy.

4.10.1 Predicting spontaneity using free energy



As we know most of the spontaneous process proceed with decrease in enthalpy (ΔH=-ve) and increase in entropy(ΔS =+ve).But this criteria cannot explain all the natural processes which are spontaneous. For example, freezing of water to ice is spontaneous but with decrease in entropy. Likewise, evaporation is spontaneous but proceed with absorption of heat (endothermic). So there must be another criterion to explain the spontaneity of all natural phenomenon.

we know

$\mathbf{\Delta S = - \Delta H/T}$ (at constant temperature)

And $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

$$= \Delta S_{sys} + \left(\frac{-\Delta H_{sys}}{T}\right)$$

Or ,

$\Delta S_{univ} = (T\Delta S_{sys} - \Delta H_{sys}) / T$

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

Or $\mathbf{-T\Delta S_{univ} = \Delta G}$

From first law of thermodynamics, it is clear that for a spontaneous process ΔS_{univ} is always positive .So ΔG should be negative .

If both T and P are constant, the relationship between the sign of gibbs free energy and the spontaneity of a reaction is as follows:

$\Delta G > 0$ If the reaction is spontaneous in the forward direction.

$\Delta G = 0$ If , the reaction is at equilibrium.

$\Delta G < 0$ If , the reaction in the forward direction is nonspontaneous (work must be done to make it occur) but the reverse reaction is spontaneous.

Boiling of water (endothermic) in which entropy of system increases and condensation of vapor (exothermic) in which entropy of system decreases. These reverse processes occur spontaneously to decrease their free energy.

In any spontaneous process carried out at constant temperature and pressure, the free energy always decreases.

When petroleum products are burnt , it does maximum amount of work on the surrounding by decreasing its free enrgy**(**ΔG is large and negative). It means ,the change in free energy for a process, , equals the maximum useful work that can be done by the system on its surroundings in a spontaneous process occurring at constant temperature and pressure.

$$\Delta G = -W_{max}$$

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

$\Delta H=\Delta E+P\Delta V$

$\Delta S=q_{rev}/T$

$q_{rev} =T\Delta S$

From first law of thermodynamics $\Delta E=q+w$

$\Delta H=q+P\Delta V$

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

$\Delta G=q+P\Delta V-T\Delta S$

$\Delta G=q+P\Delta V-q$[$T\Delta S =q$]

$\Delta G=W_{useful}$

$\Delta G=- W_{max}$ [work **on the surroundings]**

The more energy decreases, more the useful work done so is called free energy. Besides the energy used in the useful work, remaining energy enters the surrounding as a heat.

Change in free energy is the final criteria of the spontaneity and the process with any sign of enthalpy and entropy change can be spontaneous depending upon temperature .For example ,

a. **Melting of ice** ($H_2O(s)\rightarrow H_2O(l)$)

The process is endothermic with increase in entropy (*ΔH =-ve and ΔS= +ve)*

Now keeping the sign in the given equation,

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

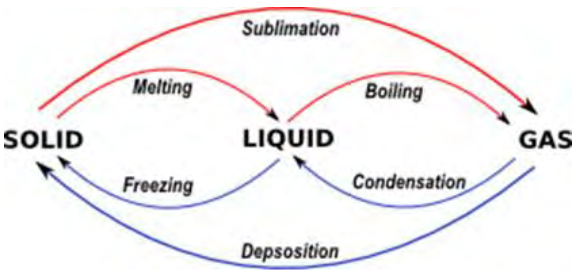
-ve = +ve – T(+ve)

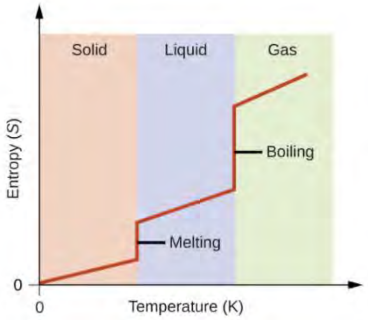
The process can be spontaneous **(**ΔG = -ve) only **at high temperature.**

b. Condensation of vapor $H_2O(g) \rightarrow H_2O(l)$)

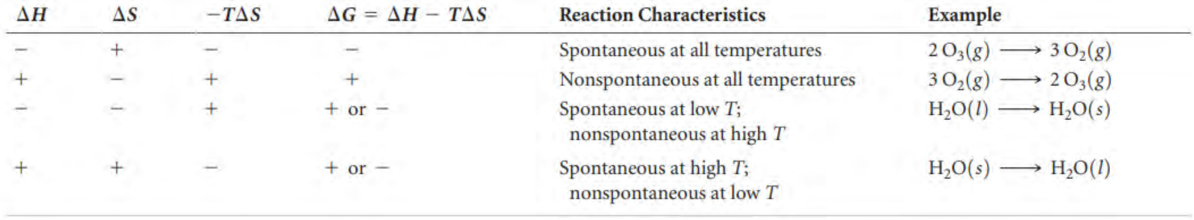
This process is spontaneous(ΔG=-ve) only at low temperatures because ΔS=-ve and ΔH=-ve

Likewise all the process moving right (shown by red curves) in the figure below are spontaneous at high temperature and all the processes moveing lefet(shown by blue curves) are spontaneou at low temperature .





Different criteria of spontaneity for various processes are shown in the table below.



ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
−	+	−	−	Spontaneous at all temperatures	$2O_3(g) \longrightarrow 3O_2(g)$
+	−	+	+	Nonspontaneous at all temperatures	$3O_2(g) \longrightarrow 2O_3(g)$
−	−	+	+ or −	Spontaneous at low *T*; nonspontaneous at high *T*	$H_2O(l) \longrightarrow H_2O(s)$
+	+	−	+ or −	Spontaneous at high *T*; nonspontaneous at low *T*	$H_2O(s) \longrightarrow H_2O(l)$

4.11 Standard Gibbs Free Energy and Equilibrium Constant

Let us consider a general chemical equation at equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium constant (K) of this equation can be written as

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

At standard conditions (*1* atm, *298K*, and *1M* concentration for solutions), the relationship relationship between equilibrium constant and change in free energy is given as :

$$\Delta G^\circ = -RT\ln K$$

$$\ln K = \frac{\Delta G^\circ}{-RT}$$

Or

$$K = e^{-\Delta G^\circ/RT}$$

$$\Delta G^\circ = -2.303RT\log K$$

where:

ΔG° = standard Gibbs free energy change (J/mol),

R = universal gas constant (8.314 J/mol·K),

T = absolute temperature (K),

K = equilibrium constant

It means

If $\Delta G^\circ < 0$ then $K > 1$ → reaction is **spontaneous** and favors products.

If $\Delta G^\circ > 0$, then $K < 1$ → reaction is **non-spontaneous** and favors reactants.

If $\Delta G^\circ = 0$, then $K = 1$ → reaction is at **equilibrium**.

Projcet work

1.

a. Measure 50.0 mL of 1.0 M HCl and Measure 50.0 mL of 1.0 M NaOH using a measuring cylinder in two different polysterene cup.
b. Record the initial temperature of both solutions separately using the thermometer.
c. Pour the NaOH solution quickly into the polysterene cup containing HCl.
d. Stir the mixture gently with a stirring rod to ensure even distribution of heat.
e. Record the highest temperature reached after mixing.
f. Repeat the process again using 25 mL ,20 mL and 100 mL of each solution
g. Fill the table given

Mass of HCl(m_1)	Mass of NaOH(m_2)	Mass of mixture ($M=m_1+m_2$)	Intial temp. of HCl(t_1)	Highest temperature(t_2)	Difference in temp($\Delta T=t_2-t1$)	Heat released ($q=Mc\Delta T$)

Remember : mass of each solution = volume (density =1)

Specific heat capacity of water(C) = 4.18 J/g°C

2. **Take a chart paper and make a a list of different thermodynamic processes in the table as shown and complete the table**

S.N	**Process**	**ΔH**	**ΔS**	**Temperature**	**ΔG**	**Spontaneous or not**
1	Melting	+ve	+ve	High low	-ve +ve	Spontaneous Non spontaneous
2	Freezing					
3	Evaporation					
4	Sublimation					
5	Condensation					
6	Crystallization					
7	Deposition					
8	Dissolution					
9	Combustion					

Exercise

A. Choose the best from the given alternatives

1. Which of the following best describes thermodynamics?
   a) Study of energy changes during chemical reactions
   b) Study of chemical properties of elements
   c) Study of nuclear reactions
   d) Study of motion of particles

2. What happens when refrigerator door is opened
   a) Room heated
   b) Room cooled
   c) More heat is passed out
   d) No effect in the room

3. If ΔH is the enthalpy change and ΔE be the change in internal energy , which of the following explains the relationship between them?
   a. $\Delta H > \Delta E$ (always)
   b. $\Delta H > \Delta E$ (change in no. of moles of gaseous product and reactant is less than zero)
   c. $\Delta H > \Delta E$ (change in no. of moles of gaseous product and reactant is more than zero)
   d. $\Delta H = \Delta E$ (always)

4. Spontaneous adsorption of gas on solid surface is exothermic .Which of the following can best explains this phenomenof?
   a. ΔH +Ve
   b. ΔS +ve
   c. ΔG +ve
   d. ΔS -ve

5. What is the ΔH of the reaction in kJ /mol for $C(s) \rightarrow C(g)$

$$C(s) + O_2(g) \rightarrow CO_2,(g); \qquad \Delta H = -94.3 \text{ kcal/mol}$$
$$CO(g) + O_2(g) \rightarrow CO_2(g); \qquad \Delta H = -67.4 \text{ kcal/mol}$$
$$O_2(g) \rightarrow 2O(g); \qquad \Delta H = 117.4 \text{ kcal/mol}$$
$$CO(g) \rightarrow C(g) + O(g); \qquad \Delta H = 230.6 \text{ kcal/mol}$$

   a. 117 b. 117
   b. 145 d .154

6. If C(diamond) → C(graphite) ΔH =453.3 cal.Which of the following best describes the properties of these allotopes

a. Diamond is chemically different from graphite
b. Graphite is more stable than diamond
c. Diamond is more stable than graphite
d. Diamond is as stable as graphite

7. Which statement correctly describes energy change in a chemical reaction?
a) Energy is always absorbed
b) Energy is always released
c) Energy is conserved but can change forms
d) Energy is created during the reaction

8. What is the significance of activation energy in a reaction?
a) It determines the feasibility of the reaction
b) It affects only exothermic reactions
c) It is required only for reversible reactions
d) It decreases with increasing temperature

9. If the internal energy of a system increases by 50 J and 20 J of work is done on the system, what is the heat absorbed?
a) 70 J
b) 30 J
c) 50 J
d) 20 J

10. Which process violates the first law of thermodynamics?
a) A machine that creates energy from nothing
b) A refrigerator using external energy
c) A compressed gas heating up
d) A car engine burning fuel

11. The enthalpy change when 1 mole of a carbon is completely burned to form 1 mole of carbon dioxide is = -393.5kJ/mol.Which of the following best defines the value ?
a) Enthalpy of formation of carbon and enthalpy of combustion of carbon dioxide.
b) Enthalpy of combustion of carbon and enthalpy of formation of carbon monooxide
c) Enthalpy of neutralization
d) Enthalpy of sublimnation of carbon

12. If enthalpy of solution is negative, which of the following condition favours the dissolution ?
a. low temperatrue
b. high temperature
c. all temperatrtue
d. no effect of temperature

13. Hess's law is also called second law of thermochemistry. Which of the following condions affect the enthalpy change of a reaction based on this Law?
   a) The nature of reactants only
   b) The nature of products only
   c) The initial and final states, not the pathway
   d) The temperature and pressure conditions only

14. Which of the following states laplace law ?
   a) Enthalpy of combustion is equal and opposite to enthalpy of formation
   b) Enthalpy of reaction is independent of path
   c) Heat capacity remains constant in all conditions
   d) Enthalpy of solution is always negative

15. Which of the following process results in an increase in entropy and decrease in enthalpy ?
   a) Freezing of water
   b) Crystallization of salt
   c) Evaporation of alcohol
   d) Formation of ice

16. Which of the following best explains second law of thermodynamics?
   a) A refrigerator transferring heat from cold to hot region
   b) Heat flowing from a hot cup of tea to air
   c) Water freezing at 0°C
   d) Conservation of mechanical energy

17. For a reaction to be spontaneous, Gibbs free energy change (ΔG) should be:
   a) Positive
   b) Negative
   c) Zero
   d) Unchanged

18. If $\Delta H = -200$ kJ/mol and $\Delta S = -50$ J/mol·K, at what temperature will the reaction become non-spontaneous?

   a) 200 K

   b) 300 K

   c) 400 K

   d) 500 K

21. The equation that relates Gibbs free energy and equilibrium constant is: $\Delta G = -RT \ln K$

   If $K > 1$, then ΔG is:

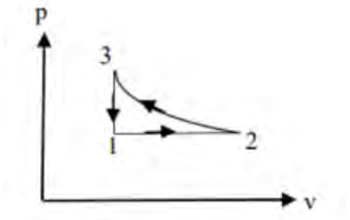
   a) Positive

   b) Negative

   c) Zero

   d) Undefined

23. Which of the process shown represents isobaric process in the graph ?



- a) 1 to 2
- b) 3 to 1
- c) 3 to 2
- d) Can not be predicted from the figure given

24. The enthalpy change for a reaction is -150 kJ and entropy change is -0.2 kJ/K. At what temperatrue will the reaction be spontaneous at?

a) 200 K
b) 500 K
c) 800 K
d) 1000 K

25. Which of the following is the cause of the spontaneous conversion of diamond into graphite?

a) High enthalpy of graphite
b) Increase in entropy
c) Decrease in pressure
d) Lower energy of diamond

26. If a system releases 200 J of heat and does 100 J of work, what is the internal energy change?

a) -300 J
b) -100 J
c) +100 J
d) +300 J

27. Which of the property /properties of the system mostly affect the spontaneity of a reaction ?

a) Only enthalpy
b) Only entropy
c) Both enthalpy and entropy
d) Volume of reactants

28. Which factor does not affect enthalpy change of a reaction?

a) Physical states of reactants
b) Temperature
c) Catalyst
d) Bond energies

Short answer questions

1. Define the following terms with their units.
    - a. Internal energy
    - b. Enthalpy
    - c. Entropy
    - d. Gibbs free energy

2. Differnetiate the following
    a. Exothermic and endothermic process
    b. Extensive and intensive properites
    c. Enthalpy of formation and enthalpy of combustion
    d. State function and path function
    e. Isobaric and isochoric process

3. State the following laws with relevant mathematical formulation and explanation
    a. First law of thermodynamics
    b. Second law of thermodynamics
    c. Laplace and lavoiser law
    d. Hess’s law of constant heat summation

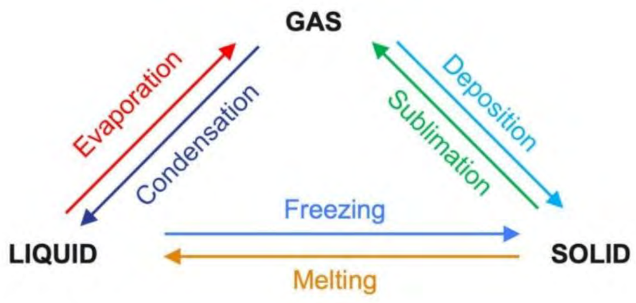
4. Define state function and give reason how are enthalpy and entropy state functions?

5. What is internal energy ? write the mathematical relationship between internal energy and enthalpy.Use this relationship to prove that change in internal energy and change in enthalpy are equal for the formaion of HCl from H_2 and Cl_2.

6. enthalpy of reaction between nitrogen and oxygen is given
   $N_2+O_2 \longrightarrow 2NO \quad \Delta H = +\ 180kJ$
    a. what do mean by enthalpy of reaction
    b. What is the meaning of $\Delta H= +180kJ$
    c. Find the enthalpy change of the given reaction
       $2NO \longrightarrow N2+O2$
    d. Calculate the enthalpy of formation of NO

7. State Laplace law and lavoiser law and write the application of these laws

8. Differnet thermodynamic processes are given in the figure
    a. Identify the process that are endothemeric and the process that are exothermic
    b. Name the process that proceeds with increase in entropy of the system
    c. Using the information of enthalpy change and entropy change identify the process that are spontaneous at low temperature wih suitable explanation



9. Uisng the information given ,calculate the enthalpy of the reaction

$$C_4H_{10}O_{(l)} \rightarrow C_4H_{8(g)} + H_2O_{(g)}$$

$4C_{(s)} + 5H_{2(g)} + ½O_{2(g)} \rightarrow C_4H_{10}O_{(l)}$ $\Delta H = -335\ kJ\ mol^{-1}$

$4C_{(s)} + 4H_{2(g)} \rightarrow C_4H_{8(g)}$ $\Delta H = -17\ kJ\ mol^{-1}$

$H_{2(g)} + ½O_{2(g)} \rightarrow H_2O_{(g)}$ $\Delta H = -242\ kJ\ mol^{-1}$

10. Calculate the enthalpy change of the given reaction using the data given

$C_6H_4(OH)_2(aq) + H_2O_2(aq) \rightarrow C_6H_4O_2(aq) + 2H_2O(\ell)$ $\Delta H=?$

$C_6H_4(OH)_{2(aq)} \rightarrow C_6H_4O_{2(aq)} + H_{2(g)}$ $\Delta H = +177{\cdot}4\ kJ\ mol^{-1}$

$H_{2(g)} + O_{2(g)} \rightarrow H_2O_{2(aq)}$ $\Delta H = -191{\cdot}2\ kJ\ mol^{-1}$

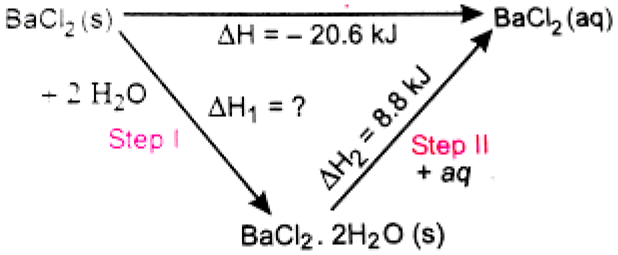
$H_{2(g)} + ½O_{2(g)} \rightarrow H_2O_{(g)}$ $\Delta H = -241{\cdot}8\ kJ\ mol^{-1}$

$H_2O_{(g)} \rightarrow H_2O_{(\ell)}$ $\Delta H = -43{\cdot}8\ kJ\ mol^{-1}$

11. $KClO_3(s) + 3Mg(s) \rightarrow KClO_3(s) + 3MgO(s)$ $\Delta H = –1852\ kJ\ mol–1$
$K(s) + ½Cl_2(g) \rightarrow KCl(s)$ $\Delta H = –437\ kJ\ mol–1$
$Mg(s) + ½O_2(g) \rightarrow MgO(s)$ $\Delta H = –602\ kJ\ mol–1$
calculate the enthalpy change in kJ mol^{-1}, for the reaction
$K(s) + ½Cl_2(g) + 1½O2(g) \rightarrow KClO_3(s)$

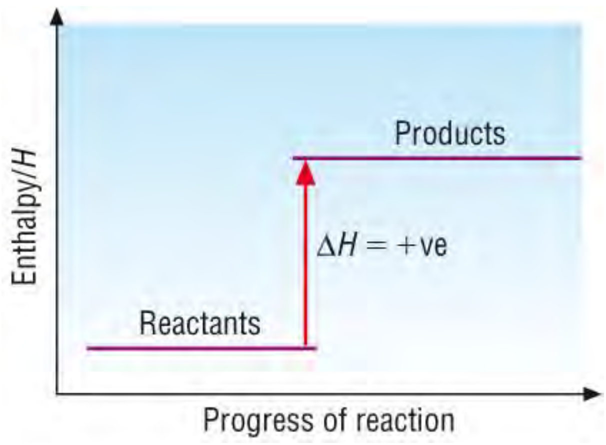
12. One of the enthalpy cycle to explain Hess's law is given .

a. How does this explain Hess's law?
b. What is the enthalpy of solution of Barium chloride ?
c. Calculate the enthalpy of hydration of $BaCl_2(s)$ frrom the cycle.



13. The enthalpy of reactants and products with the progress of reaction is shown in the graph below.

a. Identify the reaction as endothermic or exothermic and why?
b. Give any two common examples of such reactions.



14. First law of thermodynamics gives the relationship with internal energy, work and heat
    a. Write such mathematical relationship with its meaning
    b. How can such equation be varied for isothermal and adiabatic process?
    c. By what means can the internal energy of a closed system increase?
    d. Under what conditions will the quantities q and w be negative ?

15. Using the data of combustion of two allotropes of carbon are given, answer the following.

$$\begin{array}{lll} C(graphite) + O_2(g) \longrightarrow CO_2(g) & \Delta H = -393.5\ kJ \\ C(diamond) + O_2(g) \longrightarrow CO_2(g) & \Delta H = -395.4\ kJ \end{array}$$

    a. What do you mean by allotropes?
    b. Which of the allotrope is most and why?
    c. Calculate enthalpy change for the conversion of graphite to diamond and diamond to graphite.

16.

$$\begin{array}{ll} NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) & \Delta H = -198.9\ kJ \\ O_3(g) \longrightarrow \tfrac{3}{2}O_2(g) & \Delta H = -142.3\ kJ \\ O_2(g) \longrightarrow 2\ O(g) & \Delta H = 495.0\ kJ \end{array}$$

    a. Which one is easier process among the reaction (2) and (3) and why?
    b. Calculate the change in enthalpy for the reaction: $NO(g) + O(g) \rightarrow NO_2(g)$

17. Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

    (a) $NaNO_3(s)\longrightarrow Na+(aq)+NO_3^-(aq)NaNO_3(s)\longrightarrow Na^+(aq)+NO_3^-(aq)$

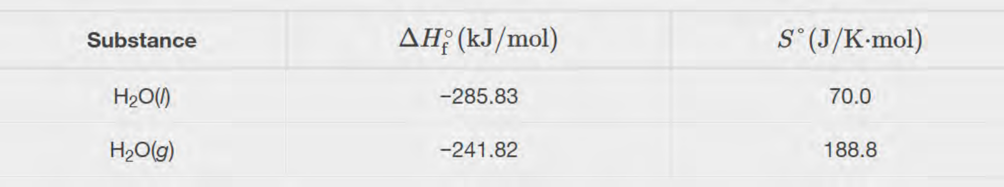
    (b) the freezing of liquid water

    (c) $CO_2(s)\longrightarrow CO_2(g)CO_2(s)\longrightarrow CO_2(g)$

    (d) $CaCO_3(s)\longrightarrow CaO(s)+CO_2(g)$

18. Using the data given, calculate the minimum temperature at which the given process is at equilibrium

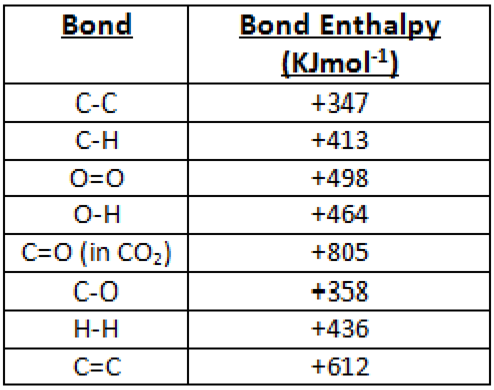
$$H_2O(l) \longrightarrow H_2O(g)$$



Substance	ΔH°_f (kJ/mol)	S° (J/K·mol)
$H_2O(l)$	−285.83	70.0
$H_2O(g)$	−241.82	188.8

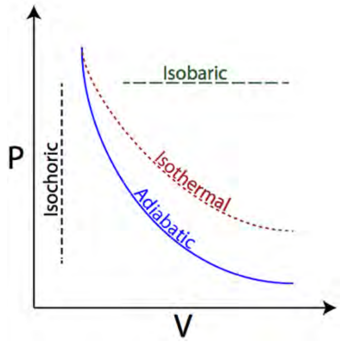
19. Use the bond energy value for some bonds in the table and answer:

   a. Which of the bond is difficult to break among the bonds given?
   b. What is the meaning of bond enthalpy of C-H bond 413kJ mol^{-1}?
   c. Calculte the enthalpy of combustion of methane using the bond enrgy in the table.



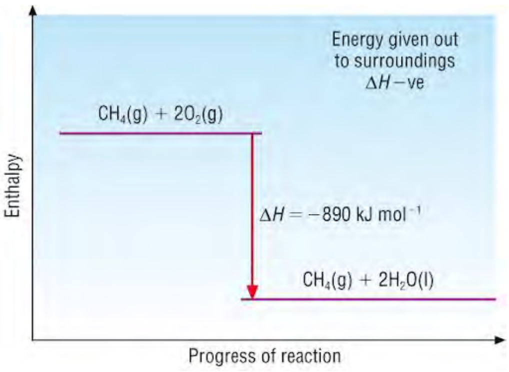
Bond	**Bond Enthalpy (KJmol^{-1})**
C-C	+347
C-H	+413
O=O	+498
O-H	+464
C=O (in CO_2)	+805
C-O	+358
H-H	+436
C=C	+612

20. Some of the thermodynamic processes are given in the figure below. Define each process with one example of each.



Long answer type questions

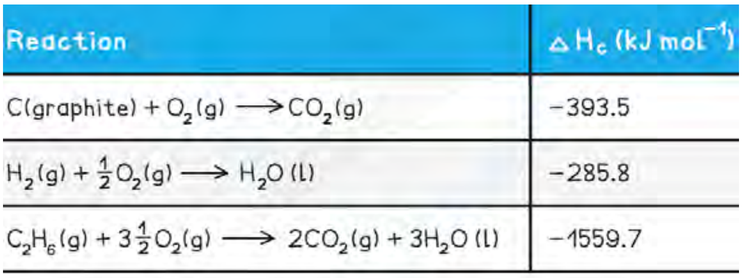
1. Using the figure given answer the question below.
   a. Define the term enthalpy.
   b. Write the balanced chemical equation for the given reaction.
   c. What is the meaning of -890kJ mol^{-}
   d. Calculate the calorific value of methane in kJ g^{-1}.
   e. How does this reaction increase the entropy of universe?



2. Define the term entropy and write its unit. Predict the sign of the entropy change of the system for each of the following reactions:

a. Molten gold solidifies.
b. Gaseous Cl_2 dissociates in the stratosphere to form gaseous Cl atoms.
c. Gaseous CO reacts with gaseous H_2 to form liquid methanol, CH_3OH.
d. precipitation reaction between Ca $(NO_3)_2(aq)$ and $(NH_4)_3PO_4(aq)$.

3. Enthalpy of combustion of carbon, hydrogen and ethane are given in the table:



Reaction	ΔH_c (kJ mol^{-1})
$C(graphite) + O_2(g) \longrightarrow CO_2(g)$	−393.5
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	−285.8
$C_2H_6(g) + 3\frac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	−1559.7

   a. Define the term enthalpy of combustion
   b. Calculate the calorific value of ethane
   c. Using Hess's law calculate the enthalpy of formation of ethane.

4. Standard enthalpy change and standard entropy change of the combustion of graphite is given as

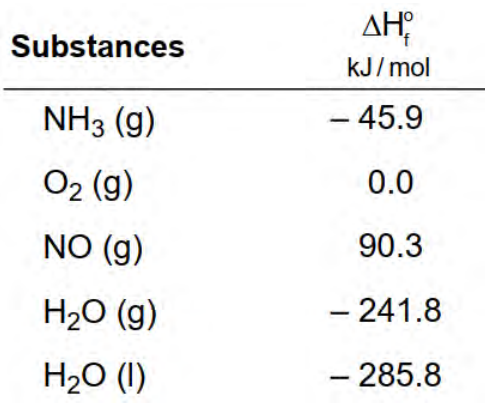
$$\Delta H° = -393 \text{ kJ and } \Delta S° = +2.9 \text{ J K}^{-1}$$

$$C_{(graphite)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$$

   d. Define the term standard enthalpy and entropy change
   e. What is the enthalpy of formation of carbon dioxide in the given process. Justify
   f. In which condition the above process is spontaneous?
   g. Calculate the temperature at which the standard free energy change ($\Delta G°$) = –394 kJ
   h. Melting and freezing are reverse processes but are spontaneous in nature. Explain the spontaneity of these processes at different temperature.

5. Standard enthalpy of formation of some substances are given

   b) What do you mean by standard enthalpy of formation?
   c) Why the value is zero for oxygen?
   d) Which of the substance is difficult of form and why?
   e) Identify the substance that is most stable and the one that is unstable.
   f) Calculate the calorific value of ammonia and Nitric oxide



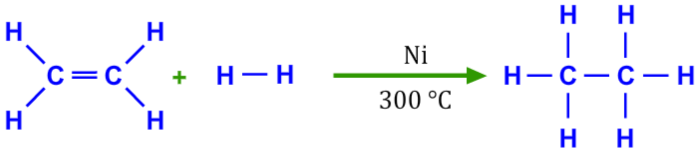
Substances	ΔH_f° kJ / mol
NH_3 (g)	– 45.9
O_2 (g)	0.0
NO (g)	90.3
H_2O (g)	– 241.8
H_2O (l)	– 285.8

6. Standard Enthalpy of formation of acetylene and ethane are given.

$$2C(s) + H_2(g) \rightarrow C_2H_2(g) \quad \Delta H_f^\circ = +226.7 \text{ kJ/mol}$$

$$2C(s) + 3H_2(g) \rightarrow C_2H_6(g) \quad \Delta H_f^\circ = -84.7 \text{ kJ/mol}$$

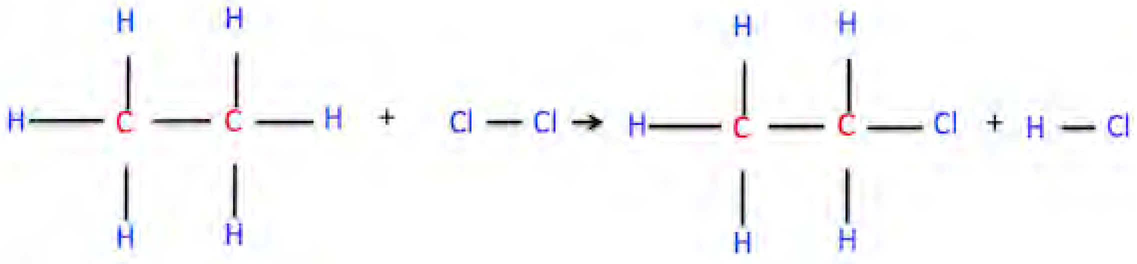
a. What do you mean by standard enthalpy of formation?
b. How can you use these values to compare the stability and reactivity of given substances
c. Calculate the enthalpy change of given reaction using Hess's law



7. Bond enthalpy of some bonds is given in the table

Bond	Enthalpy (kJ/mol)
C–H	413
C–C	347
Cl–Cl	239
H–Cl	427
C–Cl	339

a. Define the term bond enthalpy.
b. What are the factors that affect the value of bond enthalpy?
c. Which of the given bond is difficult to dissociate and why?
d. Calculate the enthalpy change of the given reaction.



8. Gibbs free energy change is the final criteria for the spontaneity of the process.
a. Define the term spontaneity and Gibbs free energy?
b. How is free energy change related with enthalpy change and entropy change?
c. In which conditions of free energy change the process are spontaneous?
d. Identify whether the following process are spontaneous or non spontaneous and mention the condition of temperature for the spontaneity.
    i. Evaporation of liquid
    j. Dissolving NaCl in water
    k. Crystallization of copper sulphate

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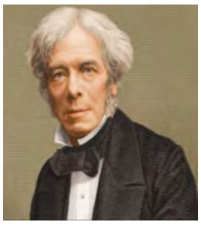
Unit 5

ELECTROCHEMISTRY

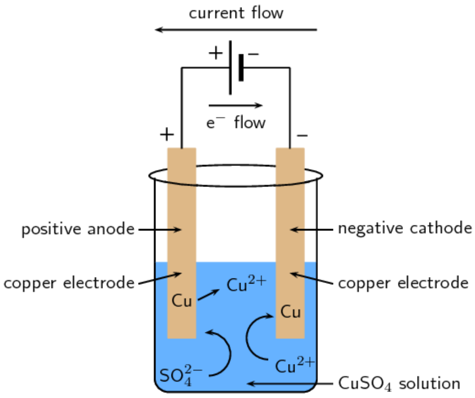


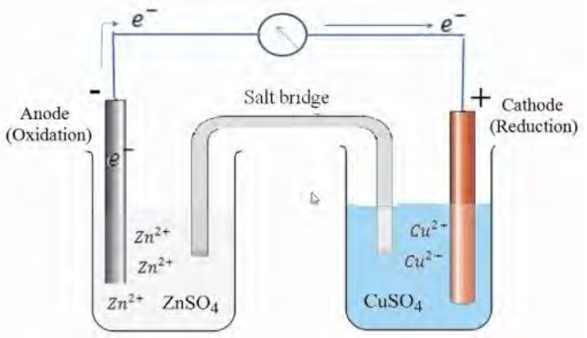
Michael Faraday (1791–1867) was a self-taught English scientist whose work in electromagnetism and electrochemistry revolutionized science. Born into a working-class family, Faraday began as a bookbinder's apprentice and educated himself by reading scientific books. His career took off when he impressed Sir Humphry Davy, a leading chemist, who hired him as an assistant. Faraday's discoveries include electromagnetic induction, which led to the development of electric generators, and his laws of electrolysis, foundational to electrochemistry. He also introduced concepts like the Faraday cage and discovered benzene. Known for his humility and deep religious faith, Faraday declined prestigious honors and focused on his research and public science education, founding the Royal Institution Christmas Lectures. His legacy endures in physics and chemistry, as his findings underpin much of modern electrical engineering and physical science.

Activity 1

You are provided a typical diagram of two types of cells.

1. Do you know cell? Could you name the following cells
2. What basic differences you can find in the two cells?
3. Identify the redox reactions in two cells.





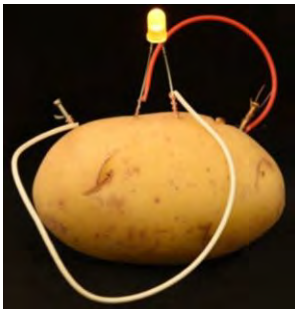
Electrochemistry is the branch of chemistry that deals with the study of relationship between electrical energy and chemical reactions. It focuses on redox (oxidation-reduction) reactions. Electrochemistry describes how chemical energy can be converted into electrical energy (as in batteries) and how electrical energy can drive chemical reactions (as in electrolysis). The main areas of electrochemistry are electrical energy storage and production, corrosion prevention, and electroplating.

There are two types of electrochemical cells: **galvanic or voltaic** and **electrolytic** cells. In electrolytic cell a redox reaction occurs non-spontaneously. Here, electrical energy is converted to chemical energy. In galvanic cells, redox reaction takes places spontaneously. Such cells convert chemical energy into electrical energy. Design wise also, two cells differ. In galvanic cells two electrodes are dipped in different electrolytic solutions but in electrolytic cells two electrodes are dipped in same electrolytic solution. The focus of this chapter will be galvanic cells and the related fundamentals.

5.1 Electrode potential and standard electrode potential

Activity 2

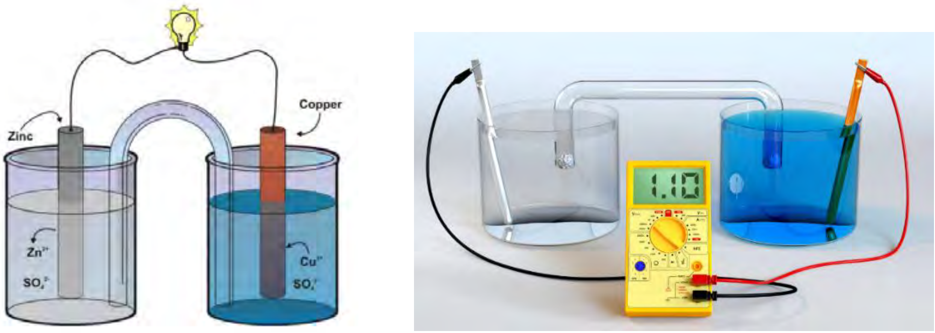
Take a potato, prick it with a copper wire at one end and iron nail to the other end. Connect them with cables to a LED bulb. The bulb will glow. Can you find the reason why the bulb glows?



Activity 3

Insert a zinc rod in 1M $ZnSO_4$ solution in a beaker and a copper rod in 1M $CuSO_4$ solution in another beaker. Connect the two beakers with a strip of filter paper soaked in concentrated potassium nitrate solution. Connect the two electrodes with copper wire to a torch light bulb.

1. Could you guess the reason behind the lighting of the bulb?
2. Remove the bulb, connect a multimeter you have in your Physics lab and note the potential.
3. Can you guess the origin of cell potential?



(a) (b)

Fig: a) Lighting of bulb using Zn and Cu half-cells. b) Measuring of electrode potential using multi-meter.

When a metallic rod is immersed in its salt solution, metal atoms get oxidized and released in to the solution in the form of positive ion leaving behind electrons in the rod. As a result metal becomes negatively charged and positive ions in solution get attracted towards it to form an **electrical double layer**. It creates potential difference between metal and ions at interface in solution, known as electrode potential. It is called single electrode potential and is measured only when a reference electrode is connected with it. Electrode potential is comparative and is measured with respect of reference electrode.

Electrode potential is defined as the potential difference between a metal and its ions at interface in solution

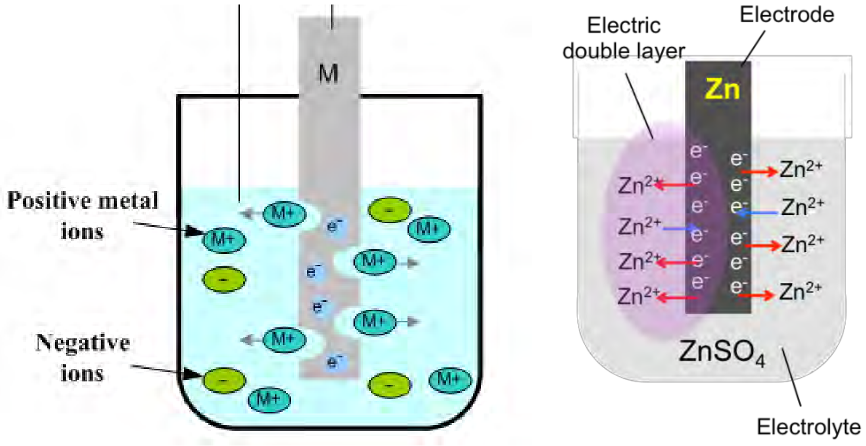
According to the tendency of a metal to get oxidize, it losses electron and goes in to the solution as positive ion. Some of the metal ions in solution will accept electron from metal where electrons are accumulated and get deposited on the rod. After some time equilibrium is established.

$$M_{(s)} \rightleftharpoons M^{++}_{(aq)} + 2e^{-}$$

It results in the separation of charges (electrical double layer). In this way electrode potential is generated.

Electrode potential depends upon

i. Concentration of ions in solution
ii. Temperature
iii. Nature of metals and ions



(a) (b)

Figure: (a) Oxidation of metal in its salt solution. (b) Formation of electrical double layer.

If we want to compare electrode potential of different metals then we need to set standard conditions. If we measure electrode potential under standard conditions then the potential is known as **standard electrode potential** (E^o). The standard conditions are: 1 M concentration of its ions, 298 K temperature, and 1 atmosphere pressure.

In fact, the standard electrode potential represents the tendency of a substance to gain or lose electrons in comparison to the standard hydrogen electrode (SHE), which is assigned a standard reduction potential of 0 volts.

It allows comparison of different electrodes' tendencies to undergo reduction or oxidation.

1. Positive standard electrode potential ($E°$) values indicate a greater tendency to gain electrons (reduction) compared to hydrogen.
2. Negative standard electrode potential ($E°$) values indicate a greater tendency to lose electrons (oxidation) compared to hydrogen.

Try yourself

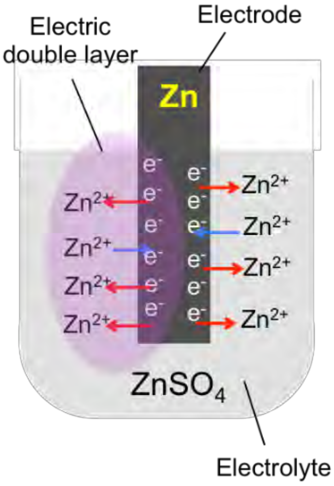
What happens when $ZnSO_4$ is added in the electrolyte of anode half-cell of the following voltaic cell?

$$Zn_{(s)} + Cu^{++}_{(aq)} \rightarrow Zn^{++}_{(aq)} + Cu_{(s)}$$

5.2 Types of reference electrodes

Activity

Take a zinc rod and dip it into the ZnSO4 solution. You know electrode potential will be generated as shown in figure below.



1. Do you think we can measured the electrode potential?
2. Do you know the term *reference* in scientific measurement?

We cannot measure single electrode potential unless we use a reference electrode. The most commonly used reference electrode are standard hydrogen electrode and calomel electrode.

5.2.2 Standard Hydrogen Electrode

The Standard Hydrogen Electrode (SHE) is the primary reference electrode, with an assigned electrode potential of 0 volts under standard conditions.

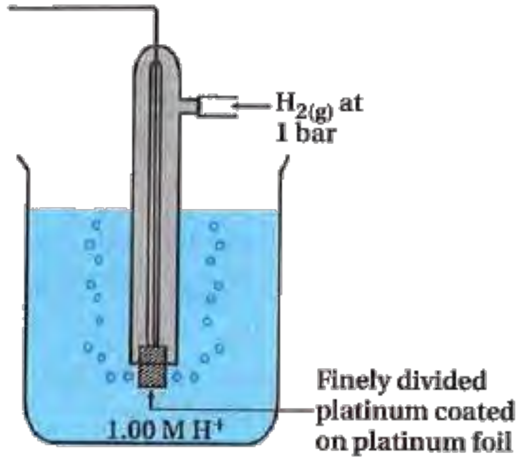


Fig 5.2: Standard hydrogen electrode

Standard Hydrogen electrode contains platinum electrode immersed in 1M solution of strong acid like HCl and hydrogen gas is bubbled continuously around platinum electrode.

$$H_{2\,(g)} \rightleftharpoons H^+ + 2e^-$$

SHE is used to measure the standard electrode potentials of other electrodes by pairing it in a cell and measuring the potential difference. Since the potential of SHE is exactly 0 volts, any measured cell potential corresponds to the electrode potential of the other half-cell.

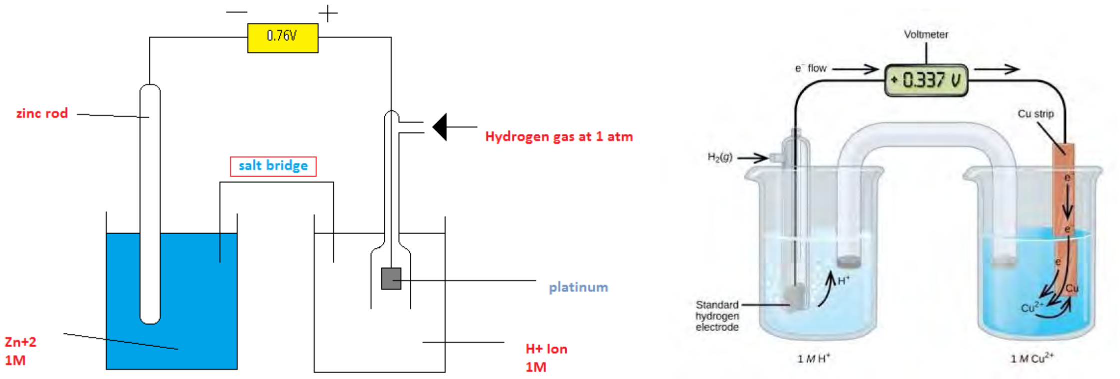


Fig 5.2.1: Measurement of electrode potential of zinc and copper

The emf of the cell (E cell) is given by:

$$E_{cell} = E_{cathode} - E_{anode}$$

Zinc is more electropositive than hydrogen so taken as anode; whereas copper is less electropositive so taken as cathode. The multi-meter measures the emf of the cell formed by connecting hydrogen with electrode whose electrode potential is to be measured.

The electrode potential of zinc electrode can be measured as:

$$0.76 = E_{Hydrogen} - E_{Zinc}$$

$$0.76 = 0 - E_{Zinc}$$

$$E_{Zinc} = -0.76V$$

The electrode potential of copper electrode can be measured as:

$0.34 = E_{Copper} - E_{Hydrogen}$

$0.34 = E_{Zinc} - 0$

$E_{Copper} = +0.34V$

Limitations of hydrogen electrode

1. Hydrogen electrode needs extra pure hydrogen and platinum electrode. This makes electrode expensive.
2. The electrode is not easy to use for routine work.

How to assign anode and cathode with reference to SHE?

As stated earlier, the electrode potential of an electrode is measured by connecting it with SHE, the electrode potential of which is assigned 0 Volt. The metal, which is more electropositive than hydrogen (i.e. having negative reduction potential), is taken as anode (negative electrode) with respect to SHE during measurement.

The metal which is less electropositive (i.e. having positive reduction potential) than hydrogen, is taken as cathode (positive electrode) with respect to SHE and assigned positive charge in electrode potential.

5.2.3 Calomel Electrode

Calomel electrode is most commonly used secondary reference electrode. It has simple design and easy to use. The reduction potential of saturated calomel electrode at 298K is +0.241 V.

In a calomel electrode, consist of a glass tube with a porous plug. A platinum electrode covered with mercury (Hg) and paste of mercurous chloride (Hg_2Cl_2, calomel) dipped in saturated KCl solution is used for electrical contact.

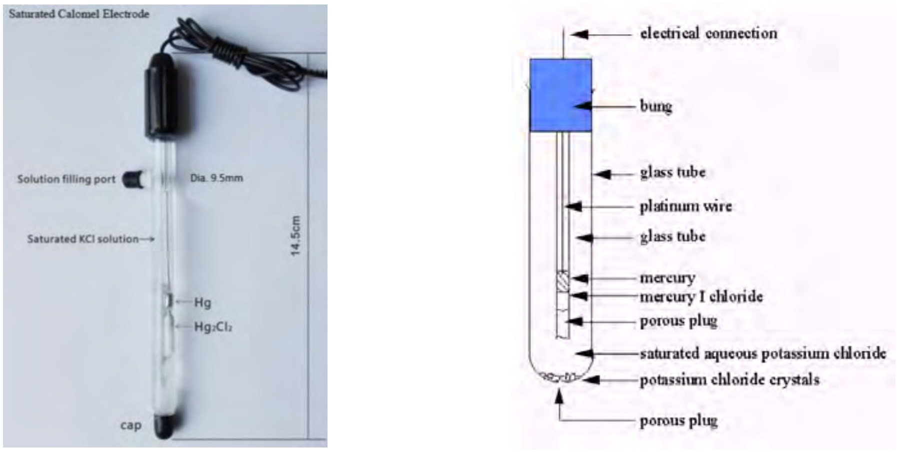


Fig 5.2.2: Calomel Electrode: a) commercial version, b) the anatomy of the electrode.

The reaction involved in this electrode is:

$$Hg_2Cl_{2\,(s)} + 2e^- \rightleftharpoons 2Hg_{(l)} + 2Cl^-_{(aq)}$$

Advantages of the calomel electrode

1. Due to its reliability and easy maintenance it is most frequently secondary reference electrode.
2. There is no need of continuous gas supply, so it is easy to use. Since the electrode contains toxic mercury and mercurous chloride, care should be taken while use.

5.3 Electrochemical series and its applications

Activity

Take two test tubes filled with $CuSO_4$ and $FeSO_4$, insert iron rod in $CuSO_4$ and copper rod in $FeSO_4$ solution containing test tubes. Observe the result.

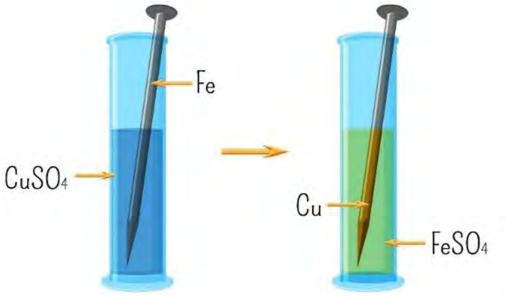


Fig 5.2.3.: Copper nail in $FeSO_4$ and iron nails in $CuSO_4$ solutions.

Electrochemical series or **activity series**, is a series in which elements are arranged in the increasing order of standard reduction potential. This series is obtained by measuring the electrode potential of various electrodes against a standard hydrogen electrode (SHE).

Fig.:- Electochemical series:

Several information can be obtaeind from an electrochemical series.

1. To identify oxidizing and reducing agent
   By observing electrochemical series reduction potential of substances can be identified. The substance with higher reduction potential is strong oxidizing agent while that with lower reduction potential is strong reducing agent.
2. To calculate cell potential
   This series helps to calculate cell potential by providing reduction potential of electrodes involved in the cell.

$$E_{cell} = E_{cathode} + E_{anode}$$

For example, for Zn-Cu cell,

$$E_{cell} = E_{(Cu^{++}/Cu)} + E_{(Zn^{++}/Zn)}$$
$$= 0.34 - (-0.76)V$$
$$= 1.10\ V$$

3. To predict spontaneity or feasibility of Galvanic cell

   To be spontaneous, electrodes of galvanic cell should be arranged as the cathode should be of higher reduction potential and anode should be of lower reduction potential. This will produce positive cell potential and current will be generated.

   For example, for Zn-Cu cell,

   Electrode potential of Zinc (Zn^{++}/Zn) is -0.76V and should be anode and that of Copper (Cu^{++}/Cu) is +0.34V and should be cathode.

4. Metal- Metal displacement

   The metal with lower reduction potential can displace the metal with higher reduction potential from their salt. So, the metal above in the series can displace the metal below in the series from their salt.

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

5. Corrosion prediction and prevention

The electrochemical series indicates which metals oxidize and corrode most readily. Sacrificial anodes (metals with even lower reduction potential) can be used to safeguard metals that are known to corrode easily.

6. Understanding electrolytic process

   This series suggests that the ions in the solution move towards the cathode, which has a higher reduction potential, and the anion moves towards the anode, which has a lower reduction potential. This concept provides a clear prediction about the formation of the product.

7. Displacement of Hydrogen from non-oxidizing acids

   The metals with negative reduction potential only can displace hydrogen from non-oxidizing acids. Such metals exist above hydrogen in the series.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

$$Cu + H_2SO_4 \rightarrow \times$$

Try yourself: *Two electrodes i.e. Fe^{3+}/Fe^{2+} and Sn^{4+}/Sn^{2+} having electrode potential of +0.77V and +0.15V respectively, are used to construct a galvanic cell. Identify anode and cathode in the cell to be spontaneous reaction with reason. Write spontaneous cell reaction.*

5.4.1: Electrochemical or Galvanic or Voltaic cell

Luigi Galvani (1737–1798) was an Italian physician and anatomist who discovered bioelectricity. While dissecting a frog, he noticed muscle twitching when touched by metal, leading to his theory of "animal electricity" generated by living tissues. This challenged existing views and sparked a debate with Alessandro Volta, who believed the electricity came from metals. Though Volta's battery gained more recognition, Galvani's work laid the foundation for bioelectricity and influenced neuroscience. Terms like galvanism and galvanometer honor his legacy.

Alessandro Volta (1745–1827) was an Italian physicist who invented the electric battery in 1800, known as the "voltaic pile." By stacking zinc and copper with brine-soaked cloth, he produced the first continuous electric current, disproving Galvani's "animal electricity" theory. His invention advanced electromagnetism and electrical circuits. Honored by Napoleon and with the unit "volt" named after him, Volta's legacy is foundational in science and technology.

Activity:

Volatic cell or **Galvanic cell** is a device which converts chemical energy into electrical energy through spontaneous reaction. It contains two electrode reactions occur separately in different containers, known as half-cells. The half-cell with higher reduction potential is taken as cathode and that with lower reduction potential is taken as anode. Two half-cells are externally connected by a thin wire through a voltmeter and internally by a salt bridge, which prevent direct contact between solutions. Combination of two electrode (half-cell) reactions give a net cell reaction.

Let us take Zn-Cu cell (Daniel cell) as an example.

At anode: Oxidation occurs at anode and metal ions are released in solution by losing electrons

$$Zn_{(s)} - 2e^- \rightarrow Zn^{++}_{(aq)} \text{ (anodic half reaction)}$$

At cathode: Reduction occurs at cathode and metal ions in solution accept electron from cathode and deposited on it.

$$Cu^{++}_{(aq)} + 2e^- \rightarrow Cu_{(aq)} \text{ (cathodic half reaction)}$$

Cell reaction: It is the sum of anodic and cathodic half reactions

$$Zn_{(s)} + Cu^{++}_{(aq)} \rightarrow Zn^{++}_{(aq)} + Cu_{(s)}$$

Here electrons flow from Zn (anode) to Cu (cathode), so current flows from Cu (cathode) to Zn (anode).

$$(-)\underbrace{Zn_{(s)}/Zn^{2+}_{(aq,1M)}}_{\text{Anodic half cell}}//\underbrace{Cu^{2+}_{(aq,1M)}/Cu_{(s)}}_{\text{Cathodic half cell}}(+)$$

This type of representation is called cell notation and it corresponds to the Daniel cell.
Galvanic or voltaic cell can also be represented by a symbolic representation, called **cell notation**. In this representation, single vertical line separates solid metal and electrolyte solution called solid-liquid interface while double vertical line represents salt bridge which connects two half cells. The anode (-) should always be on left hand side and cathode (+) should be on right hand side. The concentration of the ions is written within parentheses.

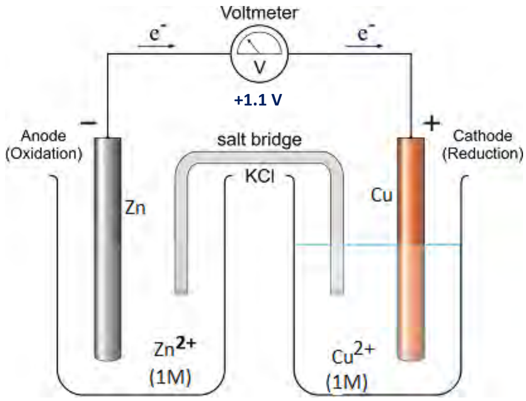


Fig5.4.1: Representation of Zn-Cu cell

The voltage or potential produced by the cell is calculated by using the relation;

$$E^o_{cell} = E^o_{Cathode} - E^o_{anode}$$

$$E^o_{cell} = 0.34 - (-0.76)\ V$$

$$E^o_{cell} = +1.10\ V$$

Positive value of cell potential shows the reaction is spontaneous and cell is feasible to produce current.

Salt Bridge

A salt bridge is a device used in electrochemical cells to connect electrolyte solutions and preserve neutrality. It is typically composed of a U-shaped glass tube filled with a concentrated solution of inert electrolyte (such as KCl or KNO_3) mixed in agar-agar gel. Filter paper soaked in this type of electrolyte solution is occasionally used as a salt bridge.
Salt bridge has following functions.

1. It connects two electrolytic solutions to a complete circuit by providing an ionic pathway.
2. It prevents direct mixing of solutions
3. Minimizes unwanted potential, for example a liquid junction potential

Note: In spite of having positive reduction potential metal can be oxidized (or can't be reduced), because reducing capacity of electrode is comparative and its reduction and oxidation depends on the electrode potential of the other electrode, with which it will be connected in the cell. The electrode with higher electrode potential will be reduced in the cell.

Let us take Cu-Ag cell as next example of electrochemical cell. In this cell, Cu electrode will be anode and Ag electrode as cathode (why?).

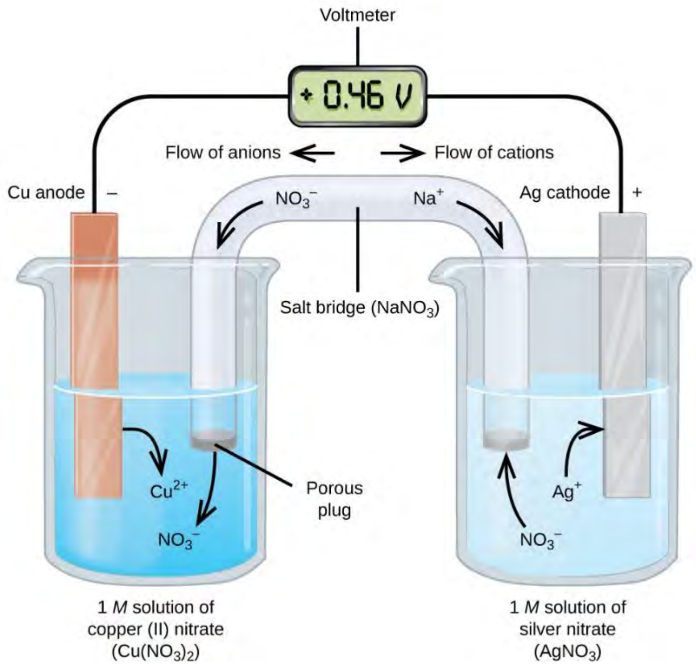


Fig 5.4.2: Representation of Cu-Ag cell

At anode: Oxidation occurs at anode and metal ions are released in solution by losing electrons

$$Cu_{(s)} - 2e^- \rightarrow Cu^{++}_{(aq)}$$

At cathode: Reduction occurs at cathode and metal ions in solution accept electron from cathode and deposited on it.

$$Ag^+_{(aq)} + 1e^- \rightarrow Ag_{(aq)}$$

Cell reaction: It is the sum of electrode reaction at anode and cathode.

$$Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{++}_{(aq)} + 2Ag_{(s)}$$

Cell notation:

$$(-) - Zn_{(s)}/Cu^{2+}_{(aq)}//Zn^{2+}_{(aq)}/Cu_{(s)} - (+)$$

The cell potential produced by the cell is calculated by using the relation;

$$E^o_{cell} = E^o_{Cathode} - E^o_{anode}$$

$$E^o_{cell} = (0.80 - 0.34)\ V$$

$$E^o_{cell} = +0.46\ V$$

Try yourself: *Is it possible for an electrode to get reduced in some cases and get oxidized in other? Explain with example.*

Activity

Construct a voltaic cell using Fe and Cu electrodes

Given,

$E_{Fe^{3+}/Fe^{2+}} = +0.77$ V

$E_{Cu^{++}/Cu} = +0.34$ V

1. Identify anode and cathode.
2. Write cell reaction.
3. Write cell notation.
4. Calculate cell potential.

.

5.5.1 Cell potential and standard cell potential

Cell potential(E_{cell})is the voltage or potential difference between two electrodes of an electrochemical cell. In the given set of conditions, it shows driving force for the electrochemical reaction.

$$E_{cell} = E_{cathode} - E_{anode}$$

Where,

$E_{cell} = cell\ potential$

$E_{cathode} = Electrode\ potential\ of\ cathode$

$E_{anode} = Electrode\ potential\ of\ anode$

It can be affected by temperature, pressure and concentration

If cell potential is measured under standard conditions of 25°C (298 K) temperature, 1 atm pressure and 1M concentration of electrolyte solution, then it called as **standard cell potential** (E^o_{cell}). It is comparative to the standard hydrogen electrode. It is specific to each reaction and helps to determine whether the reaction tends to proceed spontaneously or not.

$$E^o_{cell} = E^o_{Cathode} - E^o_{anode}$$

5.6. Relation between Cell Potential and Free Energy

The product of the cell potential and the total charge transferred during the reaction (nF) is the maximum amount of work that an electrochemical cell can produce (w_{max}).

$$w_{max} = nFE_{cell}$$

The maximum useful work that can be done by a system is equal to decrease in free energy, i.e.

$$-\Delta G = w_{max}$$

From above relations:

$$\Delta G = -nFE_{cell}$$

Under standard conditions:

$$\Delta G^\circ = -nFE^o_{cell}$$

In thermodynamics, for a process to be spontaneous the free energy change should be negative. This requires E^o_{cell} to be positive.

5.7. Commercial batteries and fuel cells

5.7.1. Commercial batteries

Commercial batteries are electrochemical cells (which convert chemical energy into electrical energy throuh chemical reaction) designed for practical or everyday use for wide rane of applications.

Commercial batteries are classified as:

1. Primary batteries: These are non-rechargeable batteries and can only be used for one time. For example

Dry cell: It is also known as Leclanche cell and used in remotes wall clocks, toys etc.

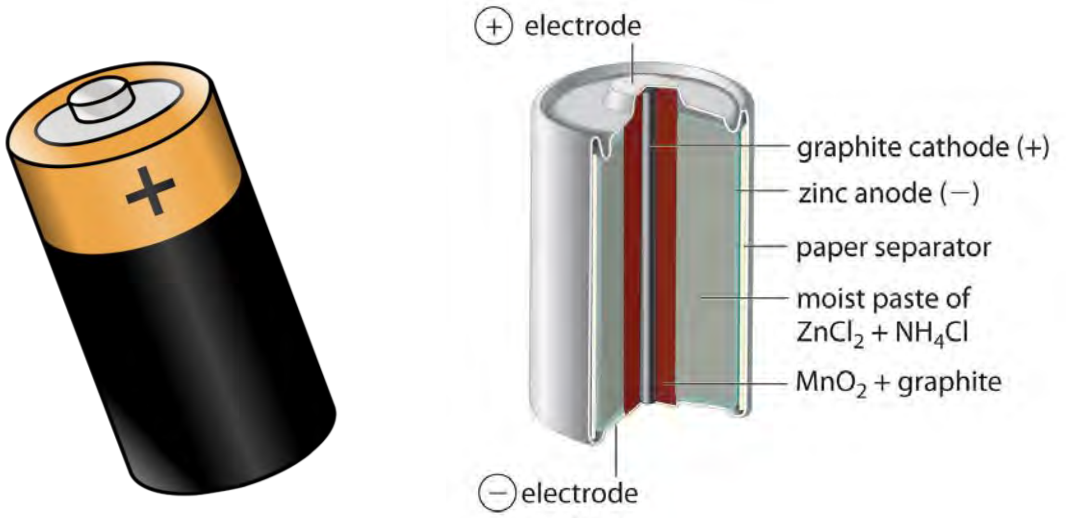


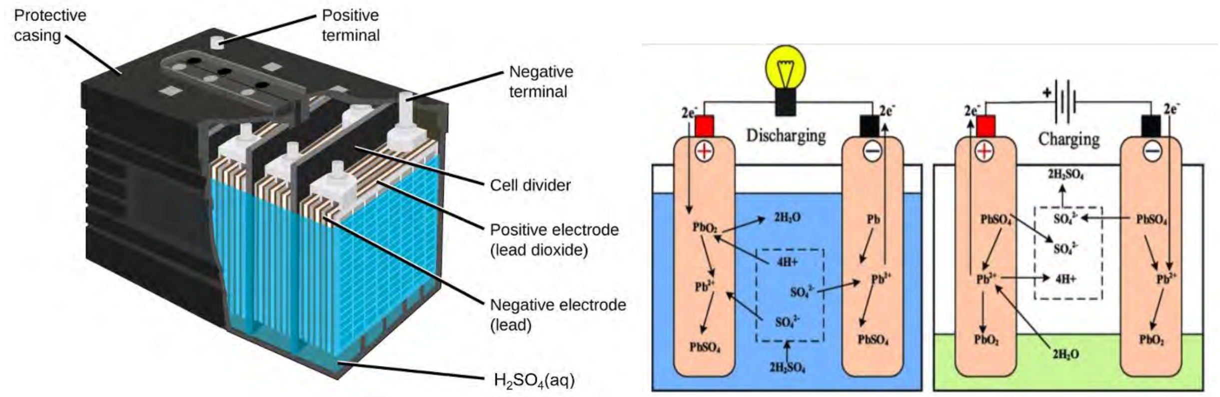
Fig 5.7.1: Leclanche dry cell

Cell reaction:

$$2MnO_{2(S)} + 2NH_4Cl_{(aq)} + Zn_{(S)} \rightarrow Mn_2O_{3(S)} + Zn(NH_3)_2Cl_{2(S)} + H_2O_{(l)}$$

2. Secondary batteries: These are rechargeable batteries and can be used multiple times. For example:

Laed acid battery: Generally used in automobiles and inverters.



$$Pb_{(S)} + PbO_{2(S)} + 2HSO^{-}_{4(aq)} + 2H^{+}_{(aq)} \longrightarrow 2PbSO_{4(S)} + 2H_2O_{(l)}$$

Fig 5.7.2: Lead storage battery

Nickel-Cadmium battery: It is the battery in which nickel oxy-hydroxide (positive plate and cadmium (negative plate) are electrodes and aqueous KOH as electrolyte.

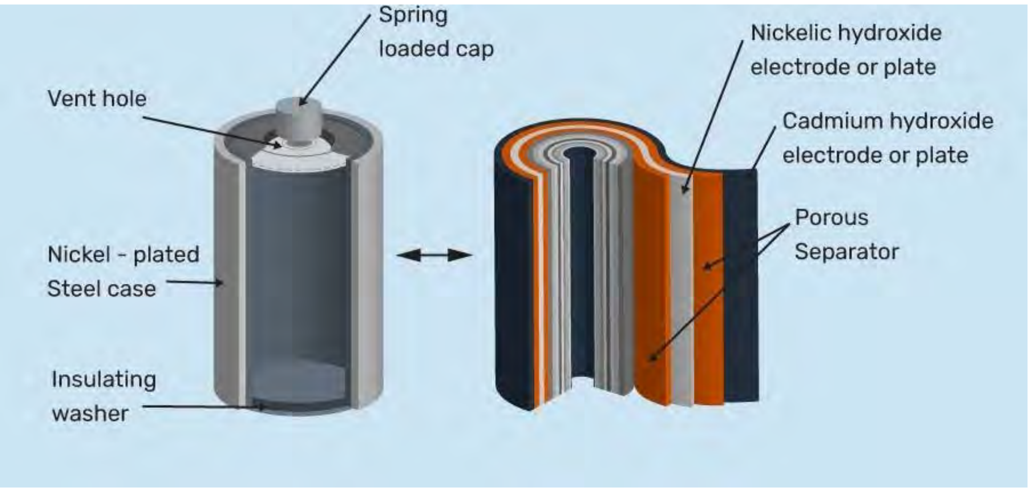


Fig 5.7.3: Ni-Cd Battery

The chemical reaction (discharge process)
At anode (cadmium)

$Cd+2OH^- \rightarrow Cd(OH)_2+2e^-$

At cathode (nickel)

$2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$

Overall reaction:
$2NiO(OH) + Cd + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + Cd(OH)_2$

3. Fuel cell: The cell which uses the chemical energy of fuel like hydrogen to produce electric energy. For example, hydrogen-oxygen cell.

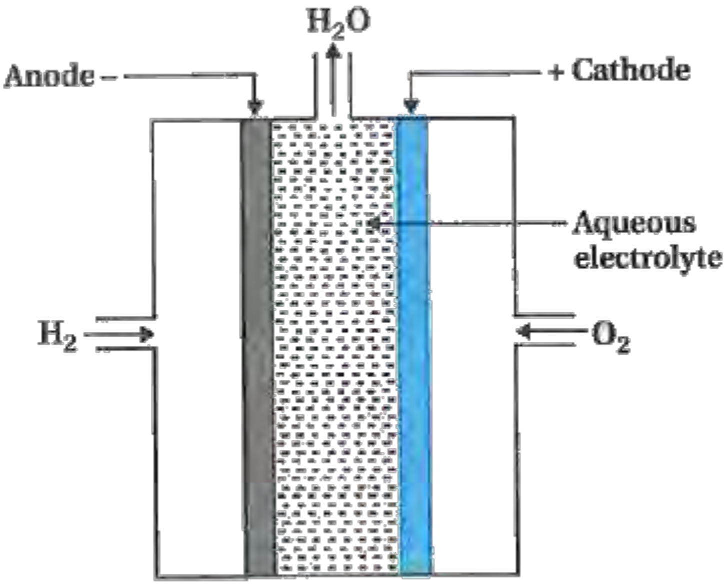
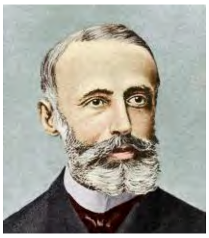


Fig 5.7.4: Hydrogen / Oxygen cell



Do you know?The first electric storage battery, or accumulator, was created in 1859 by French physicist Gaston Plante. His invention is now widely employed in cars in an enhanced form.He started conducting research in 1859 that led to the creation of a battery for electrical energy storage. His initial prototype comprised two lead sheets that were separated by rubber bands, wrapped into a spiral shape, and submerged in a solution that contained about 10% sulphuric acid. His battery was capable of producing extraordinary high currents.

1. The alkaline Hydrogen oxygen cell was used in Apollo 11 space exploration. It had weight of ~180 kg and contained 31 separate cells connected in series each cell could produce 27-31 V.

Exercise

Multiple choice questions

1. Electrode potential is
   a) The potential difference across a cell
   b) The potential of an electrode on connecting with another electrode
   c) The ability of an electrode to attract ions
   d) The measure of the ability of the electrode to gain or loss electrons

2. The conditions required for electrode potential to be standard are-
   a) 25°C, 1 atm pressure and 0.1M concentration
   b) 0°C, 1 atm pressure and 1M concentration
   c) 25°C, 1 atm pressure and 0.1M concentration
   d) 0°K, 1 atm pressure and 1M concentration

3. The standard electrode potential of hydrogen is taken as:

   a) +V b) 0V c) -1 V d) 1.5 V

4. The standerd hydrogen electrode is commonly used as:

   a) An anode only b) A cathode only

   c) A reference electrode d) A universal electrode

5. The calomel electrode is primarily used for:

   a) determining cell potenti b) As a standard reference electrode

   c) To generate gydrogen gas d) Measuring pH levels

6. Metals in electrochemical series are arranged on the basis of:

   a) Atomic number b) Atomic mass

   c) Reduction potential d) Ionization potential

7. Which of the following has the highest reduction potential?

   a) Zinc b) Copper c) Lithium d) Fluorine

8. Which of the following would displace copper from copper sulphate solution?

   a) Silver b) Gold c) Nickel d) Platinum

9. The reaction that occurs at cathode in a Zn-Cu voltaic cell is:

a) $Zn \rightarrow Zn^{2+} + 2e^-$ b) $Cu \rightarrow Cu^{2+} + 2e^-$

c) $Zn^{2+} + 2e^- \rightarrow Zn$ d) $Cu^{2+} + 2e^- \rightarrow Cu$

10. The standard reduction potential of a Zn-Cu cell is:

a) 0.34 V b) 1.10 V c) 0.76 V d) 0.42 V

11. If the cell potential of a galvanic cell is positive, the reactions is:

a) Reversible b) At equilibrium

c) Spontaneous d) Non-spontaneous

12. The relationship between cell potential and free energy is:

a) $\Delta G = nFE$ b) $\Delta G = -nFE$ c) $\Delta G = \frac{E}{nF}$ d) $\Delta G = \frac{nF}{E}$

13. The electrolyte in a lead storage battery is:

a) Potassium hydroxide b) Sulphuric acid

c) Lead hydroxide d) Hydrochloric acid

14. The battery which is commonly used in smart phones is:

a) Alkaline battery b) Ni-Cd battery

c) Lead storage battery d) Li-ion battery

15. The byproduct of hydrogen/Oxygen fuel cell is:

a) Carbon dioxideb) Oxygen c) Water d) Sulphur dioxide

16. Standard conditions are necessary during measurement of standard electrode potential because:

a) They maximizes the reaction speed

b) They ensure consistent comparison across electrodes.

c) They reduce the potential difference.

d) They prevent corrosion.

17. If the standard reduction potential of a metal is -0.76 V, on comparing it with standard hydrogen electrode, it indicates:

a) Greater tendency to gain electrons than hydrogen

b) Greater tendency to lose eletrons than hydrogen

c) it is more stable than hydrogen

d) It has a lower density than hydrogen.

18. In a voltaic cell the function of salt bridge is:
    - a) To provide electrons for the reaction
    - b) To keep the solution neutral by allowing flow of ions.
    - c) To increase the voltage of the cell
    - d) To prevent the anode from corroding.

19. For the construction of a voltaic cell using two different metals, what should be the first step in predicting the cell potential?
    - a) Comparison of atomic masses of metals
    - b) Identification of ionization potential of metals.
    - c) Identification of reduction potentials of metals
    - d) Identification of electrolyte in salt bridge.

20. In real-world contexts the use of electrochemical series is best explained by:
    - a) Determining the quality of metals for construction.
    - b) Determining the color of metal compounds.
    - c) Comparing the market price of metals.
    - d) Selecting metals for rechargeable batteries.

21. Engineers choose materials with high reduction potential for designing commercial battery to:
    - a) Ensure a lower energy density
    - b) Achieve a higher cell potential for greater power output.
    - c) Make the battery heavier and more stable.
    - d) Decrease the overall cost.

22. When metal X and Y with +0.80 V and -0.76 V respectively are used in a galvanic cell then for spontaneity of cell:
    - a) Electrons flow from X to Y
    - b) Electrons flow from Y to X
    - c) Current flow from Y to X
    - d) X should be and Y should be cathode.

23. If a voltaic cell has a cell potential +1.0 V, then
    - a) $\Delta G\ is\ positive\ indicating\ non-spontaneous\ reaction$
    - b) $\Delta G\ is\ negative\ indicating\ spontaneous\ reaction$
    - c) $\Delta G\ is\ zero\ indicating\ the\ reaction\ at\ equilibrium$
    - d) $The\ value\ of\ \Delta G\ depends\ upon\ the\ concentration\ ofreactant$

24. To prevent marine corrosion in an iron structure the metal suitable for sacrificial metal is

a) Copper b) Zinc c) Gold d) Aluminium

Exercise 5.2

1. Given:

$$E^o_{Na^+/Na} = -2.71\ V \text{ and } E^o_{Au^{3+}/Au} = +1.5\ V$$

a) Which ion a better reducing agent: Na or Au?
b) Can Au^{3+} oxidizes Na to Na^+? Write the reaction if feasible.
c) Why is gold found in nature in its elemental form?

2. Electrochemical series has many applications. It can also help in the protection of metal from corrosion.
a) Why does iron corrode faster in saline water? Use electrochemical series to explain.
b) Suggest why aluminum is used as sacrificial anode for iron ships. Even though $E^o_{Al^{3+}/Al} < E^o_{Fe^{2+}/Fe}$.
c) Write the oxidation half-reaction for aluminum acts as a sacrificial anode.

3. A galvanic cell consists of the following half-cells:

$$Ni^{2+} + 2e^- \longrightarrow Ni \quad E^o = -0.25\ V$$

$$Cr^{3+} + 3e^- \longrightarrow Cr \quad E^o = -0.74\ V$$

Answer the following questions:
a) Identify anode and cathode. Write cell notation
b) Write cell reaction showing the electrode reactions.
c) Calculate standard emf of the cell.
d) What will happen to the cell potential if the concentration of Ni^{2+} is increased to 2M while Cr^{3+} remains at 1M?

3. To construct a galvanic cell of zinc and iron, following reaction is given:

$$Zn_{(s)} + Fe^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Fe_{(s)}$$

a) Convert the above reaction in to cell notation.
b) Calculate the ΔG^o for the using the standard cell potential $E^o_{cell} = 0.32\ V$
c) Is this reaction spontaneous under standard conditions? Justify.
d) What happens to the mass of zinc electrode as the reaction proceeds?

5. The following standard reduction potentials are given:

$$E^o_{Mg^{2+}/Mg} = -2.37\ V \text{ and } E^o_{Ni^{2+}/Ni} = -0.25\ V$$

a) Design a galvanic cell using Mg and Ni. Label the anode, cathode and electron flow.
b) Write cell notation and cell reaction
c) Calculate cell potential.
d) Which metal acts as oxidizing agent? Explain

6. During the construction of a galvanic cell no voltage was observed.
   a) List three possible reasons for this observation.
   b) How can a person overcome the problem to ensure proper functioning?
   c) Explain the role of salt bridge in maintaining cell operation.

7. Five different Metals P, Q, R, S and T show the following reactivity:

R displaces P and Q from their solutions while S does not react with any of the metal solutions. T displaces hydrogen from 1 acid but not R. P displaces Q from its solution.

Answer the following:

a. Arrange the metals in an activity series with hydrogen.

b. if the standard reduction potential of the following electrodes are

$$P^{2+} + 2e^- \rightarrow P, \qquad E^o = -0.44V$$

$$T^+ + e^- \rightarrow T, \qquad E^o = +0.34V$$

i. Construct a Galvanic cell and indicate the anode and cathode
ii. Calculate the EMF of the cell with 1M ion solutions.
iii. Predict whether the reaction:

$$P^{2+} + T \rightarrow P + T^+,$$

will occur. Explain

Activity (Bingo-Game)

Instruction

1. A 5 × 5 bingo card is provided to you or draw in your notebook
2. A word bank comprising 25 terms is provided below. You should select the appropriate term that corresponds to the clue provided by the teacher.
3. The box at the center is your FREE space, which may be marked automatically.
4. Only one term should be filled per box on your Bingo card.
5. Listen carefully as your teacher reads out clues or definitions related to the terms.
6. When a clue matches a term on word bank, fill the term in that box randomly.
7. The first student to fill a full row, column, or diagonal shouts "BINGO!" and wins!

Bingo Card

		FREE		

Word Bank (Select to fill the card)

Anode, Cathode, Oxidation, Reduction, Electron, Electrode potential, Standard hydrogen electrode, Calomel electrode, Electrolyte, Salt bridge, Voltaic cell, Galvanic cell, Electrochemical series, Cell potential, Standard cell potential, EMF, Nernst equation, Redox reaction, Daniell cell, Half-cell, Electroplating, Fuel cell, Hydrogen electrode, Zn/Cu cell, Free energy, Battery, Electrolysis, Faraday's laws, Ions, Volt

Teacher Clues (Speak Aloud)

1. The electrode where oxidation occurs.
2. The electrode where reduction takes place.
3. Loss of electrons.
4. Gain of electrons.
5. Subatomic particle transferred in redox reactions.
6. A measure of the tendency of an electrode to lose or gain electrons.
7. A standard reference electrode with a potential of zero volts.
8. A commonly used reference electrode containing mercury and potassium chloride.
9. A solution that conducts electricity.
10. Connects two half-cells and maintains electrical neutrality.
11. A cell that converts chemical energy to electrical energy.
12. Another name for a voltaic cell.
13. A list of elements arranged by their electrode potentials.
14. The difference in potential between two electrodes.
15. Cell potential measured under standard conditions.
16. Electromotive force — drives the movement of electrons.
17. An equation that relates cell potential to concentration.
18. A reaction involving both oxidation and reduction.
19. A voltaic cell made using zinc and copper electrodes.
20. A single electrode and its solution.
21. A process of coating an object with metal using electricity.
22. A device that converts chemical energy from fuel into electricity.
23. A type of standard electrode involving hydrogen gas.
24. A cell made from zinc and copper electrodes in their respective solutions.
25. The capacity to do work, related to cell potential.

Project Work

1. To construct a bio-electrochemical cell: can fruit or vegetables generate electricity?

2. To Construct a battery using household materials.

Unit 6

Transitions Metals

6.1: Introduction:

1. Activity:

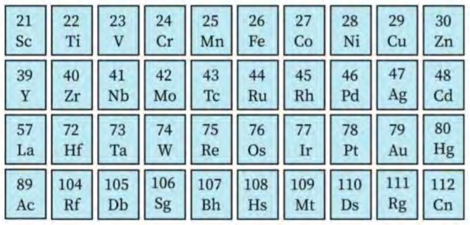
A part of modern periodic table is shown; answer the following questions based on your observation and knowledge.

a. Why these elements are called d- block element?

b. d-block elements are also known as transition metals, why?

c. Write the position of these elements in the periodic table.

d-block



21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

a	....
b	....
c	....

If you closely observe the elements shown in this part of the periodic table, you will notice they all fall in the central block and seem to share certain features. For example, many of them are metals used in tools, wires, and construction. Some form colorful compounds or are even used as catalyst in several chemical reactions. They are no ordinary metals and belong to a unique group known as **transition metals**.

Transition metals are elements found in the middle of the periodic table, specifically in group 3 to 12. They are called so because their properties lie in between s-block and p-block elements. They are d-block elements as their valence electron enters (n-1)d subshell. These metals are distinguished by their hardness, variable oxidation state, high melting and boiling points, capacity to produce colorful compounds, etc. Several transition metals like nickel, copper, iron, etc are necessary for daily life. They are significant from a chemical and commercial standpoint due to their special qualities.

6.2: Characteristics of transition metals:

Transition metals show several unique properties that distinguish them from other elements in the periodic table. The general characteristics of transition metals are-

1. **Periodic position:** They are found in the center of the periodic table occupying groups 3 to 12.

2. **Electronic configuration:** The general valence shell electronic configuration is $(n-1)d^{1-10}$, ns^{1-2}, where (n-1) d subshell is partly filled.

3. **Variable oxidation state:** They show variable oxidation states due to lose of valence electron either from (n-1)d and ns.

4. **Formation of colored compounds:** Many transition metals form colored compounds due to d-d electronic transition.

5. **Conductivity:** They are good conductor of heat and electricity.

6. **Density, belting point and boiling point:** They have high density, melting point and boiling points due to strong metallic bonding.

Transition metal objects

7. **Catalytic property:** Many of transition metals and their compounds act as catalyst in industrial and chemical reactions.

8. **Paramagnetic nature:** Many transition metals show paramagnetism due to presence of unpaired d-electrons.

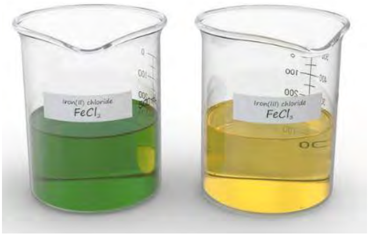
9. **Formation of complex:** They readily form complex ions with ligands because of their small size and high charge density.

10. **Alloy formation:** They easily form alloy with other metals.

11. **Metallic character:** They are typically hard, malleable, ductile and posses metallic luster.

6.3: Variable oxidation state of transition metals:

2. Activity:



Observe the color of $FeCl_2$ (pale green) and $FeCl_3$ (yellow-brown) carefully and answer the following questions based on your observation and knowledge

a. What do the different colors of $FeCl_2$ and $FeCl_3$ suggest about the oxidation state of iron?

b. Can you think of another transition element that shows more than one oxidation state?

a.	....
b.	....

One of the most remarkable features of d-block elements is their ability to exhibit variable oxidation state in their compounds. With a, few exceptions, most of the transition element show more than one oxidation state. This is mainly due to two reasons,

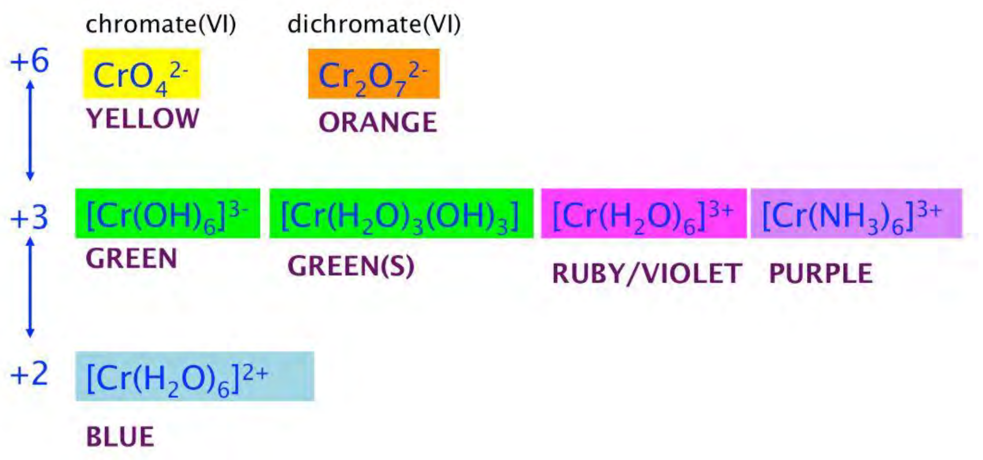
i. Since the (n-1)d and ns orbitals in the atoms of same d-block elements have very close energy difference, electrons from both of these subshells can participate in bonding. Consequently, under various conditions, transition metals may lose more than one electron showing variable oxidation state.

ii.Transition metals frequently exhibit stable electronic structures in several oxidation state because partially filled d-orbitals are generally stable. Their diverse redox activity and fluctuating valency are a result of their adaptability in electron loss.

Table: Oxidation state of 3d transition elements

Transition element	Atomic number	Oxidation state	Electronic configuration
Scandium (Sc)	21	+2, +3	Sc: [Ar]$4s^2$ $3d^1$
Titanium (Ti)	22	+2, +3, +4	Ti: [Ar]$4s^2$ $3d^2$
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar]$4s^2$ $3d^3$
Chromium (Cr)	24	+1,+2, +3, +4, +5, +6	Cr: [Ar]$4s^1$ $3d^5$
Manganese (Mn)	25	+2, +3, +4, +5, +6, +7	Mn: [Ar]$4s^2$ $3d^5$
Iron (Fe)	26	+2, +3, +4, +5, +6	Fe: [Ar]$4s^2$ $3d^6$
Cobalt (Co)	27	+2, 3,+4	Co: [Ar]$4s^2$ $3d^7$
Nickel (Ni)	28	+2, +3, +4	Ni: [Ar]$4s^2$ $3d^8$
Copper (Cu)	29	+1, +2	Cu: [Ar]$4s^1$ $3d^{10}$
Zinc (Zn)	30	+2	Zn: [Ar]$4s^2$ $3d^{10}$

Example: Common oxidation states shown by chromium



Do you know?

- ✓ **The relative stability of various oxidation states can be explained based on the stability of d^0, d^5 and d^{10} orbitals [example, Mn^{2+} ($3d^5$, $4s^0$) is more stable than Mn^{3+} ($3d^4$, $4s^0$)].**
- ✓ **+7 is the highest oxidation state shown by elements of 3d series while elements in the 4d and 5d series can exhibit oxidation state as high as +8 (for example, OsO_4)**
- ✓ **Generally transition element with lower oxidation state (+2, +3) forms ionic compounds and higher oxidation state forms covalent compounds (example, CrO is ionic whereas CrO_3 is covalent).**

Test yourself:

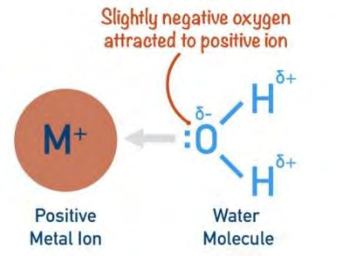
Q. Ti^{4+} is more stable than Ti^{3+}, why?

6.4: Complex ions and metal complexes:

3. Activity:

In the given figure, a water molecule is approaching the metal ion M^+ to form a complex ion. Answer the following questions based on your observation and knowledge.

a. What type of bond is likely to form between the metal ion and water molecule?

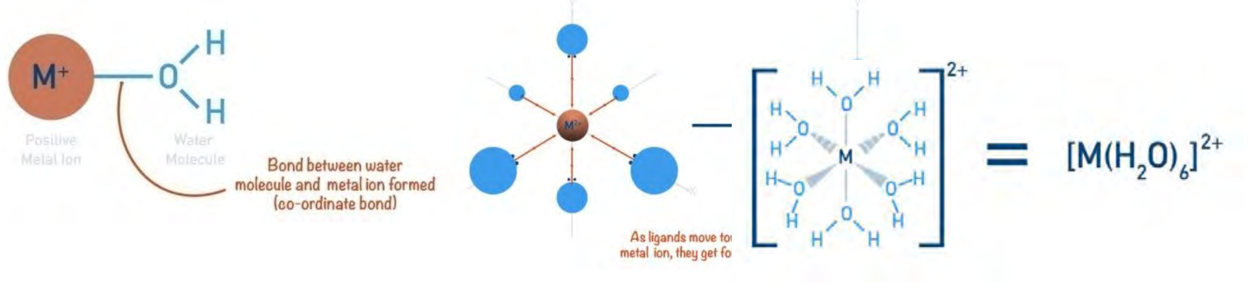


b. What property of water molecule allows it to bond with metal ion?

c. What charge would you expect the resulting complex ion to have after the attachment of several water molecules?

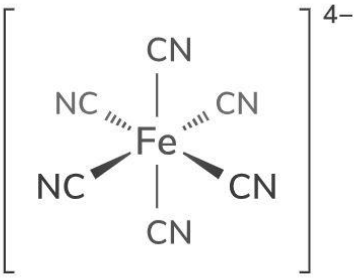
a.	....
b.	....
c.	....

As the water molecule surrounds and attach to the metal ion (M^+) in the activity, something interesting begins to happen. The oxygen atom in each water molecule, carrying, lone pairs of electrons, donates one of these pairs to the metal ion forming a special type of bond called **coordinate bond**. As more water molecules bond this way, a stable cluster begins to form around the central metal ion. This entire assembly where central metal ion is surrounded by molecules like water, is known as **metal complex** (or **coordination complex)** and if the overall structure carries charge, it is referred to as a **complex ion**. The molecule or ion that donates electron pair is called **ligands** and the number of ligands, in general, bonded to central metal ion (M+) is called **coordination number**. In this case, if six water molecules attach then coordination number would be six typically forming **octahedral geometry**. The part of the complex ion that consists of central metal ion and directly bonded ligands is called **coordination sphere**. It is usually enclosed in a **square bracket [ ]** in chemical formulas.

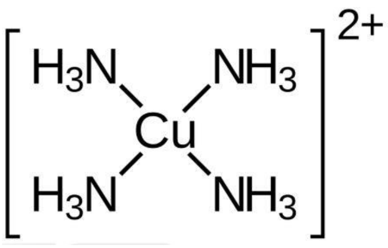


Ligands: Ligands are the atoms or ions or neutral molecucles that donate a lone pair of electron to a central metal ion to form a coordinate bond in a complex. Followings are the types of ligands-

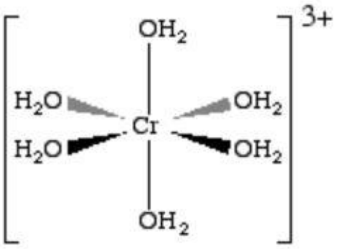
a. Monodetate ligand: The ligand that can share only one pair of electron is called monodentate ligand. For example, $X^-(F^-, Cl^-, Br^-, I^-)$, CN^-, OH^-, H_2O, NH_3, CO, NO, etc.
b. Bidentate ligand: The ligand that can share only two pair of electrons is called bidentate ligand. For example, CO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-} ,ethylenediamine ($NH_2CH_2CH_2NH_2$) etc. etc.
c. Tridentate ligand: The ligand that can share only three pair of electrons is called tridentate ligand. For example, diethyletriamine etc.
d. Polydentate ligand: The ligand that can share many electron pairs (more than three) is called polydentate ligand. For example, EDTA (Ethylenediamnie tetracetate)etc.
Some examples of metal complexes are Tetraaminecopper(II) sulphate : $[Cu(NH_3)_4]SO_4$, Tetraaquodichlorochromium (III) chloride: $[Cr(H_2O)_4Cl_2]Cl$, Potassiumhexacyanoferrate(III) or Potassium ferricyanide: $K_3[Fe(CN)_6]$ etc.



Hexacyanoferrate (II) ion



Tetraaminecopper (II) ion

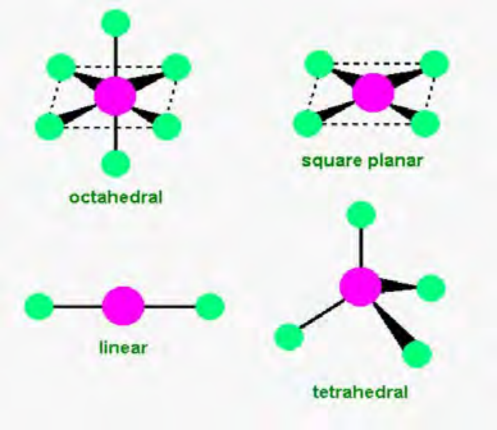


Hexaaquochromium(III) ion

Do you know?

- Complexes are classified as-
  i. Complex cation: A complex ion having net positive charge is called complex cation. Example, $[Ag(NH_3)_2]^+$ etc.
  ii. Complex anion: A complex ion ahving net negative charge is called complex anion. Example, $[Ag(CN)_2]^-$ etc.
  iii. Neutral complex: A complex having no charge is called neutral complex. Example, $Ni(CO)_4$, $Fe(CO)_5$ etc.

6.5: Shape of complexes ion:



The shape of complex ions depends on the number of ligands surrounding the central metal atom or ion which is called coordination number (C.N.). The most common C.N. of transition metal complexes are 4 and 6. Complexes with C.N. 4 adopt either tetrahedral or square planar geometry and that with C.N. 6 adopt octahedral geometries.

Common geometries based on coordination number (C.N.) are-

Coordination number	Geometry	Example
2	Linear	$[Ag(NH_3)_2]^+$, etc.
4	Square planar	$[Ni(CN)_4]^{2-}$, $[Pt(Cl)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, etc.
4	Tetrahedral	$[Co(Cl)_4]^{2-}$, $[CuCl_4]^{2-}$, $Ni(CO)_4$, $[Zn(NH_3)_4]^{2+}$, $[MnCl_4]^{2-}$, etc.
6	Octahedral	$[Cu(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$, etc.

Factors affecting the geometry (shape) of complex ions are-

i. Coordination number

ii. Size of metal ion

iii. Type and size of ligands

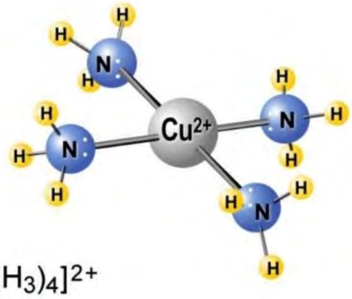
iv. Electronic configuration and oxidation state of central metal atom

v. Steric effect and ligand-ligand repulsion.

"The shape of complex ions can be explained using **VSEPR theory**, which considers electron pair repulsion, and **Crystal Field Theory (CFT)**, which considers d-orbital interactions with ligands."

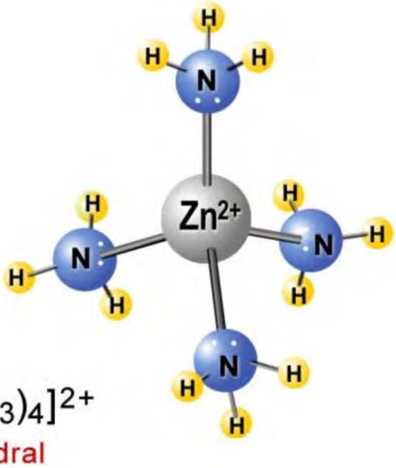
$[Ag(NH_3)_2]^+$

Linear



$[Cu(NH_3)_4]^{2+}$

Square planar



$[Zn(NH_3)_4]^{2+}$

Tetrahedral

$[Fe(H_2O)_6]^{3+}$

Octahedral

Ball and Stick model:

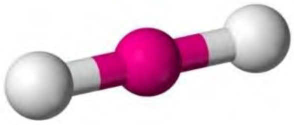


Fig: Linear shape

Fig: Square planar shape

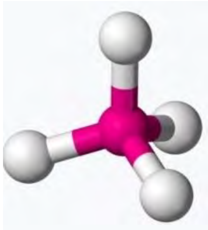


Fig: Tetrahedral shape

Fig: Octahedral shape

6.6: Crystal Field Theory (CFT) for octahedral complex:

In the early 1930s, two physicists, Hans Bethe and Van Vleck, developed crystal field theory (CFT) to examine ionic crystals. Later, they expanded it to cover the characteristics of coordination compounds. This theory assumes that the ligands are simple dipoles which occupy their position around the central metal cation. The basic postulates of CFT are-

Hans Albrecht Eduard Bethe

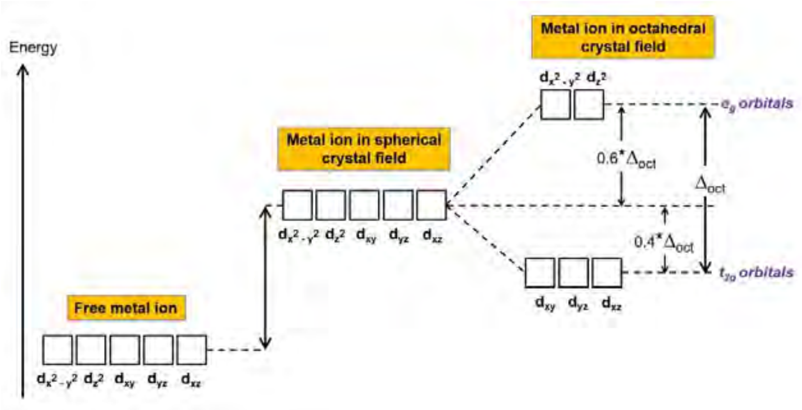
i. The metal ion is surrounded by an electric field created by the ligands.

ii. The bonding between metal cation and ligands is of electrostatic in nature.

iii. The transition metal ion is a positive ion with the same charge as the oxidation state.

iv. In the absence of ligands, the d-orbitals of the metal ions are degenerate i.e, all five d orbitals have same energies.

v. In the environment of ligands, the degeneracy of d-orbitals is lost due to splitiing of d-orbitals into lower energy state t_{2g} and higher energy state e_g.. In the case of octahedral complexes, the d_{xy}, d_{zx} and d_{yz} orbitals form lower energy set t_{2g} and $d_{x^2-y^2}$ and d_{z^2} orbitals form higher energy set e_g as shown below.



Splitting of d orbitals in octahedral complexes

John Hasbrouck van Vleck

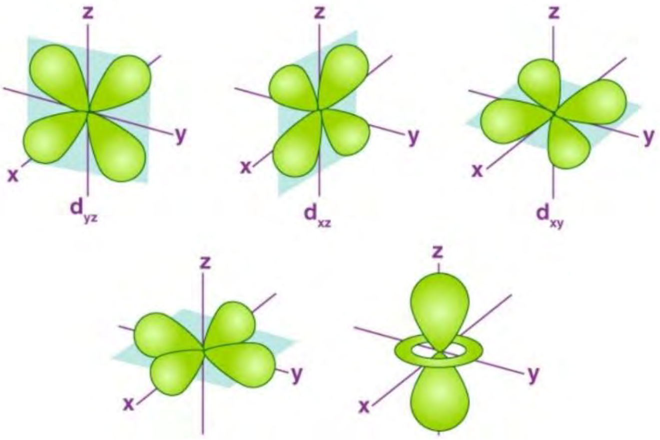
vi. The extent of this splitting depends on the nature of ligands and their position around the metal ions.

vii. The difference in energies between the splits orbitals give rise to Crystal Field Stabilization Energy (CFSE), which contributes to the complexes' stability, color, magnetism and other properties.

viii. High spin complexes occur with weak field ligands (like H_2O, OH^-, X^- etc.), leading to more unpaired electrons due to minimal splitting.

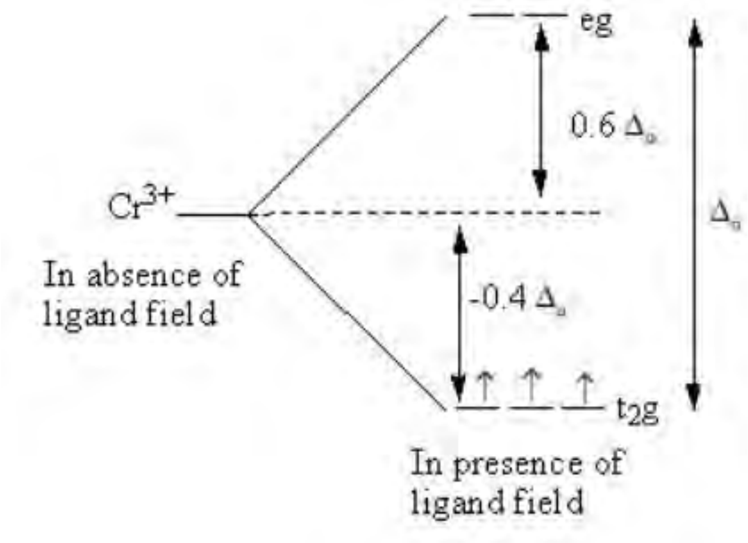
ix. Low spin complexes occur with strong field ligands (like CO, CN^-, NH_3 etc), causing greater splitting and more electron pairing in lower orbitals.

- **Splitting of d-orbitals in octahedral complexes:**



The splitting d-orbitals of metal in the presence of ligands is called crystal field splitting (CFT). The The d-orbitals **(**$d_{x^2-y^2}$ and d_{z^2}) pointing towrds the axes along the direction of ligands are raised to higher energy state denoted by e_g and the d-orbitals (d_{xy} d_{zx} and d_{yz}) which are directed between the axes are depressed to lower energy sate denoted by t_{2g}.The energy difference of these two states is denoted by Δ_o, where o is for octahedral.

For example,



Octahedral field splitting of Cr^{3+}

Test yourself:

Q. What is the cause of crystal field splitting?

6.7: Color of transition metal compounds:

4. Activity:

Observe the picture of different metal ion solution displayed in the image and answer the following questions on the basis of your observation and prior knowledge.

a. Why do these metal ion solution appear colorful?

b. Can you think of an example of metal ion that forms colorless solution?

a.	....
b.	....

Transition metal ions get their color from the absorption of particular light wavelengths, which causes the metal ion to move between different energy levels. is due to the absorption of specific wavelength of light, which causes electrons in the metal ion to jump between energy levels. This phenomenon is influenced by the type of metal, its oxidation state, and the ligands surrounding it.

The color of transition metals primarily arises due to d-d electronic transitions within partially filled d-orbitals of the metal ion. Followings are the key reasons to explain the color of metal ions-

1. Crystal Field Theory (CFT): According to this theory, the transition metal complexes exhibit different color due to splitting of their degenerate d-orbitals in to two sets by the surrounding ligands. This splitting causes electrons to move in between the energy levels by absorbing light if specific wavelength. The observed color of the complex is the complementary color of the absorbed light by the metal ions. In addition, oxidation state of metal ion, nature of ligands and geometry of the complex all affect the color of metal ions.

For example, aqueous solution of copper (II) sulphate is blue. This is because when copper sulpahte is dissolved in water it forms hydrated ion $[Cu(H_2O)_6]^{2+}$ where under the influence of ligands H_2O the d-orbital of Cu (d^9) gets split into lower (t_{2g}) and higher (e_g) orbitals . When radiations of visible light fall on this complex, it absorbs radiation in the orange region and transmits blue color which is complementary color of orange.

2. Electronic configuration: Ions with completely full (d^{10}) or empty (d^0) d- orbitals typically, as d-d electronic transition is not possible.

For example, Cu^{2+} complexes are colored because Cu^{2+} has $3d^9$ electronic configuration allowing d-d electronic transition whereas Zn^{2+} complexes are colorless which has $3d^{10}$ electronic configuration and no d-d electronic transition occurs.

3. Charge transfer theory (Secondary factor): In some cases, the color of transition metal ions arises due to charge transfer transition between the metal ion and ligands. These transitions are typically stronger and more intense than d-d transition, resulting in more vivid color. For example, in $[TiO_6]^{4-}$, an electron is transformed from the oxide ligand to the titanium ion leading to intense color absorption.

Test yourself:

Q. Sc^{3+} , V^{5+} complexes are white even all are transition metals. Why?
Q. Anhydrous copper sulphate is white, why?

6.8: Catalytic property of transition metals:

5. Activity

Study the given reaction carefully and answer the following questions based on your knowledge

$$CH_2{=}CH_2 \xrightarrow{Hydrogen\,/Nickel} CH_3\text{-}CH_3$$

a. What is the role of nickel in the reaction? Why is it used?
b. Can you suggest another transition metal that could replace nickel in the reaction?
c. Is nickel consumed in the reaction?

a.	....
b.	....
c.	....

In the above activity, we observed how nickel metal faciliated the addition of hydrigen to ethene in order to get ethane.This is the essence of catalysis- a process in which a substance (catalyst) alters the rate of reaction. Transition metals and their compounds exhibit the catalytic property. The catalytic property is due to following reasons-

i. Variable oxiation state: Transition metals can gain or lose electrons momentarily during a reaction because they can exist in many oxidation states. This makes it possible for them to minimize activation energy and promote the creation of chemical intermediates.

ii. Surface adsorption: Both transition metals and transition metal compounds offer large surface area for reactants to adsorb onto. This adsorption helps to weaken the bonds in the reactant molecules facilitating the formation of intermediate complex which quickly turns into final products.

Table: List of some catalytic activity of transition metals and their compounds:

Catalyst	Applications
Fe-Mo	In the manufacture of ammonia by Haber's process
Ni or Pd	In the manufacture of vansapati ghee (Hydrogenation of vegetable oil)
MnO_2	Thermal decomposition of $KClO_3$/ Also in the decomposition of H_2O_2
TiCl4 (in Ziegler Natta catalyst)	In preparation of polyethene polymer from alkene
Cu	In the dehydrogenation of alcohols
V_2O_5 or Pt	In the manufacture of sulphuric acid by contact process.

Exercise

A. Multiple choice questions

1. What is the maximum oxidation state shown by transition elements?

   a. +5   b. +6   c. +7   d. +8

2. What the maximum oxidation state shown by 3d series?

   b. +9   b. +8   c. +7   d. +6

3. Which of the following does not form colorful compound?

   a) Cu^{2+} b) Fe^{2+} c) Cu^{+} d) Co^{2+}

4. What is the general electronic configuration of transition metals?

   a. ns^{1-2} $(n-1)d^{1-9}$ b. ns^{1-2} $(n-1)d^{10}$ c. ns^{2} $(n-1)d^{1-10}$ d. ns^{1-2} $(n-1)d^{1-0}$

5. Which of the following element shows maximum number of oxidation state?

   a. Mn   b. Ni   c. Cr   d. Cu

6. Find the number of unpaired electron in iron metal ion of $[Fe(H_2O)_6]^{2+}$?

   a. 2   b. 3   c. 4   d. 5

7. What is the coordination number of of octahedral complexes?

   a. 2   b. 4   c. 5   d. 6

8. Which of the following ion has no d electron?

   a. Cr^{3+} b. Cu^{+} c. Sc^{3+} d. Fe^{2+}

9. What do we call the energy difference between the two sets of d-orbitals in an octahedral field splitting?

   a. Bond enthalpy   b. Crystal field splitting energy

   c. Ligand field energy   d. Coordination energy

10. Which of the following ligand produces a strong crystal field?

    a. CN^{-} b. H_2O c. NH_3 d. I^{-}

B. Short answer questions:

11. Give reason,

    a. Zinc is non typical transition element.

    b. Transition element exhibits variable oxidation state.

    c. Transition metals behave as good catalyst.

12. Write the characteristics of transition metals.
13. What do you mean by crystal field splitting?
14. What are transition elements? Why are they called so?
15. Define- a. Ligands b. Coordination sphere c. Complex ion
16. Which of the Fe^{2+} and Cr^{3+} has more number of unpaired electrons?
17. What do you mean by degenerate orbitals?.
18. What is crystal field splitting energy?
19. Give any two examples of complex ions.
20. Transitions metal ions are paramagnetic, why?

C. Long answer question:

21. What is CFT? Write its postulates.
22. Explain how CFT accounts for the splitting of d-orbitals in octahedral complexes.
23. What are transition metals? Write their general characteristics.
24. Explain why transition metals and their compounds exhibit catalytic property.
25. Why do most transition metals form colorful compounds? What factors affect the color of transition metals?
26. Draw the shape of complex ions having coordination number 4 and 6.

PROJECT WORK

1. Take a chart paper and draw the shapes of linear, tetrahedral, square planar and octahedral complexes taking one example of each."
2. Prepare a written or visual presentation on any two real life application of transition metal complexes or catalyst in industry or biology.

Unit 7
Study of Heavy Metals

Sub-unit-7.1: Copper (Cu)

1.Activity:

Complete the table about copper and discuss in group to answer the following questions:

Element	Copper
Symbol	....
Atomic Number	....
Atomic Mass	....
Electronic Configuration	....
Group	....
Period	....
Valency	....

a. What is the role of copper in our daily life?

b. Write the name of some copper minerals.

c. Why is copper called coinage metal?

a.	....
b.	....
c.	....

7.1.1: Introduction:

Fig: Copper wire

Fig: Copper utensil

Fig: Copper coin

Copper is a metal that has been known since ancient times. It derives its name from the island of Cyprus, where Romans and Greeks first extracted it, calling it 'Cuprum'. In Nepali, copper is referred to as "Tama" (तामा). Along with silver and gold, copper is classified as a coinage metal, owing to its historical use in making coins for currency. Copper's atomic number is 29, with an atomic mass 63.57 amu. It has melting point of 1083 ^{0}C and boiling point of 2350 ^{0}C and a specific gravity of 8.85.

7.1.2: Occurrence:

2. Activity:

Take a blank map of Nepal and answer the following questions-

a. Locate the major copper mines in the map.
b. What is the chief ore of copper? Write its molecular formula.

a.	....
b.	....

Copper occurs in both native and combined state. In its native form, it is primarily found in countries like Canada, China, USA, Mexico and Russia. In Nepal, copper is commonly found in minerals such as chalcopyrite, malachite, azurite, cuprite, etc. Notable, copper mines in Nepal, includes Okharbot (Myagdi), Gyazi (Gorkha), and Wapsa (Solukhumbu). Some major ores of copper are-

S. N.	**Name of copper ore**	**Formula**
1	Chalcopyrite or Copper pyrite	$CuFeS_2$ or $Cu_2S.Fe_2S_3$
2	Chalcocite or Copper glance	Cu_2S
3	Malachite (green)	$CuCO_3.Cu(OH)_2$
4	Cuprite or Ruby copper	Cu_2O
5	Azurite (blue)	$2CuCO_3.Cu(OH)_2$
6	Bronite or Peacock ore	Cu_3SFeS_4

7.1.3: Extraction of Copper from Copper pyrites:

3. Activity:

Discuss in a group and answer the following questions-

a. How do you think we can extract pure copper from its chief ore?
b. Why is cooper pyrite chosen as a chief ore for the extraction of copper?

a.	....
b.	....

The extraction of pure copper from its chief ore chalcopyrite ($CuFeS_2$) involves pyrometallurgy. The various steps involved in the extraction of Cu are-

1. Crushing and Pulverization:

The big lumps of chalcopyrite ore are first broken down in to small pieces by jaw crusher or hammer and then changed in to powder form in the ball mill. This entire process is called crushing and pulvarization.

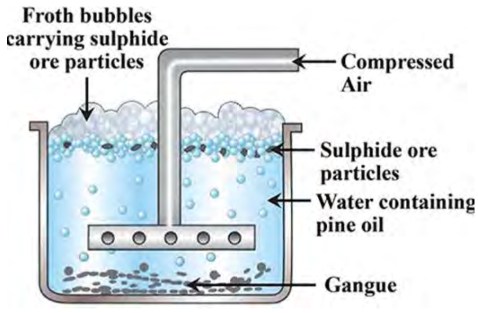


Fig: Froth floatation

2. Concentration:

The powdered ore from step 1 is concentrated by froth floatation process where ore is mixed with pine oil and water and kept in a tank. When the mixture in the tank is agitated by passing compressed air, ore particles float on the surface in the form of froth and earthy impurities settle at the bottom.

3. Roasting:

The concentrated ore from step 2 is strongly heated in excess supply of air in a reverberatory furnace where copper pyrite is converted into a mixture of cuprous sulphide and ferrous sulphide.

$$2CuFeS_2 + O_2 \xrightarrow[\Delta]{} Cu_2S + 2FeS + SO_2\uparrow$$

The ferrous sulphide further gets oxidized to ferrous oxide and cuprous sulphide partially oxidized to cuprous oxide.

$$2FeS + 3O_2 \xrightarrow[\Delta]{} 2FeO + 2SO_2\uparrow$$

$$Cu_2S + O_2 \xrightarrow[\Delta]{} Cu_2O + SO_2\uparrow$$

During roasting impurities like P, As, S, Sb etc are removed as their volatile oxides.

$$4P + 5O_2 \xrightarrow[\Delta]{} 2P_2O_5\uparrow$$

$$S + O_2 \xrightarrow[\Delta]{} SO_2\uparrow$$

$$4As + 3O_2 \xrightarrow[\Delta]{} 2As_2O_3\uparrow$$

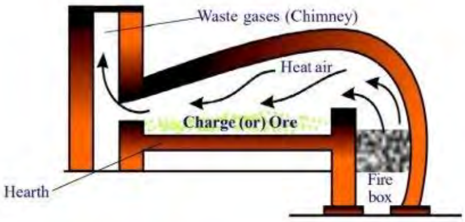


Fig: Reverberatory furnace for roasting

4. Smelting:

The mixture of roasted ore from step 3 is mixed with sand and coke and charged in a blast furnace. When hot air is blown from the lower part of the furnace coke burns producing a temperature about 1000 ^{0}C as a result following reactions occur-

$$2FeS + 3O_2 \xrightarrow[\Delta]{} 2FeO + 2SO_2 \uparrow$$

It should be noted that complete removal of FeS is most important for the extraction of cooper because, Cu_2O formed in step 3 reacts with un-reacted FeS to produce Cu_2S again.

$$2FeS + Cu_2O \xrightarrow[\Delta]{} 2Cu_2S + FeO$$

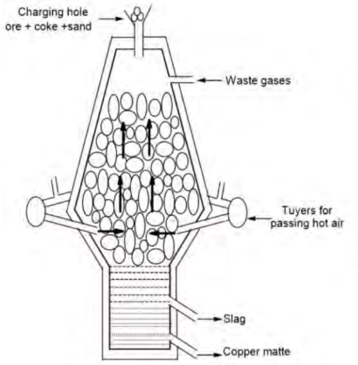


Fig: Blast Furnace

FeO is removed by the action of sand forming a slag.

$$FeO + SiO_2 \xrightarrow[\Delta]{} FeSiO_3 \text{ (slag)}$$

At the beneath (just below the slag) of the blast furnace molten mass copper is obtained which is known as **"Matte"**. Matte is mixture of sulphide of copper and iron. It contains 50% copper.

Test yourself:

Q. Why is it necessary to remove ferrous sulphide from blast furnace during extraction of copper?

5. Bessemerisation:

Bessemerization is carried out to recover metallic copper from copper matte. This process is carried out in a Bessemer converter which is an egg or pear shaped furnace lined with basic materials. In this step matte is mixed with silica and charged into the converter. When the mixture is heated by passing hot air from the tuyer then following changes occur.

$$2FeS + 3O_2 \xrightarrow[\Delta]{} 2FeO + 2SO_2\uparrow$$

$$FeO + SiO_2 \xrightarrow[\Delta]{} FeSiO_3 \text{ (slag)}$$

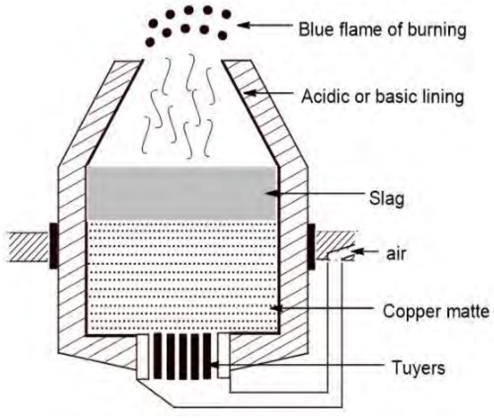


Fig: Bessemer converter

When entire iron is removed as a slag, then cuprous sulphide partly get oxidized to cuprous oxide. Thus formed cuprous oxide reacts with left over cuprous sulphide to produce metallic copper.

$$Cu_2S + 3O_2 \xrightarrow[\Delta]{} Cu_2O + 2SO_2\uparrow$$

$$Cu_2S + Cu_2O \xrightarrow[\Delta]{} Cu + SO_2\uparrow$$

The metallic copper thus obtained is allowed to cool slowly where dissolved SO_2 gas escapes out forming large blisters on the surface of copper metal which is 98-99% pure copper.

6. Purification:

Thus obtained blister of copper may contains certain impurities like oxides and sulphides of copper and iron along with some trace elements like Ag, Zn, Au, Ni etc which can be removed by either of the following methods-

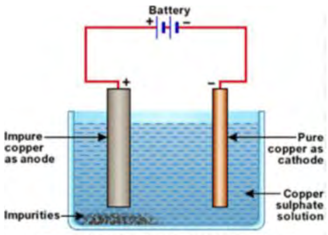
(i) Poling:

In this method the molten mass of copper is stirred with a green pole of bamboo where hydrocarbon presents in it reduces oxides of copper into metallic copper. The copper thus obtained is 99.5% pure. However this method of refining copper is outdated.

$$Cu_2O + C \rightarrow Cu + CO\uparrow$$

(ii) Electro-refining:

This is the modern method of refining many metals including copper. In this method an impure copper which is to be purified is suspended as an anode and a thin pure copper metal is used as a cathode. Acidified copper sulphate solution is used as an electrolyte. When electricity is passed then impure copper dissolves from anode and get deposited at cathode. A muddy mass is deposited just below anode which is known as anode mud.



Experimental set up for the electrolytic refining of copper.

$$CuSO_4 \xrightarrow{Electrolysis} Cu^{++} + SO_4^{--}$$

At anode,

$$\underset{(impure)}{Cu} \rightarrow Cu^{++} + 2e^-$$

At cathode

$$Cu^{++} + 2e^- \rightarrow Cu\ (pure)$$

Thus obtained copper is 99.9% pure.

Test yourself:

Q. Why is an impure rod of copper used as anode instead of cathode in electrolytic refining of copper?

Q. What happens if graphite rod is used instead of copper at anode during electrolytic refining of copper?

7.1.4: Physical properties of copper:

Copper is a reddish brown colored metal having following physical properties-

i. Appearence: It is solid at room temperature.

ii. Conductivity: It is good conductor of heat and electricity.

iii. Workability: It can be easily shaped (malleable) and drawn in to wire (ductile).

iv. Density: Its specific gravity is 8.85 g/cc.

v. Melting and Boiling point: Its melting point is 1083 ^{0}C and boiling point is 2350 ^{0}C.

7.1.5: Chemical properties of copper:

1. Action of air:

Copper is unaffected by dry air, but it reacts with moist air in presence of carbondioxide to give basic carbonate. Due to this Cu turns green on long standing in air.

$$2Cu + H_2O + CO_2 + O_2 \rightarrow CuCO_3 . Cu(OH)_2$$

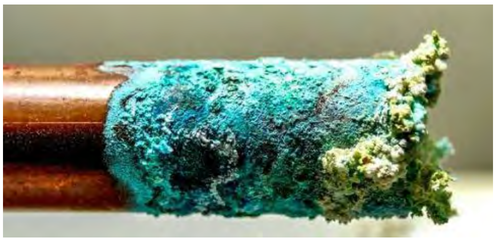


Fig: Green coating deposited on Cu

Test yourself:

Q. What causes a copper coin to develop a green patina after long exposure?

2. Action of heat:

When copper is heated with air below 1100^{0}C it gives cupric oxide and when heated above 1100^{0}C produces cuprous oxide.

$$2Cu + O_2 \xrightarrow{<1100oC} 2CuO \text{ (cupric oxide)}$$

$$4Cu + O_2 \xrightarrow{>1100oC} 2Cu_2O \text{ (cuprous oxide)}$$

3. Action of acids:

i) Cu gets dissolve in dil. HCl and dil. H_2SO_4 in presence of air.

$$2Cu + 4HCl + O_2 \rightarrow 2CuCl_2 + 2H_2O$$

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O$$

But, Cu does not react with these acids in absence of air.

ii) Cu reacts with nitric acid under different conditions to produce copper nitrate and oxides of nitrogen. The formation of oxides of nitrogen depends upon the strength of nitric acid. For example,

a) With conc. HNO_3: $Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

b) With cold & dil. HNO_3: $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

4. Action with metal ions:

Cu can reduce or displace metals lying below it in electrochemical series from their aqueous solution. For example,

$Cu + 2\,AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$

Fig: Cu coil in silver nitrate solution

Test yourself:

Q. Can you store copper sulphate solution in a vessel made up of Zinc?

5. Action with aqueous ammonia:

Pure Cu does not react with ammonia. However Cu reacts with aqueous ammonia in presence of oxygen to produce a complex.

$Cu + 8NH_3 + 2H_2O + O_2 \rightarrow 2\,[Cu(NH_3)_4](OH)_2$

7.1.6: Uses of copper:

Copper coin

i) Copper is essential in electrical manufacturing, used for coating other metals (electroplating), and for making pots and pans.

ii) Copper is a key ingredient in creating alloys like brass, bronze, and gun metal.

iii) Copper compounds are used in farming to kill insects and pests.

iv) Copper is used to make coins, hence it also termed as "coinage metal."

v) Copper is a component of enzymes and proteins in our bodies, which help regulate bodily functions.**)**

7.1.7: Compounds of copper:

A. Blue vitriol ($CuSO_4.5H_2O$) :

4. Activity:

Observe the given picture of copper salt and answer the following questions-

a. Write the formula of each copper salt.
b. What could be the reason behind the color of these salts?
c. What happens when you add few drops of water to white colored copper salt?

a.	....
b.	....
c.	....

Introduction :

Copper sulphate pentahydrate is called blue vitriol. Its molecular formula is $CuSO_4.5H_2O$. It is commonly known as "Nilo tutho" in Nepali.

Preparation of Blue vitriol :

Blue vitriol can be prepared by the action of dilute sulphuric acid on metallic copper (Cu) or copper oxide (CuO) or copper hydroxide $Cu(OH)_2$ or copper carbonate ($CuCO_3$) followed by crystallization of the resulting salt solution.

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O$$

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

$$Cu(OH)_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O$$

$$CuCO_3 + H_2SO_4 \rightarrow CuSO_4 + H_2O + CO_2$$

The copper sulphate solution is now subjected to crystallization in order to obtain the crystals of blue vitriol.

$$CuSO_4 \xrightarrow[\Delta]{Crystallization} CuSO_4.5H_2O \text{ (Blue vitriol)}$$

Physical properties of Blue vitriol :

i. It is crystalline blue colored solid soluble in water.
ii. It is insoluble in alcohol.
iii. Its anhydrous form is white in color.

Chemical properties of Blue vitriol:

1. Action of heat:

When blue vitriol is heated, it loses its water of crystallization turning from blue to white anhydrous copper sulphate. On further heating the anhydrous copper sulphate decomposes to produce CuO and SO_3.

$$CuSO_4.5H_2O \xrightarrow{100\ oC} CuSO_4.H_2O \xrightarrow{250\ oC} CuSO_4 \xrightarrow{750\ oC} CuO + SO_3$$

2. Action with alkali:

When copper sulphate solution is treated with alkali, it gives bluish white precipitate of copper (II) hydroxide.

$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2\downarrow + Na_2SO_4$

3. Action with ammonia (Formation of complex):

When ammonia is passed through copper sulphate solution , a bluish white precipitate of copper (II) hydroxide is obtained. On further passing of ammonia, deep blue soluble complex of tetrammine copper sulphate is produced.

$NH_3 + H_2O \rightarrow NH_4OH$

$CuSO_4 + 2\,NH_4OH \rightarrow Cu(OH)_2\downarrow + (NH_4)_2SO_4$

$Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

(Terammine copper sulphate)

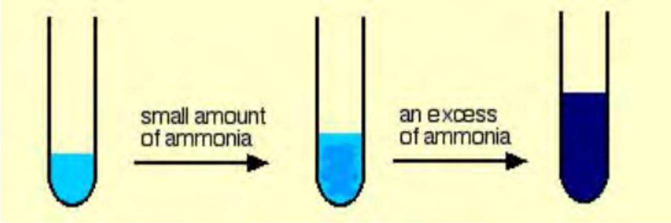


Fig: Formation of deep blue complex

Do you know?

Tetrammine copper sulphate is called Schweitzer's reagent which is one of the few solutions that is capable of dissolving cellulose, making it useful in the production of artificial fibers like Rayon.

4. Action with KI (Oxidizing nature):

Copper sulphate oxidizes KI solution into I_2 and itself gets reduced to cuprous iodide (Cu_2I_2).

$CuSO_4 + KI \rightarrow CuI_2 + K_2SO_4\ ]\times 2$

$\underline{2CuI_2 \rightarrow Cu_2I_2 + I_2}$

$CuSO_4 + 2KI \rightarrow K_2SO_4 + Cu_2I_2 + I_2\downarrow$

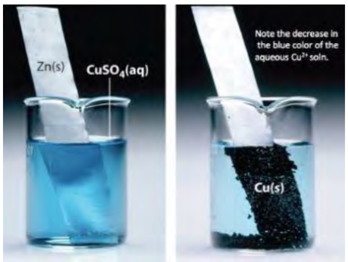


Fig: Zn displacing Cu from $CuSO_4$

5. Displacement reaction:

Electropositive metals like Fe, Zn, etc, that lie above Cu in electrochemical series displace the copper from its salt solution.

$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

Due to this property copper sulphate solution cannot be stored in a vessel of Zn.

Test yourself:

Q. Why copper sulphate solution cannot be transported in iron container?

6. Action with H_2S :

When hydrogen sulphide gas is passed through acidified solution of copper sulphate solution, black precipitate of copper sulphide is obtained.

$$CuSO_4 + H_2S \rightarrow CuS \downarrow + H_2SO_4$$

Uses of Blue vitriol:

i. It is used as a laboratory reagent.
ii. It is used in electroplating and electrotyping.
iii. It a component of Benedict and Fehiling's solution which are used to test reducing sugars.
iv. It is used as fungicide and insecticides.
v. It is used to preserve woods and gums.
vi. Anhydrous copper sulphate is used to detect the traces of traces of water.

Do you know?

Blue vitriol is used in the creation of Bordeaux mixture, a fungicide used on grape vines, potatoes, and other crops. A Bordeaux mixture is prepared by mixing blue vitriol, calcium hydroxide and water.

B. Black Oxide (CuO) & Red Oxide (Cu_2O) :

Cupric oxide is commonly known as black oxide whereas cuprous oxide is called red oxide.

Uses of Black oxide:

i. It is used as an oxidizing agent.

ii. It is used to provide blue or green color to glass.

iii. It is used to estimate carbon and hydrogen present in organic compound.

Uses of Red oxide

i. It is used to prepare cuprous chloride.

ii. It is used to prepare red colored glass.

iii. It is used as antirust paint.

Exercise

A. Multiple choice questions

1. Which of the following is ore of copper?

a. Calamine b. Philosopher wool c. Chalocopyrite d. Rinmann green

2. Which of the following metallurgical principle is applied to extract copper?

b. Hydrometallurgy b. Pyrometallurgy c. Electrometallurgy d. Mond's process

3. Which of the following method is used to purify blister copper?

a) Zone refining b) Distillation c) Electrolytic refining d) Fractional crystallization

4. In electrolytic refining where does the pure copper deposit?

a. Anode b. Anode mud c. Cathode mud d. Cathode

5. What do we call the impurities that settle during electro refining of cooper?

a. Anode mud b. Cathode mud c. Slag d. Flux

6. Which of the following dressing method is used for the chief ore of copper?

a. Leaching b. Magnetic separation c. Gravity separation d. Froth flotation

7. Which of the following composition represent copper matte?

a. $CuFeS_2 + SO_2$ b. $CuS + FeS$ c. $Cu_2O + CuS$ d. $FeS + CuO$

8. Which of the following is not a coinage metal?

a. Ag b. Cu c. Co d. Au

9. What is the formula of malachite?

a. $CuCO_3.Cu(OH)_2$ b. Cu_2O c. $CuFeS_2$ d. Cu_2S

10. What is the composition of bell metal?

a. Cu+Zn+Sn b. Cu +Sn c. Zn + Sn d. Cu + Pb +Sn

B. Short answer questions:

11. Give reason,

    a. Statue of copper becomes green on long standing.

    b. Copper sulphate is not recommended to store in nickel vessel.

    c. A brown gas evolves when copper is treated with conc. nitric acid.

12. Give the balanced chemical equation for the preparation of blue vitriol from metallic copper. Write one use of blue vitriol.

13. What happens when ammonia is passed through copper sulphate solution?

14. Write down the molecular formula of -
    a. Blue vitriol b. Malachite c. Ruby copper d. Black oxide

15. Write the formula and one important use of- a. Black oxide b. Red oxide c. Blue vitriol

16. Pentahydrate copper sulphate is called Blue vitriol.

    a. Starting from metallic copper how would you prepare blue vitriol?
    b. Write the action of heat on blue vitriol.
    c. What happens when aqueous solution of this compound treated with KI?
    d. Why is this compound considered as vitriol?

17. Write the balanced chemical equation for-
    a. Roasting of copper sulphide ore.
    b. Thermal decomposition of blue vitriol.
    c. Action of air on copper coin.

18. Write a note on- Blue vitriol.

19. Starting from copper pyrite, how would you obtain pure copper? Explain the steps involved in this metallurgy with necessary diagram.

20. What is blister of copper? How is it extracted from the chief ore of copper?

C. Long answer question:

21. A transition metal 'M' having atomic mass 63.5 amu lies in group 11 of periodic table.

    a. Identify the metal 'M'.
    b. Write the formula of the chief ore of 'M'.
    c. How would you extract 'M' starting from its chief ore?
    d. What happens when 'M' is treated with dilute sulphuric acid followed by crystallization?
    e. What happens when 'M' is heated with dry air below and above **1100 ^{o}C ?**
    f. Write any two uses of 'M'.

22. A blue crystalline compound 'X' is commonly referred to as blue vitriol.
    a. Identify the chemical formula of 'X'.
    b. Describe the preparation of 'X' from copper(II) oxide.
    c. Write the physical properties of 'X'.
    d. What chemical changes occur when 'X' is heated?
    e. What happens when excess of ammonia gas is passed through the aqueous solution of 'X'?
    f. Outline two agricultural uses of 'X'.

PROJECT WORK

1. Prepare a project on, " Applications of copper in electrical wiring and electronics".

2. Take a chart paper and write the steps involved in extraction of copper from its chief ore along with necessary diagrams".

3. Many of the utensils and utility items used in home are made up of copper. Take a chart paper and prepare the list of those items that contain copper as one of the main component.

4. Some alloys are listed below. Prepare a chart showing their composition and uses.

   Brass, Gun metal, German silver, Bronze, Coin

Sub-unit-7.2: Zinc (Zn)

1.Activity:

Complete the table about zinc and discuss in group to answer the following questions:

Element	Zinc
Symbol	....
Atomic Number	....
Atomic Mass	....
Electronic Configuration	....
Group	....
Period	....
Valency	....

a. What is the role of zinc in our daily life?

b. Why is zinc regarded as non typical transition element?

c. Write the name of some zinc minerals.

a.	....
b.	....
c.	....

7.2.1: Introduction:

Zinc metal

Zinc battery

Zinc roof

Brass utensils

Zinc is a bluish white metal used for a long time in the manufacture of brass which is called "**pital**" in Nepali. It was first industrially produced in India and its name is derived from German word "**Zink**" which means "tooth" or "prong". It is a non typical transition element because its d-orbital is completely filled as a result it does not exhibit variable oxidation state and form colorful compounds like other transition elements. Its atomic number is 30 and atomic mass 65.37 amu. It has melting point of 429.4 ^{0}C, boiling point of 907 ^{0}C and a specific gravity of 7.14.

Test yourself:

Q. Why is zinc used in dry cell?

7.2.2: Occurrence:

2. Activity:

Take a blank map of Nepal and answer the following questions-

a. Locate the major zinc mines in the map.
b. What is the chief ore of zinc? Write its molecular formula.

a.	....
b.	....

Zinc does not occur in free state. It is mostly found in combined state in the form sulphide, oxide and carbonate ore. In Nepal, zinc is found in the form its sulphide ore in places like Ganesh himal, Pulchwoki, and some Mahabharat range etc. Some major ores of zinc are-

S. N.	Name of zinc ore	Formula
1	Zinc blende	ZnS
2	Calamine	$ZnCO_3$
3	Zincite or Zinc oxide	ZnO
4	Wellemite	$2\ ZnO.SiO_2$
5	Fraklinite	$ZnO.Fe_2O_3$

7.2.3: Extraction of Zinc from Zinc blende:

3. Activity:

Discuss in a group and answer the following questions-

a. How do you think we can extract pure zinc from its chief ore?
b. Why is zinc blende chosen as a chief ore for the extraction of zinc?

a.	....
b.	....

The extraction of pure zinc from its chief ore zinc blende(ZnS) involves pyrometallurgy. The various steps involved in the extraction of Zn are-

1. Crushing and Pulverization:

The big lumps of zinc blende ore are first broken down in to small pieces by jaw crusher or hammer and then changed in to powder form in the ball mill. This entire process is called crushing and pulverization.

2. Concentration:

The powdered ore from step 1 is concentrated by froth floatation process where ore is mixed with pine oil and water and kept in a tank. When the mixture in the tank is agitated by passing compressed air, ore particles float on the surface in the form of froth and earthy impurities settle at the bottom.

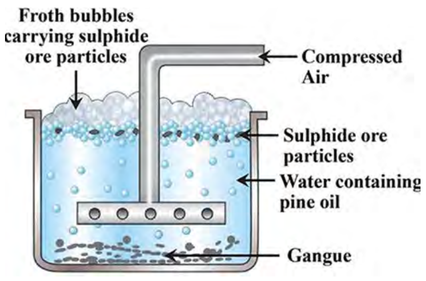


Fig: Froth floatation

3. Roasting:

The concentrated ore from step 2 is strongly heated in excess supply of air in a reverberatory furnace where zinc sulphide is converted into zinc oxide .

$$2ZnS + 3O_2 \xrightarrow[\Delta]{} 2ZnO + 2SO_2\uparrow$$

Some of the zinc sulphide may first oxidized to zinc sulphate and then into zinc oxide.

$$ZnS + 2O_2 \xrightarrow[\Delta]{} ZnSO_4$$

$$2ZnSO_4 \xrightarrow[\Delta]{} 2ZnO + SO_2\uparrow$$

During roasting impurities like P, As, S, Sb etc are removed as their volatile oxides.

$$4P + 5O_2 \xrightarrow[\Delta]{} 2P_2O_5\uparrow$$

$$S + O_2 \xrightarrow[\Delta]{} SO_2\uparrow$$

$$4As + 3O_2 \xrightarrow[\Delta]{} 2As_2O_3\uparrow$$

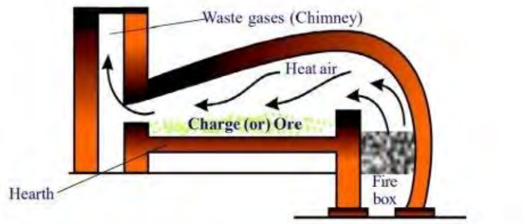


Fig: Reverberatory furnace for roasting

Test yourself:

Q. What chemical transformation takes place in reverberatory furnace when calamine is present along with zinc sulphide?

4. Reduction:

The zinc oxide obtained by roasting is now heated with carbon in the form of coke in vertical retort furnace. Small briquettes of zinc oxide powder and coke are prepared in the ratio 2:1 and fed in to the retort furnace. When the retort is heated externally by burning producer gas ($CO + N_2$) at 1400-1500 °C then zinc oxide gets reduced to metallic zinc. Following reactions occur in the retort-

$$ZnO + C \xrightarrow[\Delta]{} Zn + CO\uparrow$$

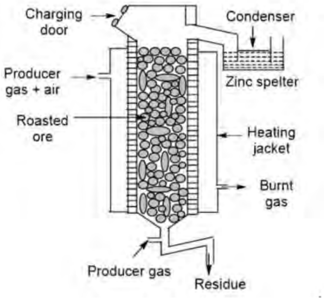


Fig: Vertical retort process for reduction of ZnO to Zn

Here zinc is obtained in the form of vapor. Zinc vapor along with CO gas is swept out by producer gas and subsequently condensed in to molten zinc called **spelter zinc**, while the CO gas is released. The zinc thus obtained is 97.8% pure.

Do you know?

Reduction of zinc oxide can be carried out by any of the following methods-
1. Continuous vertical retort process
2. Belgian method (uses elliptical retort or circular retort)
3. Silesian process(uses reverberatory furnace)

Among these three, vertical retort process is modern and economical process.

5. Purification:

Thus obtained spelter zinc may contain impurities like iron, lead, cadmium, arsenic etc. These impurities can be removed by any of the following methods-

(i) Fractional Distillation:

The boiling point of zinc is 907 °C whereas boiling point of cadmium, lead and iron are 767, 1620 and 3000 °C respectively. When the impure zinc is subjected to distillation at about 1000 °C, cadmium and zinc are collected as distillate leaving behind lead and iron. Finally, the distillate containing zinc and cadmium is again subjected to re-distillation at 800 °C where cadmium is obtained as distillate leaving behind the pure zinc. The zinc thus obtained is 99.5% pure.

(ii) Electro-refining:

This is the modern method of refining many metals including zinc. In this method, impure zinc which is to be purified is suspended as an anode and a thin pure zinc metal is used as a cathode. Acidified zinc sulphate solution is used as an electrolyte. When electricity is passed, impure zinc dissolves from anode and get deposited at cathode. A muddy mass is deposited just below anode which is known as anode mud.

$$ZnSO_4 \xrightarrow{Electrolysis} Zn^{++} + SO_4^{--}$$

At anode,

$$\underset{\text{(impure)}}{Zn} \rightarrow Zn^{++} + 2e^-$$

At cathode

$$Zn^{++} + 2e^- \rightarrow Zn\ (pure)$$

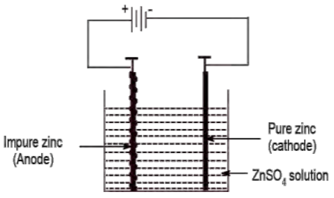


Fig: Electrolytic refining of zinc

Thus obtained zinc is 99.9% pure.

Test yourself:

Q. Why is an impure rod of zinc used as anode instead of cathode in electrolytic refining of zinc?

Q. What happens if graphite rod is used instead of zinc at anode during electrolytic refining of zinc?

7.2.4: Physical properties of zinc:

Zinc is a bluish white metal having following physical properties-

i. Appearance: It is solid at room temperature. It gets tarnished to grey color on exposure to moist air.

ii. Conductivity: It is good conductor of heat and electricity.

iii. Workability: It can be easily shaped (malleable) and drawn in to wire (ductile).

iv. Density: Its specific gravity is 7.14 g/cc.

v. Melting and Boiling point: Its melting point is 429.4 ^{0}C and boiling point is 907^{0}C.

7.2.5: Chemical properties of zinc:

1. **Action of air:**

Zinc is unaffected by dry air, but it reacts with moist air in presence of carbondioxide to give basic zinc carbonate. Due to this Zn gets tarnished to grey color on long standing in air.

$$2Zn + H_2O + CO_2 + O_2 \rightarrow ZnCO_3.Zn(OH)_2$$

But when zinc is heated with air at 500 ^oC, it burns with bluish flame producing dense white smoke of zinc oxide called **philosopher's wool**.

$$2Zn + O_2 \xrightarrow{500oC} 2ZnO(\text{philosopher's wool})$$

Test yourself:

Q. What causes the dull appearance of zinc roof over time?

2. **Action of acids:**

Since, zinc lies above hydrogen in electrochemical series it can liberate hydrogen gas from dilute mineral acids and non-oxidizing agents.

i) Zn reacts with dilute hydrochloric acid and sulphuric acid to produce hydrogen gas.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$$

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$$

But, Zn reacts with concentrated sulphuric acid to produce sulphur dioxide gas.

$$Zn + \underset{(conc.)}{2H_2SO_4} \rightarrow ZnSO_4 + 2SO_2\uparrow + 2H_2O$$

ii) Zn reacts with nitric acid under different conditions to produce zinc nitrate and different oxides of nitrogen depending upon the concentration of the acid. For example,

a) With conc. HNO_3:

$$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

b) With moderately conc. (1:1) HNO_3:

$$3Zn + 8HNO_3 \rightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

c) With dil. HNO_3:

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

d) With very dil. HNO_3:

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

4. Action with alkali:

Zn reacts with hot and conc. NaOH solution to produce sodium zincate and hydrogen gas.

$$Zn + 2\,NaOH \rightarrow Na_2ZnO_2 + H_2\uparrow$$

5. Displacement reaction:

Zn can displace less reactive metals that lie below it in electrochemical series. For example,

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

Test yourself:

Q. Can you store silver nitrate solution in a vessel made up of zinc?

7.2.6: Uses of zinc:

i) Zinc is used for making anode material in dry cell.

ii) Zinc is a key ingredient in creating alloys like brass, German silver, etc.

iii) Zinc is used as a reducing agent in the extraction of Ag and Au.

iv) Zinc is used in galvanization of iron and steel that prevents from rusting.

v) Granulated zinc is used in chemistry laboratory for the preparation of hydrogen gas.

Do you know?

Zinc is important for boosting immune system, wound healing, cell growth and other sensory functions.

7.2.7: Compounds of zinc:

A. White vitriol ($ZnSO_4.7H_2O$) :

Fig: White vitriol

4. Activity:

Observe the given picture of zinc sulphate and answer the following questions-

a. What could be the reason behind white color of the salt?

b. What happens when you heat the salt?

a.	....
b.	....

Introduction :

Zinc sulphate heptahydrate is called white vitriol. Its molecular formula is $ZnSO_4.7H_2O$. It is commonly known as "Seto thuto" in Nepali.

Preparation of White vitriol :

White vitriol can be prepared by the action of dilute sulphuric acid on metallic zinc (Zn) or zinc oxide (ZnO) or zinc carbonate ($ZnCO_3$) followed by crystallization of the resulting salt solution.

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$

$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$

$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + H_2O + CO_2\uparrow$

The zinc sulphate solution is now subjected to crystallization in order to obtain the crystals of white vitriol.

$ZnSO_4 \xrightarrow[\Delta]{Crystallization} ZnSO_4.5H_2O$ (white vitriol)

Physical properties of White vitriol :

i. It is crystalline white colored solid soluble in water.

ii. It is an efflorescent solid i.e, it loses its water of crystallization when exposed to atmosphere.

Chemical properties of White vitriol:

1. Action of heat:

When white vitriol is heated, it loses its water of crystallization turning from anhydrous zinc sulphate. On further heating the anhydrous zinc sulphate decomposes to produce ZnO and SO_3.

$ZnSO_4.7H_2O \xrightarrow{100\ oC} ZnSO_4.H_2O \xrightarrow{300\ oC} ZnSO_4 \xrightarrow{800\ oC} ZnO + SO_3$

2. Action with alkali:

When zinc sulphate solution is treated with NaOH, it gives white precipitate of zinc hydroxide which dissolves in excess of NaOH to produce sodium zincate.

$ZnSO_4 + 2NaOH \rightarrow Zn(OH)_2\downarrow + Na_2SO_4$

$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$

3. Action with Barium sulphide (Formation of lithopone):

When zinc sulphate is treated with barium sulphide, double salt called lithopone is obtained. This lithopone is used as white pigment.

$ZnSO_4 + BaS \rightarrow ZnS.BaSO_4$

Do you know?

Lithopone is commonly used as a white pigment in interior wall paints, paper coating, providing the necessary opacity and brightness for smooth even finish.

4. Action with potassium ferrocyanide:

When zinc sulphate is treated with potassium ferrocyanide, a white precipitate of zinc ferrocyanide is obtained.

$$2\,ZnSO_4 + K_4[Fe(CN)_6] \rightarrow \underset{\text{(white ppt.)}}{Zn_2[Fe(CN)_6]\downarrow} + 2K_2SO_4$$

Uses of White vitriol:

i. Zinc sulphate solution is used as eye lotion.
ii. It is used as fungicide.
iii. It is used in zinc electroplating.
iv. It is used as a key ingredient to prepare lithopone.
v. It is used as preservative of animal skin.
vi. It is used as laboratory reagent.

Exercise

A. Multiple choice questions

1. Which of the following is an ore of zinc?

a. Zinc blende b. Philosopher wool c. Chalocopyrite d. Ruby copper

2. What is the formula of Rinmann's green?

a. $ZnCO_3$ b. $CoZnO_2$ c. $Co(NO_3)2.ZnO$ d. ZnO

3. What is the formula of white vitriol?

a) $ZnSO_4.5H_2O$ b) $ZnSO_4.7H_2O$ c) $MgSO_4.7H_2O$ d) $FeSO_4.6H_2O$

4. In electrolytic refining of zinc, cathode what is cathode made up of?

a. Impure zinc b. Impure Carbon c. Pure zinc d. Pure copper

5. Which of the following reducing agent is used in the smelting of zinc oxide?

a. Aluminium b. Copper c. Carbon dioxide d. Carbon

6. Which of the following reaction takes place during smelting of zinc oxide?

a. $ZnO + C \rightarrow Zn + CO$ b. $ZnCO_3 \rightarrow ZnO + CO_2$

c. $ZnSO_4 \rightarrow ZnO + SO_2$ d. $ZnS + O_2 \rightarrow ZnO + SO_2$

7. Which of the following is an ore of zinc?

a. Haematite b. Lunar caustic c. Calamine d.Calomel

8. Which of the following is major use of zinc?

a. Electrical wiring b. Galvanizing iron c. Making jewelry d. Manufacturing glass

9. Which of the following is not a transition element?

a. Zn b.Cu c. Ni d. Cu

10. What is X in the given reaction?

$ZnSO_4 + BaS \rightarrow X$

a. White vitriol b.Lithopone c. Philosopher'swool d. Zinc blende

B. Short answer questions:

11. Give reason,

    a. Iron is coated with zinc.

    b. Zinc is not considered as typical transition element.

    c. Zinc does not form colored salts.

12. What is spelter of zinc? How is pure zinc obtained from spelter of zinc?.

13. What is lithopone? How is it prepared? Write its one application.

14. Write down the molecular formula of -

    a. Zincite b. Calamine c. Zinc blende d. White vitriol

15. A student mistakenly used an iron vessel to evaporate zinc sulphate solution. Predict and explain the likely outcome, including relevant chemical equations and observations. How would you modify the procedure to prevent this error?

16. Heptahydrate zinc sulphate is called white vitriol.

    a. Starting from metallic zinc how would you prepare white vitriol?

    b. Write the action of heat on white vitriol.

    c. What happens when aqueous solution of this compound treated with barium sulphide?

17. Write the balanced chemical equation for-

    a. Roasting of zinc sulphide ore.
    b. Thermal decomposition of white vitriol.
    c. Action of air on zinc.

18. Write a note on- White vitriol.

19. Starting from zinc blende, how would you obtain pure zinc? Explain the steps involved in this metallurgy with necessary diagram.

C. Long answer question:

20. A non typical transition metal 'M' having atomic number 30 lies in group 12 of periodic table It is most commonly used for roofing house.

    a. Identify the metal 'M'.
    b. Write the formula of the chief ore of 'M'.
    c. How would you extract 'M' starting from its chief ore?
    d. What happens when 'M' is treated with dilute sulphuric acid followed by crystallization?
    e. What happens when 'M' is heated with steam at 5**00 °C ?**
    f. Write any two uses of 'M'.

21. A recently discovered ore deposit contains a complex mixture of a sulfide, a carbonate, and silica (SiO_2). Chemical analysis reveals the presence of a non-typical transition element lying in group 12. This element is known to form compounds where it exhibits a +2 oxidation state predominantly. The sulfide and carbonate components are the primary sources of this element. The silica is considered a significant impurity.
    a. Identify the element and write its chief ore.
    b. Describe the steps required to extract this element from its chief ore with necessary diagram.
    c. How does this element react with nitric acid under different conditions?
    d. Write any two uses of this element.

PROJECT WORK

1. Take a chart paper and write the steps involved in extraction of zinc from its chief ore along with necessary diagrams".

2. Some alloys are listed below. Prepare a chart showing their composition and uses.

Brass, Zamak, Solder, Galvanized steel

3. Take a chart paper and make a comparative analysis on the use of vertical retort furnace for zinc extraction Vs blast furnace.

Sub-unit-7.3: Mercury (Hg)

1. Activity:

Complete the table about zinc and discuss in group to answer the following questions:

Element	Mercury
Symbol	....
Atomic Number	....
Atomic Mass	....
Electronic Configuration	....
Group	....
Period	....
Valency	....

a. What is the role of mercury in our daily life? Give some examples.

b. Write the name of some mercury minerals.

c. How mercury contaminates environment?

a.	
b.	
c.	

7.3.1: Introduction:

Fig: Mercury metal

Fig: Mercury thermometer

Fig: Use of mercury as vermilion

Fig: Hg as dental filling

Mercury is the only metal that exists in liquid state at room temperature. It is a silvery-white metal having melting point, boiling point and density -38.85 ^{0}C, 357 ^{0}C and 13.6 g/cc respectively. In ancient time mercury was used in alchemy, medicine, cosmetics, gold and silver extraction. Today mercury is widely used in thermometer, barometer, fluorescent light and some electrical switches despite of its health and environmental issues. In Nepali mercury is called "***paro***".

Test yourself:

Q. Why, is mercury called quick silver?
Q. What is the purpose of using mercury in thermometer?

7.3.2: Occurrence:

2. Activity:

Take a blank map of Nepal and answer the following questions-

a. What is the chief ore of mercury? Write its molecular formula.
b. Look around, where do you think mercury is present in your area?

a.	....
b.	....

Mercury occurs in a free state in a very small amount. It is mostly found in combined state in the form sulphide, halide, and amalgam. In Nepal, mercury is primarily found in the form of sulphide ore Cinnabar (HgS) in places like Khimti river, Tirche pani/ Taruka etc. The major ore of mercury is cinnabr.

7.3.3: Extraction of Mercury from Cinnabar:

3. Activity:

Discuss in a group and answer the following questions-

a. How do you think we can extract pure mercury from its chief ore?
b. Why is cinnabar chosen as a chief ore for the extraction of mercury?

a.	....
b.	....

The extraction of pure mercury from its chief cinnabar (HgS) involves pyrometallurgy. The various steps involved in the extraction of Hg are-

1. Crushing and Pulverization:
The big lumps of cinnabar ore are first broken down in to small pieces by jaw crusher or hammer and then changed in to powder form in the ball mill. This entire process is called crushing and pulverization.

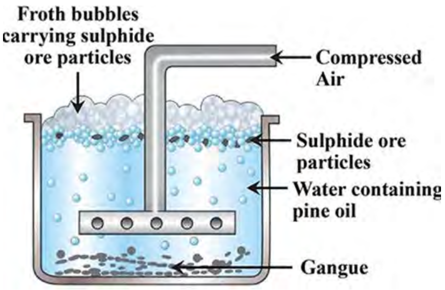


Fig: Froth floatation

2. Concentration:

The powdered ore from step 1 is concentrated by froth floatation process where ore is mixed with pine oil and water and kept in a tank. When the mixture in the tank is agitated by passing compressed air, ore particles float on the surface in the form of froth and earthy impurities settle at the bottom.

3. Roasting and Distillation:

Due to low boiling point of mercury and easy separation of mercury vapor shaft furnace is used to carry out roasting and distillation. A shaft furnace contains 'Y' shaped iron tube for condensing mercury vapor. The concentrated ore from step 2 is mixed with charcoal and heated in excess supply of air in a shaft furnace where mercuric sulphide is converted into mercuric oxide which subsequently gets decomposed into mercury vapor. This mercury vapor gets condensed to give liquid mercury.

$$2HgS + 3O_2 \xrightarrow[\Delta]{} 2HgO + 2SO_2\uparrow$$

$$2HgO \xrightarrow[\Delta]{} 2Hg + O_2\uparrow$$

During roasting impurities like P, As, S, Sb etc are removed as their volatile oxides through outlet of the receiver or condenser.

$$4P + 5O_2 \xrightarrow[\Delta]{} 2P_2O_5\uparrow$$

$$S + O_2 \xrightarrow[\Delta]{} SO_2\uparrow$$

$$4As + 3O_2 \xrightarrow[\Delta]{} 2As_2O_3\uparrow$$

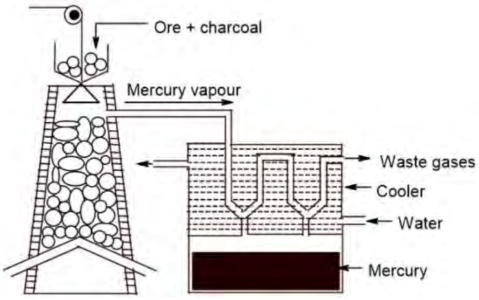


Fig: Shaft furnace for roasting & distillation

Test yourself:

Q. Reverberatory furnace is not ideal for roasting cinnabar, why?

4. Purification:

Thus obtained liquid mercury may contain several impurities like copper, lead, zinc, bismuth etc, and other suspended particles. Followings are the steps to remove impurities present in mercury-

(i) Filtration:

Filtration is applied to remove fine particles like soot, HgO and other metal oxides. In this method impure mercury is filtered through chamois leather or thick canvas as a result suspended impurities are removed.

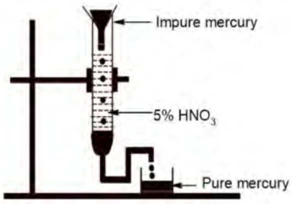


Fig: Purification of mercury

(ii) Chemical Washing (Treatment with 5% nitric acid):

In this method filtrate obtained from above is passed through a long tube containing 5% dilute nitric acid where mercury reacts with HNO_3 to form mercurous nitrate. Metallic impurities like Zn, Pb, Fe etc which are more reactive than Hg form soluble nitrate salt displacing pure mercury.

$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

$$Zn + Hg_2(NO_3)_2 \rightarrow Zn(NO_3)_2 + 2Hg$$

(Impurities present in mercury)

(iii) Vacuum Distillation

Distillation of mercury helps to remove impurities like Pb, Cu, Cd, etc. that have higher boiling point than mercury (357^0C). In this method, when the impure mercury is subjected to distillation under reduced pressure, mercury gets distilled off leaving behind the impurities. Mercury obtained is about 99.9% pure.

Test yourself:

Q. How would you remove iron impurity present in mercury?

7.3.4: Physical properties of mercury:

Mercury is a silvery white metal having following physical properties-

i. Appearance: It is liquid at room temperature. It gets tarnished to grey color on exposure to moist air.

ii. Conductivity: It is good conductor of heat and electricity.

iii. Solubility: It is insoluble in water but soluble in organic solvent.

iv. Density: Its specific gravity is 13.6 g/cc.

v. Melting and Boiling point: Its melting point is - 38.83 ^0C and boiling point is 356.73^0C.

vi. Toxicity: Its vapor is deadly poisonous.

7.3.5: Chemical properties of Mercury:

1. Action of air:

Mercury is unaffected by air under normal condition, but it produces mercuric oxide when heated with air (oxygen) at about 350 ^0C.

$$2Hg + O_2 \xrightarrow{350oC} 2HgO\text{(mercuric oxide)}$$

When the temperature exceeds beyond 350 ^0C then HgO decomposes to give metallic mercury.

$$2HgO \xrightarrow{>350oC} 2Hg + O_2$$

Test yourself:

Q. What causes the dull appearance of zinc roof over time?

2. Action of acids:

Since, mercury lies below hydrogen in electrochemical series it cannot liberate hydrogen gas from dilute mineral acids and non-oxidizing agents.

i) Action with HCl:

Hg does not react with hydrochloric acid alone. However in the presence of oxidizing agents like chlorine gas, nitric acid it react differently.

$Hg + Cl_2 \rightarrow HgCl_2$ (mercuric chloride)

(present in HCl)

ii) Action with HNO_3:

Hg reacts with nitric acid under different conditions to produce nitrate salt of mercury. For example,

a) With dil. HNO_3:

$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O$

b) With conc. HNO_3:

$3Hg + 4HNO_3 \rightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$

iii) Action with Aqua regia:

Aqua regia is a mixture of one part of concentrated nitric acid and three parts of concentrated hydrochloric acid. It is commonly known as **'Kingly water'** or **'Royal water'**. It is known for its ability to dissolve noble metals like gold and platinum.

Aqua regia is highly oxidative and reacts with mercury to give mercuric chloride.

$HNO_3 + 3HCl \rightarrow NOCl + 2H_2O + 2[Cl]$

$Hg + 2[Cl] \rightarrow HgCl_2$

Test yourself:

Q. What is the use of aqua regia in gold refining in jewelry making?

iii) Action with H_2SO_4: Hg reacts with hot and conc. H_2SO_4 to produce mercuric sulphate.

$Hg + 2H_2SO_4 \rightarrow HgSO_4 + 2H_2O + SO_2\uparrow$

3. Action with water and alkali:

Hg does not react with water and alkali.

4. Action with ozone:

Hg reacts with O_3 to produce mercurous oxide.

$$O_3 \rightarrow O_2 + [O]$$

$$Hg + [O] \rightarrow Hg_2O \text{ (mercurous oxide)}$$

Due to the formation of mercurous oxide when mercury is allowed to run through an inclined plane it leaves a tail (i.e, meniscus of mercury gets depressed) which is called **tailing of mercury**.

5. Formation of amalgam:

Hg forms amalgam with many metals like gold, silver, copper, zinc, sodium etc. For example,

$$Na + Hg \rightarrow NaHg \text{ (sodium amalgam)}$$

$$Ag + Hg \rightarrow AgHg \text{ (Silver amalgam)}$$

Do you know?

Iron is the only metal which cannot form amalgam. This is because iron neither dissolve in mercury nor react with mercury to form stable alloy.

7.3.6: Uses of mercury:

i) Mercury is used in the extraction of gold and silver through amalgamation process.
ii) Mercury is used as a thermometric and barometric liquid.
iii) Mercury is used in the preparation of various amalgam including dental filling.
iv) Mercury is used in the production of chlorine and caustic soda.
v) Mercury is used in laboratory experiments involving thermodynamics and fluid mechanics for scientific research.
vi) Mercury is used in electrical switches to control electrical circuit.
vii) Mercury is used in small devices like hearing aids and cameras as mercury batteries.
viii) Mercury is used to impart bluish light rich in UV rays in mercury vapor lamps.

7.2.7: Compounds of mercury:

A. Calomel (Mercurous chloride) :

Fig: Calomel

4. Activity:

Observe the given picture of calomel and answer the following questions-

a. Can you give one method of preparing calomel?
b. How do you think calomel is used in electrochemical experiments, especially in reference electrodes?

a.	…………………………………………………………………………………………………
b.	…………………………………………………………………………………………………

Introduction:
Mercurous chloride or mercury (I) chloride, also known as calomel, is mercury based non toxic substance that has long being utilized in medicine and as an element in electrochemical reference electrodes. Its molecular formula is Hg_2Cl_2.

Test yourself:

Q. Why does calomel have molecular formula Hg_2Cl_2 and not $HgCl_2$?

Preparation of Calomel :

1. From mercurous nitrate:

Calomel is prepared by treating mercurous nitrate with soluble chlorides like NaCl, HCl etc.

$$Hg_2(NO_3)_2 + 2HCl \rightarrow Hg_2Cl_2 + 2HNO_3$$

This is the laboratory method of preparation of calomel.

Test yourself:

Q. Complete the reaction,

$Hg_2(NO_3)_2 + NaCl \rightarrow$ …………+ ……….

2. From mercuric chloride:

Calomel is prepared by heating mercury with mercuric chloride.

$$Hg + HgCl_2 \xrightarrow[\Delta]{} Hg_2Cl_2$$

3. From mercuric chloride:

Mercuric chloride can be used to prepare calomel, as-

a. Calomel is prepared by heating mercury with mercuric chloride.

$$Hg + HgCl_2 \xrightarrow[\Delta]{} Hg_2Cl_2$$

b. Calomel is prepared by reduction of mercuric chloride with the use of reducing agent stannous chloride.

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$

4. From mercuric sulphate:

Calomel is prepared by heating the mixture of mercuric sulphate, mercury and sodium chloride.

$$Hg + HgSO_4 + 2NaCl \xrightarrow[\Delta]{} Hg_2Cl_2 + Na_2SO_4$$

Physical properties of calomel:

i. It is white amorphous solid insoluble in water.
ii. It is soluble in aqua-regia.
iii. It is tasteless and non-toxic in nature.

Chemical properties of Calomel:

1. Action of heat:

When calomel is strongly heated, it sublimes and decomposes to give mercuric chloride.

$$Hg_2Cl_2 \xrightarrow[\Delta]{} HgCl_2 + Hg$$

2. Action with alkali:

When calomel is dissolved in NaOH solution, it produces grey black ppt. of Hg_2O which slowly decomposes in presence of light to give HgO and Hg.

$$Hg_2Cl_2 + 2NaOH \rightarrow \underset{\text{(grey-black ppt.)}}{Hg_2O\downarrow} + 2NaCl + H_2O$$

$$Hg_2O \rightarrow HgO + Hg$$

3. Action with ammonia:

When calomel is treated with ammonia solution, it turns black due to formation of finely divided mercury (black) and amino mercuric chloride.

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{(grey-black)}}{[Hg + Hg(NH_2)Cl]} + NH_4Cl + 2H_2O$$

Test yourself:

Q. What happens when a piece of paper is soaked in ammonia solution and allowed to react with calomel?

4. Action with aqua regia:

Calomel gets oxidized to mercuric chloride (corrosive sublimate) when dissolve in aqua regia.

$$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2[Cl]$$

$$Hg_2Cl_2 + 2[Cl] \longrightarrow 2HgCl_2 \text{ (corrosive sublimate)}$$

5. Action with stannous chloride:

Calomel gets reduced to metallic mercury when treated with reducing agents like stannous chloride.

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\textbf{(black)}}{Hg} + SnCl_4$$

Uses of calomel:

i. Calomel is used as laxative (purgative) in medicine.
ii. It is used to make secondary reference electrode called calomel.
iii. It is used as antiseptic (outdated).

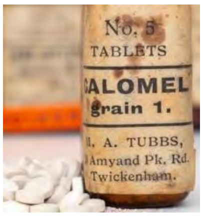


Fig: Bed pill

Fig: Calomel electrode

Do you know?

> **Historically calomel was used as 'Bed pill' in medicine as a purgative (laxative). A purgative (or laxative) is a medicine often used to cleanse the intestine and treat severe constipation.**

B. Corrosive sublimate (Mercuric chloride) :

Fig: Corrosive sublimate

5. Activity:

Observe the given picture of corrosive sublimate and answer the following questions-

a. Can you give one method of preparing corrosive sublimate?
b. Can you write reactions of inter conversion of calomel and corrosive sublimate?

a.	....
b.	....

Introduction:
Mercuric chloride or mercury (II) chloride, also known as corrosive sublimate, is mercury based toxic crystalline substance that has long being utilized as disinfectant, antiseptic and pesticide. Its use has been discontinued due to its toxicity. Its molecular formula is $HgCl_2$.

Preparation of Corrosive sublimate :

1. From calomel:

When calomel is dissolved in aqua regia, corrosive sublimate is produced.

$3HCl + HNO_3 \rightarrow NOCl + 2H_2O + 2[Cl]$
$Hg_2Cl_2 + 2[Cl] \rightarrow 2HgCl_2$ (corrosive sublimate)

2. From mercury:

Corrosive sublimate is prepared by heating mercury with excess of chlorine.

$Hg + Cl_2 \xrightarrow[\Delta]{} HgCl_2$

3. From mercuric oxide:

Corrosive sublimate is prepared by dissolving mercuric oxide in dil. HCl.

$HgO + 2HCl \rightarrow HgCl_2 + H_2O$

4. From mercuric sulphate:

Corrosive sublimate is prepared by heating mercuric sulphate with sodium chloride in presence of manganese dioxide.

$HgSO_4 + 2NaCl \xrightarrow[\Delta]{MnO2} HgCl_2 + Na_2SO_4$

Here, use of MnO_2 prevents the formation of calomel.

Physical properties of corrosive sublimate:

i. It is white crystalline solid sparingly soluble in cold water and readily soluble in hot water.
ii. It is soluble in aqua-regia.
iii. It is toxic in nature.

Chemical properties of Corrosive sublimate:

1. Action of heat:

When corrosive sublimate is strongly heated, it decomposes to give free metallic mercury and chlorine gas.

$HgCl_2 \xrightarrow[\Delta]{} Hg + Cl_2 \uparrow$

2. Action with alkali:

When corrosive sublimate is treated with NaOH solution, it produces yellow ppt. of HgO.

$HgCl_2 + 2NaOH \rightarrow \underset{\text{(yellow ppt.)}}{HgO\downarrow} + 2NaCl + H_2O$

3. Action with ammonia:

When corrosive sublimate is treated with ammonia solution, it produces white ppt. of mercuric amino chloride.

$HgCl_2 + 2NH_4OH \rightarrow \underset{\text{(white ppt.)}}{Hg(NH_2)Cl\downarrow} + NH_4Cl + 2H_2O$

Test yourself:

Q. What happens when corrosive sublimate is treated with NH_3?

4. Action with potassium iodide:

Corrosive sublimate reacts with KI solution to produce scarlet ppt. of HgI_2 which further dissolves in excess of KI solution to form a **Nessler's reagent** (i.e, potassium mercuric iodide).

$HgCl_2 + KI \rightarrow HgI_2 \downarrow + 2KCl$

$HgI_2 + \underset{\textbf{(excess)}}{2KI} \rightarrow K_2[HgI_4]$ (Nessler's reagent)

Test yourself:

Q. What is Nessler's reagent? Write its one application.

5. Action with potassium thiocyanate:

Corrosive sublimate reacts with KSCN to produce mercuric thiocyanate.

$HgCl_2 + 2KSCN \rightarrow Hg(SCN)_2 + KCl$

Do you know?

When mercuric thiocyanate is dried and ignites, it produces snake like tube called a *pharoach's serpents.*

Uses of corrosive sublimate:

i. Corrosive sublimate is used as pesticide (especially fungicide).

ii. Its 5% solution is used as disinfectant.

iii. It is used to prepare calomel and Nessler's reagent

iv. It is used as a preservative of timber and leather.

Do you know?

Traditionally egg white or milk were used as antidote for corrosive sublimate poisoning as it was believed that egg and milk bind with mercury and neutralize the adverse effect of mercury.

Exercise

A. Multiple choice questions

1. Which of the following is a chief ore of mercury?

a. Calomel b. Corrosive sublimate c. Cinnabar d. Livingstonite

2. What is the formula of corrosive sublimate?

b. $HgCl_2$ b. Hg_2Cl_2 c. HgI_2 d. $Hg(NH_2)Cl$

3. What is the formula of calomel?

a) HgS b) $HgCl_2$ c) $Hg(NH_2)Cl$ d) Hg_2Cl_2

4. What happens when mercury combines with other metals?

a. It dissolves in other metals b. It forms stable alloy with other metals

c. It does not react with metals d. It forms volatile compounds with other metals

5. Which of the following is used as antidote for mercury poisoning from corrosive sublimate?

a. Potassium nitrate b. Sodium hydroxide c. Egg white d. Sodium carbonate

6. In the extraction of mercury which gas is released from cinnabr?

a. CO_2 b. SO_2 c. NO_2 d. O_2

7. Which of the following is an ore of mercury?

a. Cinnabar b. Livingstone c. Calamine d.Calomel

8. Which of the following is also known as quick silver?

a. Ag b. Zn c. Na d. Hg

9. Which of the following undergoes sublimation on heating?

a. $CuSO_4.5H_2O$ b. $HgCl_2$ c. NaHg d. $FeSO_4.7H_2O$

10. What is X in the given reaction?

$HgCl_2 + 2KI \rightarrow X$

a. $K_2HgI_4 + Hg$ b.K_2HgI_2 c. K_2HgI_4 d.HgI_4

B. Short answers questions:

11. Give reason,

a.Mercury (II) chloride is called corrosive sublimate.

b. Mercury (II) chloride is more toxic than mercury (I) chloride.

c. Most common and efficient method of purification of mercury is distillation.

12. What is the chief ore of mercury? How is pure mercury obtained from its chief ore?.

13. What is Nessler's reagent? How is it prepared? Write its one application.

14. Write down the molecular formula of -

a. Cinnabar b. Nessler's reagent c. Corrosive sublimate d. Calomel

15. A student added ammonia solution to the solution of mercury (II) chloride solution. Predict and explain the likely outcome, including relevant chemical equations and observations.

16. Mercury (II) chloride is called corrosive sublimate.

a. Starting from metallic mercury how would you prepare corrosive sublimate?
b. Write the action of heat on corrosive sublimate.
c. What happens when aqueous solution of this compound treated with excess of KI?
d. Write any two uses of corrosive sublimate.

17. Write the balanced chemical equation for-

a. Roasting of cinnabar.
b. Action of aqua regia on mercury.
c. Action of ozone on mercury.

18. Write a note on- Calomel.

19. Starting from cinnbar, how would you obtain pure mercury? Explain the steps involved in this metallurgy with necessary diagram.

20. Write the chemistry of corrosive sublimate.

21. Discuss the purification of mercury during its extraction from cinnabar.

C. Long answer question:

22. A liquid metal 'M' having atomic number 80 lies in group 12 of periodic table. It is used as a thermometric and barometric liquid.

a. Identify the metal 'M'.
b. Write the formula of the chief ore of 'M'.
c. How would you extract 'M' starting from its chief ore?
d. What happens when 'M' is treated with aqua regia?

e. What happens when 'M' is heated with air at 350 **°C ?**

f. Write any two uses of 'M'.

23. A recently discovered ore deposit contains sulfide and some impurities. Chemical analysis reveals the presence of a metal lying in group 12 with atomic number 80. This element is known to form compounds where it exhibits +1 and +2 oxidation states.
a. Identify the element and write its chief ore.
b. Describe the steps required to extract this element from its chief ore with necessary diagram.
c. Write the formula of two important compounds of this element showing oxidation state +1 and +2.

d. Write any two uses of this element.

PROJECT WORK

1. Take a chart paper and write the steps involved in extraction of mercury from its chief ore along with necessary diagrams".

2. Many of utility items used in home are made or contain mercury. Take a chart paper and prepare the list of those items that contain mercury as one of the main component.

3. Prepare a chart paper to present your logic for not using coke as a reducing agent for the extraction of mercury from cinnabar.

Sub-unit-7.4: Iron (Fe)

1. Activity:

Complete the table about iron and discuss in group to answer the following questions:

Element	Iron
Symbol	....
Atomic Number	....
Atomic Mass	....
Electronic Configuration	....
Group	....
Period	....
Valency	....

a. What is the role of iron in our daily life?

b. Write the name of some iron minerals.

c. Why are stainless steel utensils preferred over iron utensils for everyday use in cooking and serving?

a.	
b.	
c.	

7.4.1: Introduction:

Fig: Iron metal

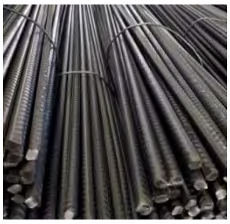


Fig: Iron rod for construction

Fig: Various items of iron

Fig: Stainless steel utensils

Iron is one of the most prevalent metallic elements in the Earth's crust. It has been used for a long time in the manufacture of steel and construction work. It is called "**Falam**" in Nepali. Its symbol Fe has been derived from Latin word ***ferrum*** which means iron. It is a transition metal belonging to the 3d series located in period 4 and group 8 of the periodic table. Its atomic number is 26 and atomic mass 55.85 amu. It has melting point of 1530 ^{0}C, boiling point of 2750^{0}C and a specific gravity of 7.86.

Test yourself:

Q. What is the biological importance of iron?
Q. Write two common oxidation states of iron.

7.4.2: Occurrence:

2. Activity:

Take a blank map of Nepal and answer the following questions-

a. Locate the major iron mines in the map.
b. What is the chief ore of iron? Write its molecular formula.
c. Look around, where do you think iron is present in your area?

a.	....
b.	....
c.	....

Iron does not occur in free-state as it is easily attacked by moisture and air. It is mostly found in combined state in the form sulphide, oxide and carbonate ore. In Nepal, iron ore deposits are found in Phulchoki (Lalitpur), Thoshe (Ramechhap), Jhumlabang (Rukum east), Dhaubadi (Nawalparasi east), etc. Some major ores of iron are-

S. N.	Name of iron ore	Formula
1	Haematite	Fe_2O_3
2	Limonite (Brown Haematite)	$2Fe_2O_3.3H_2O$
3	Magnetite	Fe_3O_4
4	Copper pyrite	$CuFeS_2$
5	Iron pyrite	FeS_2
6	Siderite	$FeCO_3$

7.4.3: Extraction of Iron from Haematite:

3. Activity:

Discuss in a group and answer the following questions-

a. How do you think we can extract pure iron from its chief ore?
b. Why is haematite chosen as a chief ore for the extraction of iron?
c. What are pig iron, cast iron and wrought iron?

a.	....
b.	....
c.	....

The extraction of pure iron from its chief ore haematite(Fe_2O_3) involves pyrometallurgy. The various steps involved in the extraction of Fe are-

1. Crushing and Pulverization:

The big lumps of haematite ore are first broken down in to small pieces by jaw crusher or hammer and then changed in to powder form in the ball mill. This entire process is called crushing and pulverization.

2. Concentration:

The powdered ore from step 1 is concentrated by gravity separation technique. In gravity separation method, pulverized ore is washed with running water as a result heavy ore particles settle down and lighter particles of impurities are washed away. If magnetic impurities are present then magnetic separation technique is followed to clean the ore.

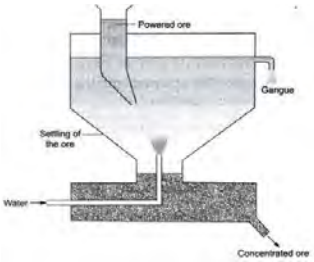


Fig: Gravity Separation

3. Calcination:

The concentrated ore from step 2 is heated with small amount of coal in limited supply of air shaft furnace (or rotary kiln) where following changes take place.

$2Fe_2O_3.3H_2O \xrightarrow[\Delta]{} 2Fe_2O_3 + 3H_2O$ (moisture is removed)

If ferrous carbonate is present, it changes to ferric oxide.

$FeCO_3 \longrightarrow FeO + CO_2$

$4FeO + O_2 \longrightarrow 2Fe_2O_3$

It should be noted that, the FeO formed may react with silica to produce ferrous silicate.

$FeO + SiO_2 \longrightarrow FeSiO_3$ (slag)

During calcination impurities like P, As, S, Sb etc are removed as their volatile oxides.

$4P + 5O_2 \xrightarrow[\Delta]{} 2P_2O_5\uparrow$

$S + O_2 \xrightarrow[\Delta]{} SO_2\uparrow$

$4As + 3O_2 \xrightarrow[\Delta]{} 2As_2O_3\uparrow$

Test yourself:

Q. Why is the conversion of FeO to Fe_2O_3 preferred over the formation of ferrous silicate during extraction of iron from haematite?

4. Reduction (Smelting or Carbon reduction process):

The calcined ore obtained from step 3 is reduced to metallic iron in a blast furnace by smelting or carbon reduction process. A blast furnace is a big, tall cylindrical tower made up of steel lined with fire bricks to withstand high temperature. The blast furnace consists of the **stack** (where raw materials are added), the **bosh** (the middle section where most reaction occurs), **tuyares** (pipes that blow hot air in to the furnace), the **hearth** (where molten iron collects), **cowper** stoves (which preheat the air) and **bells** & **spouts** (which control the flow of molten iron and slag).

The lime stone, coke and calcined ore are mixed in the ratio 1:4:8. This mixture is called charge. Here limestone acts as flux and coke acts as reducing agent. The changes that takes place at different zones of the furnace are-

i. Zone of Combustion (1300-1500 ^{0}C):

This region lies near the hearth of the furnace where combustion of carbon (coke) takes place to produce large amount of heat such that the temperature of this zone reaches upto 1500 ^{0}C.

$$2C + O_2 \xrightarrow[\Delta]{} 2CO + Heat$$

$$2CO + O_2 \xrightarrow[\Delta]{} 2CO_2 + Heat$$

The main function of this zone is to provide necessary heat for the reduction of iron ore into iron and to maintain high temperature required for the entire iron making process.

ii. Zone of Fusion (1200-1300 ^{0}C):

This region lies near the bottom of the furnace, just above the zone of combustion. In this region, the CO_2 gas from the zone of combustion reacts with hot coke to produce CO which is an endothermic reaction.

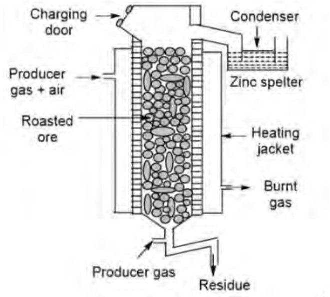


Fig: Vertical retort process for reduction of ZnO to Zn

$CO_2 + C \rightarrow 2CO$ -Heat

This endothermic reaction causes fall in temperature which is sufficient to fuse the spongy iron sliding down from zone of reduction. In this region the molten iron and slag are removed from different outlets. The molten iron may absorb impurities like carbon, phosphorous, silicon, sulphur etc. in this region.

$3Fe + C + Heat \rightarrow Fe_3C$ (cementitie)

If Fe_2O_3 is present, it will be reduced in this zone.

$Fe_2O_3 + C \rightarrow 2Fe + 3CO$

The main function of this zone is to produce molten iron and separating impurities into slag.

iii. Zone of Slag formation(700-1000 ^{0}C):

This region lies at the middle part of the furnace, just above zone of fusion. In this region limestone decomposes to produce calcium oxide (basic flux) and carbon dioxide.

$$CaCO_3 \xrightarrow[\Delta]{} CaO + CO_2$$

The CaO produced combines with silica to form slag.

$CaO + SiO_2 \rightarrow CaSiO_3$ (calcium silicate)

(flux) (gangue) (slag)

The main function of this zone is to remove silica impurities from the molten iron by forming slag with limestone.

vi. Zone of Reduction (400-700 ^{0}C):

This region lies near about the top of the furnace, just above zone of slag formation. In this region, CO gas coming from the bottom of the furnace reduces iron ore into spongy iron. Since the temperature of this zone is low therefore iron does not melt in this zone. The reduction reaction takes place as-

$$\underset{}{Fe_2O_3} + CO \rightarrow \underset{\text{(spongy iron)}}{2\,Fe} + 3CO_2$$

The main function of this zone is to reduce iron ore (haematite or magnetite) into metallic iron with the help of reducing agent carbon monoxide.

In this way spongy iron is obtained at zone of reduction which melts at zone of fusion. The molten iron is allowed to solidify into big lumps, which is called **pig iron**.

When pig iron is melted and small quantity of carbon and other elements are added followed by pouring the mixture into mould to solidify then the iron obtained is called **cast iron.**

Test yourself:

Q. What are the differences between pig iron, cast iron, wrought iron and steel?
Q. What is the function of lime stone in the smelting process during the extraction of iron?

Do you know?

In the past, the iron that was extracted from the furnace was poured into molds that were shaped like a sow and her young, which gave the name "pig iron".

7.4.4: Different forms of iron:

On the basis of carbon content, iron is classified into three types-

a. Cast Iron: It contains 2- 4.5% of carbon as the major impurity. It is hard and brittle.
b. Steel: It contains 0.2- 2% of carbon as major impurity. It is malleable and brittle.
c. Wrought iron: It contains less than 0.1% carbon as major impurity. It is malleable and soft. It is the purest form of iron (99.5%).

7.4.5: Physical properties of iron:

Pure iron is soft white metal having following physical properties-

i. Appearance: It is grey crystalline solid at room temperature. It becomes hard due to presence of carbon**.**

ii. Conductivity: It is good conductor of heat and electricity**.**

iii. Workability: It can be easily shaped (malleable) and drawn in to wire (ductile). However, it is less ductile than copper.

iv. Density: Its specific gravity is 7.87 g/cc.

v. Melting and Boiling point: Its melting point is 1530 ^{0}C and boiling point is 2750^{0}C.
vi. Ferromagnetism: It possesses strong magnetic property. It loses its magnetic property when heated at about 760 ^{0}C.

7.4.6: Chemical properties of iron:

1. Action of air:

Pure iron is not affected by dry air, but impure iron reacts with moist air to produce a reddish brown layer on its surface which is called rust.

$$4Fe + 3O_2 + xH_2O \rightarrow \underset{\text{(rust)}}{2Fe_2O_3.xH_2O} \text{ (hydrated ferric oxide)}$$

On the other hand, when finely divided iron is heated with oxygen, it gives ferrosoferric oxide.

$$3Fe + 2\,O_2 \underset{\Delta}{\rightarrow} Fe_3O_4 \text{ (ferrosoferric oxide)}$$

2. Action of water:

Cold water has no effect on iron. But, red hot iron decomposes steam to produce hydrogen gas.

$$\underset{\text{(red hot)}}{3Fe} + \underset{\text{(steam)}}{4H_2O} \rightarrow Fe_3O_4 + 4H_2\uparrow$$

3. Action with alkali:

Alkali has no action on iron.

4. Action of acids:

Since, iron lies above hydrogen in electrochemical series it can liberate hydrogen gas from dilute mineral acids and non-oxidizing agents.

i) Action with HCl:

Fe reacts with dilute hydrochloric acid to produce hydrogen gas.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$$

ii) Action with H_2SO_4:

Fe reacts with dilute sulphuric acid to produce hydrogen gas.

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2\uparrow$$

But, iron reacts with concentrated sulphuric acid to produce sulphur dioxide gas.

$$Fe + \underset{\text{(conc.)}}{2H_2SO_4} \rightarrow FeSO_4 + SO_2\uparrow + 2H_2O$$

iii) Action with HNO_3:

Fe reacts with nitric acid under different conditions to produce ferrous nitrate and different oxides of nitrogen depending upon the concentration of the acid. For example,

a) With conc. HNO_3: Fe reacts with hot and conc. HNO_3, a film of ferroso-ferric oxide (Fe_3O_4) is formed on the surface of iron and iron becomes passive as a result of which the reaction is ceased. This phenomenon is called **passivity of iron.**

b) With moderately conc. (1:1) HNO_3:

$Fe + 4HNO_3 \rightarrow Fe(NO_3)_2 + 2NO_2 + 2H_2O$

c) With dil. HNO_3:

$4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$

Do you know?

Oxidizing agents like $KMnO_4$, $K_2Cr_2O_7$ etc can also make iron passive.

5. Displacement reaction:

Fe can displace less reactive metals that lie below it in electrochemical series. For example,

$Fe + CuSO_4 \rightarrow FeSO_4 + Cu$

Test yourself:

Q. Can you store silver nitrate solution in a vessel made up of iron?

6. Reaction with carbon monoxide:

Fe on heating with CO at about 1200 ^{0}C gives iron pentacarbonyl.

$Fe + 5\,CO \xrightarrow[\Delta]{} Fe(CO)_5$ (iron pentacarbonyl)

7.4.7: Uses of iron (cast iron):

Fig: Iron pipes

Fig: Stainless steel utensils

Fig: Magnetic tape

i) Iron is used as a constructive material for roads, bridges and buildings.

ii) Iron is used to make steel and other alloys.

iii) Iron is used as an essential ingredient in hemoglobin in blood for oxygen transport.

iv) Iron is used for making ships, pipes, vehicles, and many other domestic articles.

v) Iron is used in the production of magnetic tapes and hard drives for data storage.

vi) Iron is used for making pots, pans and other cooking utensils.

7.4.8: Manufacture of steel by Open hearth process and Basic oxygen process:

Fig: Steel sink set

4. Activity:

Observe the given picture of steel sink set and answer the following questions-

a. Why do you think steel is preferred over pure iron for this item?

b. What materials do you think are used to make steel?

List some other common examples where steel is used.

a.	....
b.	....
c.	....

Introduction:

Pure iron is soft and can be bent easily. When carbon is added to iron, it becomes hard and stronger, turning it into steel. Thus steel is an alloy of iron that contains 0.2 - 2% carbon and traces of some other impurities like S, P, V, Cr, Ni, Mn, Co etc. If only carbon is present then the steel is called plain steel and if some other elements like Ni, Mn, Cr etc are present along with carbon then the steel is called special steel. For example, stainless steel is made up of iron, carbon, chromium, Nickel and some other trace impurities etc. Chromium is universal component of all steel as it increases corrosion resistance at high temperature.

Manufacture of steel:

Since the steel has carbon content in between that of cast iron and wrought iron therefore steels are manufactured either by reducing the percentage of carbon in cast iron or by raising the percentage of carbon in wrought iron. Steel can be manufactured by any of the following methods-

i. Bessemer process (from cast iron)
ii. Open hearth process (from cast and wrought iron)
iii. Basic oxygen process (from cast iron)
iv. Crucible process (from wrought iron)
v. Cementation process (from wrought iron)
vi. Electrical process (from pure ore and carbon)

Here, we discuss open hearth process and basic oxygen process only.

Manufacture of steel by open hearth process:

Sir Carl Wilhelm Siemens (4 April 1823-19 November 1883) was a German-British electrical engineer and businessman. He is renowned for his important contributions to electrical engineering and steelmaking. He created the Siemens-Martin open-hearth furnace, which improved the efficiency and controllability of steel manufacturing and completely changed the industry. In addition, he contributed to the installation of the transatlantic telegraph wire and worked on developments in telegraphy, electrical power transmission, and thermodynamics. In 1883, Queen Victoria knighted him and elected him a Fellow of the Royal Society (FRS) and a Fellow of the Royal Society of Arts (FRSA) for his scientific and industrial accomplishments.

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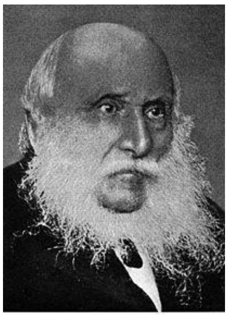


Pierre-Émile Martin (18 August 1824- 23 May 1995) was a French industrial engineer. He used the Carl Wilhelm Siemens-invented technology of recovering the hot gas in an open hearth furnace. He developed the method that bears his name in 1865, based on the Siemens process, for making steel in a hearth by re-melting waste steel and adding cast iron to dilute impurities. He was awarded a Gold Medal at the Paris Exhibition for his contribution in producing better quality of steel.

Siemen and Martin together invented the open hearth process which is a contemporary way to make steel using 70–80% cast iron, 20–30% waste iron, and a little amount of haemtite. This method involves charging a mixture of lime, iron ore (haematite), and cast (pig) iron in an open hearth furnace. To eliminate acidic impurities, calcined dolomite (CaO, MgO) is used to line the furnace and if basic impurities are present then the furnace is coated with silica (SiO_2). Thus depending upon the nature of impurities open hearth process may be acidic process or basic process.

Acidic Process: In acidic process the furnace is lined with acidic material like sand (SiO_2) that removes basic impurities like Manganese, silicon etc. or low content of phosphorous. All the impurities are oxidized by haematite and removed as a slag or gas.

$2Fe_2O_3 + 3S \rightarrow 4Fe + 3SO_2\uparrow$ (S is removed)

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO\uparrow$ (C is removed)

$2Fe_2O_3 + 3Si \rightarrow 4Fe + 3SiO_2\uparrow$ (Si is removed)

$10Fe_2O_3 + 6P \rightarrow 20Fe + 6P_2O_5\uparrow$ (P is removed due to its low content)

$\underset{\text{(gangue)}}{MnO} + \underset{\text{(flux)}}{SiO_2} \rightarrow MnSiO_3$ (slag)

In order to obtain desire quality of steel a calculated mixture of Fe, Mn and C is added after the impurities have been removed. This mixture of Fe, Mn and C is called **spiegeleisen.** Finally the molten steel is removed from the furnace and poured in to mould to obtain steel of desired shape.

Basic Process: In basic process the furnace is lined with basic material like dolomite ($CaCO_3$, $MgCO_3$) that removes acidic impurities and high content of phosphorous. All the impurities are oxidized by haematite and removed as a slag or gas.

$$2Fe_2O_3 + 3S \rightarrow 4Fe + 3SO_2\uparrow \text{ (S is removed)}$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO\uparrow \text{ (C is removed)}$$

$$10Fe_2O_3 + 6P \rightarrow 20Fe + 6P_2O_5$$

$$CaCO_3 \xrightarrow[\Delta]{} CaO + CO_2$$

$$\underset{\text{(gangue)}}{P_2O_5} + \underset{\text{(flux)}}{3CaO} \rightarrow Ca_3(PO_4)_2 \text{ (slag)}$$

In order to obtain desire quality of steel a calculated mixture of Fe, Mn and C is added after the impurities have been removed. This mixture of Fe, Mn and C is called **spiegeleisen.** Finally the molten steel is removed from the furnace and poured in to mould to obtain steel of desired shape

Advantages of open hearth process: Since open hearth process is a modern process, it has following advantages-

i. It can produce high quality of steel in a large scale.
ii. It allows control over carbon content.
iii. It uses pig iron as well as scrap iron as raw materials.
iv. It helps to remove impurities like Si, P, S etc. more effectively.
v. It is cost effective and versatile grade of steel can be produced.

Disadvantages of open hearth process: Open hearth process has following disadvantages-

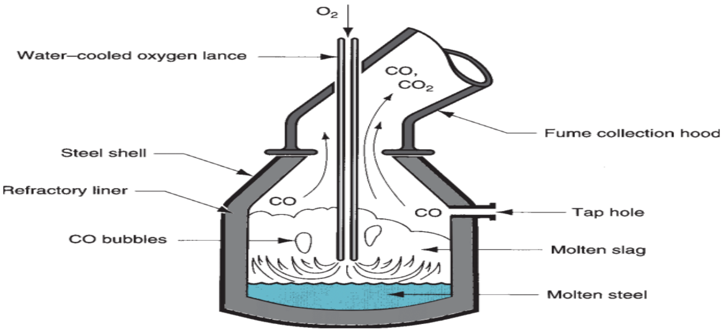
i. It is a slow and time consuming process.
ii. It requires large amount of fuel and energy.
iii. It requires high investment.
iv. It is not eco friendly as it generates harmful gases like CO, CO_2, SO_2 etc.
v. It is cost effective and versatile grade of steel can be produced.

Manufacture of steel by Basic Oxygen Process (BOP):

Robert Durrer (1890- 1978) was a Swiss engineer. He discovered the basic oxygen process for steel making process known as Linz -Donawitz (LD process) process. The name of this process was placed after the name of towns in Nazi Germany where the technology was commercialized. Later on, the method was modified and scaled up to industrial size by a team in Austria under the direction of Dr. Theodor Eduard Suess. Durrer received the Rinman Medal from the Swedish iron and steel industry in 1959 and the Bessemer Gold Medal from the British Iron and Steel Institute in 1957.

The basic oxygen process uses carbon rich molten pig iron to produce steel. Actually BOP is a modified version of Bessemer process.

As seen in the figure, this method involves pouring molten cast iron into a specialized vessel known as an LD converter and blowing extremely pure oxygen through a lance. Cast iron's carbon undergoes oxidation to produce carbon dioxide and carbon monoxide. P, Si, and other impurities are also oxidized to their corresponding oxides.



$$C + O_2 \rightarrow CO_2$$
$$CO_2 + C \rightarrow 2CO$$
$$2CO + O_2 \rightarrow 2CO_2$$
$$Si + O_2 \rightarrow SiO_2$$
$$4P + 5O_2 \rightarrow 2P_2O_5$$

After certain time the supply of oxygen is paused and suitable basic flux like CaO is added to remove oxides of P, Si etc in the form of slag. Sulphur if present as impurity gets dissolve in the slag and removed.

$$CaO + SiO_2 \rightarrow CaSiO_3 \text{ (slag)}$$

$$2CaO + P_2O_5 \rightarrow 2Ca_3(PO_4)_2\text{(slag)}$$

When molten steel with required amount of carbon is achieved then it is tilted and steel is tapped off from the furnace below the slag level. Finally slag is removed by tilting the vessel in the opposite direction. The whole process is completed in 40-45 minutes.

Advantages of basic oxygen process: Since basic oxygen process is a modified version of Bessemer process, it has following advantages-

i. It can produce high quality of steel in a large scale within 30 -45 minutes.

ii. It can produce high quality of steel than open hearth process.

iii. Majority of steel is manufactured by this method.

iv. This process is **autogeneous** i.e, required thermal energy generated during oxidation.

v. It causes very less air pollution.

Test yourself.

Q. Compare open hearth process and basic oxygen process.

Do you know?

- **Quenching of steel:** It is a process of rapid cooling of heated steel in water or oil. It is done to increase the hardness of steel
- **Tempering of steel:** It is a process of reheating quenched steel to a lower temperature and cooling it slowly. It is done to reduce brittleness and improve toughness of steel.

7.4.9: Corrosion of iron and its prevention:

5. Activity:

Observe the given picture of iron tap and answer the following questions-

a. What do you think has happened to the iron tap over time?

b. What do you think could be done to prevent rusting of iron?

c. What are some other common examples where rusting or corrosion might be a problem in everyday life?

a.	
b.	
c.	

Introduction :

Under some environmental circumstances, metals deteriorate or wear away due to unintended chemical reactions or electrochemical attack. This process is referred as corrosion. When corrosion takes place in iron metal, it is called rusting. A reddish brown film of hydrated ferric oxide

When iron is exposed to moist air over a long period of time, its surface gets covered with a reddish brown layer of hydrated ferric oxide ($Fe_2O_3.xH_2O$) is formed on the surface of iron after prolonged exposure to moist air. The brown layer formed on the iron surface is called rust and this phenomenon is called rusting.

$4Fe + 3O_2 + xH_2O \rightarrow 2Fe_2O_3.xH_2O$ (rust)

Theory:

The phenomena of rusting are explained by a number of hypotheses. Among those two crucial theories are-

1. Electrochemical Theory:

According to this theory, a tiny voltaic cell develops on the surface of iron itself due to uneven surface of iron with impurities or stains. On the surface of iron, the portion with lower reduction potential acts as anode while the portion with higher reduction potential acts as cathode. The moisture present on the surface of iron dissolves gases like oxygen, carbon dioxide , sulphur dioxide, hydrogen sulphide together behaves as electrolytic solution.

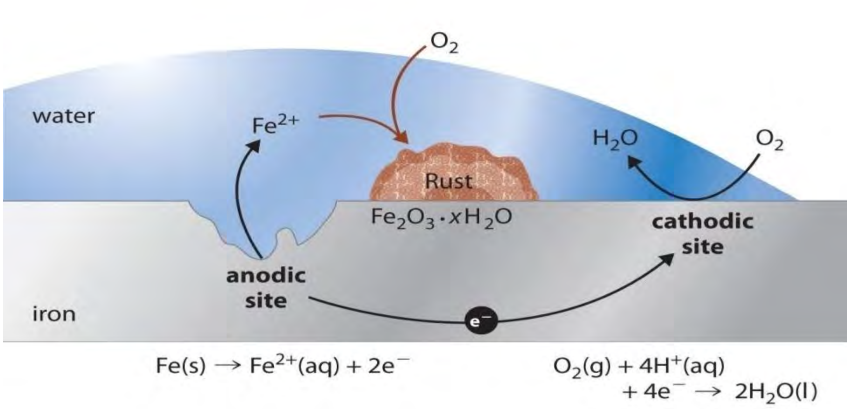


Fig: Electrochemical theory of rusting

At **anode**,

Fe atoms are oxidized to ferrous ions leaving electrons on the metal. The electrons move towards the region of cathode through the metal as shown in figure. The anodic half cell reaction is-

$$\mathbf{Fe \rightarrow Fe^{++} + 2e^{-}}$$

(s) (aq)

At **cathode**,

The electrons are taken up by hydrogen ions produced either from water or carbonic acid.

$$H_2O \leftrightarrow H^+ + OH^-$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \leftrightarrow 2H^+ + CO_3^{--}$$

$H^+ + e^- \rightarrow H$ **(cathodic half cell reaction)**

Thus, hydrogen atoms on the iron surface reduce dissolved oxygen to give water.

$$4H + O_2 \rightarrow 2H_2O$$

Hence, overall redox reaction is-

$$Fe \rightarrow Fe^{++} + 2e^{-} \textbf{ (oxidation half reaction)}$$

$$4H^{+} + O_2 + 4e^{-} \rightarrow 2H_2O \textbf{ (cathodic half reaction)}$$

$$\overline{2Fe + 4H^{+} + O_2 \rightarrow 2Fe^{++} + 2H_2O}$$

Now ferrous ions are further oxidized by atmospheric oxygen to form rust.

$$4Fe^{++} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^{+}$$

$$Fe_2O_3 + xH_2O \rightarrow \underset{\text{(rust)}}{Fe_2O_3.xH_2O}$$

2. Chemical theory of rusting:

According to this theory, rusting of iron takes place when iron reacts with carbon dioxide dissolved in water as explained below-

The presence of carbon dioxide and water form carbonic acid which combines with iron to form ferrous bicarbonate.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$Fe + H_2CO_3 \rightarrow Fe(HCO_3)_2 + H_2\uparrow$$

This ferrous bicarbonate is precipitated to ferric hydroxide in presence of water and oxygen.

$$Fe(HCO_3)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3\downarrow + 8CO_2$$

$$2Fe(OH)_3 \rightarrow \underset{\text{(rust)}}{Fe_2O_3.xH_2O}$$

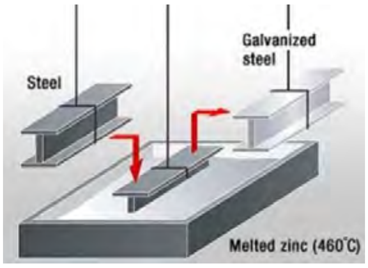
It should be noted that, this theory could not explain rusting of iron in absence of CO_2.

Prevention of rusting:

Iron should not be allowed to rust because this weakens the metal and reduces its strength and durability. It poses a safety issue since it can harm vital infrastructure like buildings, bridges and machinery. In addition to making items appear outdated and ugly, rust often results in financial losses from repairs or replacements. Preventing rust helps to enhance the life span of iron objects, safeguard them and saves money. Followings are some methods of preventing rusting of iron-

i. Galvanization:

Galvanization is one of the best ways to protect iron from rusting. In this process the iron (or steel) object is coated with thin layer of zinc. Here, zinc layer provides a barrier between iron surface and atmosphere. This process is also known as sacrificial protection or cathodic protection as more electropositive metals like Zn, Al, Mg etc are kept in contact with iron which sacrfifice themselves to protect rusting of iron.



Test yourself.

Q. What type of iron nail will you use for constructing wooden fence in your garden and why?

ii. Forming Alloys:

Alloying iron with metals like Cr, Ni, Mn, Si etc prevents rusting. Chromium is the most effective metal added to iron to prevent rusting. For example it is used in making stainless steel which corrosion resistant.

iii. Forming protective barrier:

Thin coating of paint, grease, oil, enamel, varnishes, etc are used to prevent rusting. This process is called barrier protection. Coating the iron surface with red oxide (Cu_2O) also prevents rusting.

iv. Bower-Barff process:

In this method iron is intentionally exposed to steam to form a thin layer of flash rust on its surface which avoids further rusting of iron. This process is called Barff's protection.

v. Use of corrosion inhibitors:

Some chemicals like phosphates, chromates, amines, soap etc work by neutralizing corrosive elements or create a protective layer to stop or slow down metal rusting. Such chemicals are called corrosion inhibitors.

Test yourself.

Q. Why is stainless steel more resistant to rust?

Exercise

A. Multiple choice questions

1. Iron is extracted from which ore in the blast furnace?

a. Haematite b. Cryolite c. Siderite d. Copper pyrite

2. Which of the following is main reducing agent in the blast furnace during extraction of iron?

a. CO_2 b. CO c. C d. Zn

3. Which of the following substance is used as a flux in the blast furnace during extraction of iron?

a) Quartz b) Silica c) Magnesia d) Limestone

4. Which of the following reactions is responsible for the actual reduction of iron ore in the blast furnace?

a. $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
b. $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$
c. $Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$
d. $FeO + CO_2 \rightarrow Fe + CO$

5. Which of the following is also called open hearth process?

a. LD process b. Bessemer process c. Siemen-Martin process d. Electrolytic process

6. Which of the following is used as refractory lining in the acidic open hearth process?

a. MgO b. CaO c. $CaCO_3$ d. SiO_2

7. What is the raw material in BOP?

a. Scrap iron b. Haematite c. Molten pig iron d. Scrap steel only

8. What is the function of pure oxygen in BOP?

a. To add flux b. To oxidize impurities c. To increase carbon content d. To cool the furnace

9. Which of the following best describes rusting of iron?

a. Oxidation b.Reduction c. Combustion d. Sublimation

10. What is the chemical formula of rust?

a. Fe_3O_4 b.$Fe_2O_3.xH_2O$ c. $FeCO_3$ d. $Fe(OH)_2$

11. In electrochemical theory of rusting what does iron behave as?

a. Cathode b. Salt bridge c. Anode d. Electrolyte

12. Which of the following substance accelerates the rusting of iron?

a. Sodium chloride b.Sugar c. Alcohol d. Oil

13. Which of the following is not required for rusting of iron?

a. Oxygen b.Water c. Carbon dioxide d. Iron

14. Which of the following method is not effective in preventing rusting?

a. Oiling b. Galvanizing c. Exposing to salt water d. Painting

15. Which of the following is hottest part zone of blast furnace?

a. Zone of combustion b. Zone of reduction c. Zone of fusion d. Zone of slag formation

B. Short answers questions:

16. Give reason,

a. Iron is coated with zinc.
b. Coke acts as both fuel and reducing agent in blast furnace.
c. Pure iron is not commonly used for making tools or structure.
d. Water and oxygen are essential for rusting of iron.

17. What is spiegleisen? Write its importance.

18. What is rusting? Write a balanced chemical equation for rusting of iron and suggest any two methods of preventing rusting.

19. Write down the molecular formula of -

a. Haematite b. Magnetite c. Limonite d. Siderite

20. A student mistakenly used an iron vessel to store silver copper sulphate solution. Predict and explain the likely outcome, including relevant chemical equations and observations. How would you modify the procedure to prevent this error?

21. A farmer noticed that the iron tools left in the field over the rainy season had developed a reddish-brown coating and became weaker over time.
He plans to buy new tools and wants to prevent this from happening again.

a) What is the reddish-brown coating, and how is it formed?

b) Why did the tools rust more during the rainy season?

c) Suggest any two methods the farmer can use to protect the new tools from rusting.

d) If the farmer decides to coat the tools with paint, what should he keep in mind to ensure long-term protection?

22. Write the balanced chemical equation for-

a. Action of dilute nitric acid on iron.
b. Action of steam on iron.
c. Reduction of ferric oxide in the blast furnace.

23. Write a note on- Electrochemical theory of rusting of iron.

24. Starting from haematite, how would you obtain pure iron? Explain the steps involved in this metallurgy with necessary diagram.

25. What do you mean by tempering and quenching of steel?

26. What is steel? Write the principle involved in the manufacture of steel by open hearth process.

27. Describe the theory behind the manufacture of steel by basic oxygen process.

28. Differentiate between open hearth process and basic oxygen process.

29. What are the advantages of-

a. Open hearth process

b. Basic oxygen process

30. A heavy metal is extracted from its oxide ore. During extraction, smelting of calcined ore is done in blast furnace.

a. Identify the metal and write the formula of the ore.

b. Draw the clean and labelled diagram of the blast furnace showing different zones.

c. Write the chemical reactions occurring in the zone of slag formation.

C. Long answer question:

31. A transition metal 'M' having electronic configuration [Ar] $3d^6\ 4s^2$ lies in group 8 of periodic table. It is most commonly used for making tools and structures.

    a. Identify the metal 'M'.
    b. Write the formula of the chief ore of 'M'.
    c. How would you extract 'M' starting from its chief ore?
    d. What happens when 'M' is treated with sulphuric acid?
    e. What happens when 'M' is exposed to moist air for long time**?**
    f. Write any two uses of 'M'.

32. A geologist studying a newly found ore deposit in a hilly region discovers that the ore contains a mixture of **iron carbonate**, **iron oxide**, and impurities such as **silica (SiO_2)** and **alumina (Al_2O_3)**. The local government is planning to set up a **blast furnace** to extract iron from this ore. Based on this scenario, answer the following questions-

    a. Identify the suitable ore of iron from deposits and write the impurities present in it.
    b. What suitable method of concentration is applied to clean the ore?
    c. Describe the steps required to extract this element from blast furnace with necessary diagram.
    d. What are cast iron and wrought iron? Write their uses.

    e. What is this element coated with zinc?

33. Recently, a steel manufacturing company improved its production facilities to produce high-quality steel using the Open Hearth Process. Since strength and formability are essential in vehicle body parts, the company is interested in creating low-carbon steel.

    Based on this scenario, answer the following questions-

    a. Write the principle involved in the manufacture of steel by this process.

    b. What are the raw materials for this process?

    c. Mention the impurities present in the raw materials and how are they removed?

    d. Why is this process suitable for producing low carbon steel?

    e. Write the merits and demerits of this process.

34. A modern steel plant has adopted the **Basic Oxygen Process (BOP)** for steel production to replace older methods. The plant focuses on producing high-strength steel for use in construction materials, such as beams and reinforcements.

    Based on this scenario answer the following questions-

a. Write the principle involved in the manufacture of steel by this process.

b. Mention the key raw materials used in this process.

c. What environmental advantages does this process offer?

d. List the advantages of this process.

35. A construction company has recently used **iron pillars** in a coastal area for building a bridge. After a few months, they noticed that the pillars had developed reddish-brown patches, which weakened the structure.

Based on this fact answer the following questions,

a. What causes the formation of reddish-brown patches on the iron pillars?

b. Write the formula of these reddish-brown patches.

c. Why does iron corrode faster in coastal areas compared to inland areas?

d. Explain the electrochemical theory of rusting of iron.

e. What are some of the methods of preventing rusting of iron?

PROJECT WORK

1. Take a chart paper and draw a detail diagram of blast furnace showing different zones including their functions and temperature ".
2. Many of utility items used in home are made or contain iron and steel. Take a chart paper and prepare the list of those items that contain iron/steel.
3. Prepare a chart paper to provide real life examples where various methods are adopted to prevent rusting.
4. Prepare a chart paper to explain the principle involved in the manufacture of steel by open hearth process with necessary diagram. List the advantages and disadvantages of this process.
5. Prepare a chart paper to explain the principle involved in the manufacture of steel by BOP process with necessary diagram. List the advantages and disadvantages of this process.

Sub-unit-7.5: Silver (Ag)

1. Activity:

Complete the table about silver and discuss in group to answer the following questions:

Element	Silver
Symbol	....
Atomic Number	....
Atomic Mass	....
Electronic Configuration	....
Group	....
Period	....
Valency	....

a. What is the role of silver in our daily life?

b. Write the name of some silver minerals.
c. Can you list some silver item used in your home?

a.	....
b.	....
c.	....

7.5.1: Introduction:


Fig: Silver metal


Fig: Silver jewelry


Fig: Silver utensil


Fig: Silver coin

Silver is a white shiny soft and malleable metal used for centuries for its beauty and utility, making it popular in jewelry, coins, utensils and other decorative items. It is called "**Chandi**" in Nepali. It is d-block element lying in group 11 with atomic number is 47 and atomic mass 107.87 amu. It has melting point of 956 ^{0}C, boiling point of 1955 ^{0}C and a specific gravity of 10.52.

7.5.2: Occurrence:

2. Activity:

Make a peer group and answer the following questions-

a. List some coinage metals along with silver.
b. What is the chief ore of silver? Write its molecular formula.
c. Why does silver statue or coin get tarnished on long standing?

a.	....
b.	....
c.	....

Silver is found in native state in Canada, Mexico, USA etc. In combined state silver is found as sulphide and chloride ore. Some major ores of silver are-

S. N.	Name of silver ore	Formula
1	Argentite (or Silver Glance)	Ag_2S
2	Horn silver	$AgCl$
3	Argentiferrous galena	$PbS. Ag_2S$
4	Ruby silver	Ag_2SbS_3
5	Silver copper glance	$(CuAg)_2S_2$

7.5.3: Extraction of Silver from Argentite by Cyanide Process:

3. Activity:

Discuss in a group and answer the following questions-

a. What is hydrometallurgy?
b. What is Mac-Arthur Forrest process?
c. Why is argentite chosen as a chief ore for the extraction of silver?

a.	....
b.	....
c.	....

Pure silver is extracted from its chief ore argentite (Ag_2S) by cyanide process that involves hydrometallurgy. The various steps involved in the extraction of silver are-

1. Crushing and Pulverization:
The big lumps of argentite ore are first broken down in to small pieces by jaw crusher or hammer and then changed in to powder form in the ball mill. This entire process is called crushing and pulverization.

2. Concentration:

The powdered ore from step 1 is concentrated by froth floatation process where ore is mixed with pine oil and water and kept in a tank. When the mixture in the tank is agitated by passing compressed air, ore particles float on the surface in the form of froth and earthy impurities settle at the bottom.

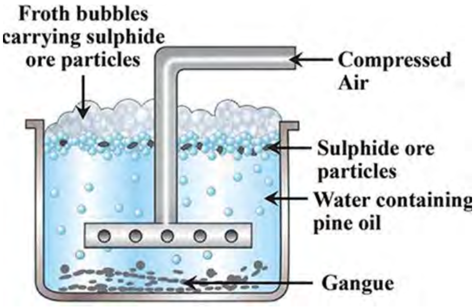


Fig: Froth floatation

3. Formation of complex cyanide:

The concentrated ore from step 2 is treated with dilute sodium cyanide solution in presence of air and water to form a soluble complex of silver called sodium argentocyanide.

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

(sod.argentocynaide)

Since the reaction is reversible and in order to shift the above equilibrium in the forward direction air is blown which removes Na_2S as Na_2SO_4.

$$Na_2S + 2O_2 \rightarrow Na_2SO_4$$

Test yourself:

Q. Write the balanced chemical reaction when horn silver is dissolve in sodium cyanide.

4. Reduction by precipitation method:

The solution from step 3 is now filtered to remove if any insoluble impurities are present. When the filtrate is treated with zinc, silver gets precipitated in the form of dark amorphous powder. Actually the silver obtained in this method is "spongy silver".

$$2Na[Ag(CN)_2] + Zn \rightarrow 2Ag + Na_2[Zn(CN)_4]$$

Thus obtained silver is separated by filtration and the precipitate is dried out.

Test yourself:

Q. What do you mean by cementation?

5. Purification:

The silver obtained from step 4 may contains some impurities. There are mainly two methods of refining silver.

(i) Cupellation Method:

When lead is present as impurity then cupellation method is applied to free lead from silver. This technique is actually applied for refining silver and gold. Here, when silver is heated in a special furnace, lead is blown away as PbO by air. The process is continued until bright shining silver is obtained.

(ii) Electro-refining Method:

This is the modern method of refining many metals including silver. In this method, impure silver which is to be purified is suspended as an anode and a thin pure silver metal is used as a cathode. Acidified silver nitrate solution is used as an electrolyte. When electricity is passed, impure silver dissolves from anode and get deposited at cathode. A muddy mass is deposited just below anode which is known as anode mud.

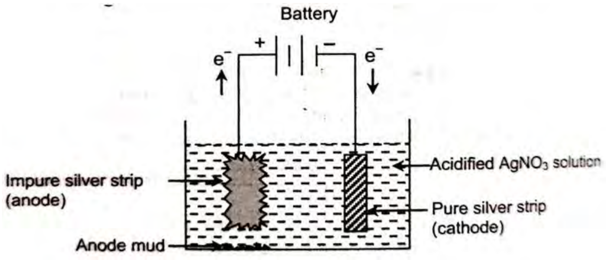


Fig: Electrolytic refining of silver

$$AgNO_3 \xrightarrow{Electrolysis} Ag^+ + NO_3^-$$

At anode,

$Ag \rightarrow Ag^+ + e^-$

(impure)

At cathode

$Ag^+ + e^- \rightarrow Ag$ (pure)

Thus obtained zinc is 99.9% pure.

Test yourself:

Q. Why is an impure rod of silver used as anode instead of cathode in electrolytic refining of silver?

Q. What happens during electrolytic refining if impure silver contains copper as impurity?

7.5.4: Physical properties of silver:

Silver is a shiny white metal having following physical properties-

i. Appearance: It is soft solid at room temperature. It gets tarnished (turns black) on exposure to moist air.

ii. Conductivity: It is good conductor of heat and electricity.

iii. Workability: It can be easily shaped (malleable) and drawn in to wire (ductile).

iv. Density: Its specific gravity is 10.52 g/cc.

v. Melting and Boiling point: Its melting point is 956 ^{0}C and boiling point is 1955^{0}C.

7.5.5: Chemical properties of silver:

1. **Action of air:**

Silver is normally unaffected by dry air, but it becomes tarnished when reacts with air containing minute of hydrogen sulphide forming black ppt. of silver sulphide.

$2Ag + H_2S \rightarrow Ag_2S(\text{black ppt.}) + H_2$

Test yourself:

Q. What is it necessary to clean silver ware from time to time?

2. **Action of acids:**

Since, silver lies below hydrogen in electrochemical series it cannot liberate hydrogen gas from dilute mineral acids and non-oxidizing agents.
Ag does not react with dilute hydrochloric acid and sulphuric acid.

$Ag + HCl \rightarrow$ No reaction
$Ag + H_2SO_4 \rightarrow$ No reaction

But, Ag reacts with concentrated sulphuric acid as

$$\underset{}{Ag} + \underset{(conc.)}{2H_2SO_4} \rightarrow Ag_2SO_4 + 2SO_2\uparrow + 2H_2O$$

Similarly, Ag reacts with nitric acid as

$$Ag + \underset{(conc.)}{2HNO_3} \rightarrow AgNO_3 + NO_2\uparrow + 2H_2O$$

$$3Ag + \underset{(dil.)}{4HNO_3} \rightarrow 3AgNO_3 + NO\uparrow + 2H_2O$$

It should be noted that silver does not dissolve in aquaregia.

4. **Action with non metals:**

Ag reacts with some non metals like S, P, Cl etc as
$Ag + S \rightarrow Ag_2S$
$2Ag + Cl_2 \rightarrow 2AgCl$

7.5.6: Uses of Silver:

i) Silver is used for making electrodes..
ii) Silver is used for making coins.
iii) Silver is used for making utensils, decorative items, and jewelry.
iv) Silver is used in photography.
v) Silver is used to prepare alloy.
vi) Silver is used in dentistry for filling cavities.

7.5.7: Compounds of silver:

A. Lunar caustic ($AgNO_3$) :

Fig: Silver nitrate

3. Activity:

Observe the given picture of silver nitrate and answer the following questions-

a. Why is it called lunar caustic?

b. Why is silver nitrate stored in dark colored bottle?

c. What causes a black stain if silver nitrate touches your skin?

a.	**…………………………………………………………………………………**
b.	**…………………………………………………………………………………**
c.	**…………………………………………………………………………………**

Introduction :
Silver nitrate is a colorless crystalline solid having molecular formula $AgNO_3$. It is highly soluble in water possessing photosensitive and caustic (corrosive) property. It is called lunar caustic because it contains silver, which was symbolically linked to the moon (*luna*), and it has a caustic (burning) effect on organic tissue.

Preparation of silver nitrate :
Silver nitrate can be prepared by the action of nitric acid on silver.

$$Ag + 2HNO_3 \rightarrow AgNO_3 + NO_2\uparrow + H_2O$$

(hot & conc.)

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + 8NO\uparrow + 2H_2O$$

(cold & dil.)

The reaction should be carried out in fume cupboard or fume hood to expel toxic oxides of nitrogen.

Physical properties of silver nitrate :
i. It is crystalline white colored solid soluble in water.
ii. In presence of light silver nitrate solution darkens slowly therefore both silver nitrate crystals and silver nitrate solution is stored in dark bottles.
iii. It is also soluble in organic compounds like alcohol, pyridine, acetone etc.

Chemical properties of silver nitrate:
1. Action of heat:
When silver nitrate is heated above 200^0C, it decomposes to produce silver nitrite and oxygen.

$$2AgNO_3 \xrightarrow{>200\ oC} 2AgNO_2 + O_2$$

If heating is continued up to red, metallic silver is obtained.

$$2AgNO_3 \xrightarrow{\text{Red } hot} 2Ag + 2NO_2 + O_2$$

2. Action with alkali:

When silver nitrate is treated with NaOH, it gives brown precipitate of silver oxide along with sodium nitrate and water.

$$2AgNO_3 + 2NaOH \rightarrow \underset{\text{(brown ppt.)}}{Ag_2O\downarrow} + 2NaNO_3 + H_2O$$

Similar reaction takes place with ammonia solution.

$$2AgNO_3 + 2NH_4OH \rightarrow \underset{\text{(brown ppt.)}}{Ag_2O\downarrow} + 2NH_4NO_3 + H_2O$$

But, with excess of ammonia solution soluble complex of diamminesilver(I) nitrate is obtained.

$$Ag_2O + 2NH_4OH + 2NH_4NO_3 \rightarrow \underset{\text{Diamminesilver(I)nitrate}}{2[Ag(NH_3)_2NO_3]} + 3H_2O$$

3. Action with organic matter:

When organic matters like skin, wood, paper, cloth etc comes in contact with silver nitrate in presence of light, black stain is produced on the organic matter due to decomposition of silver nitrate in to silver (black).

$$2AgNO_3 + \text{Organic matter} \xrightarrow{\text{Red } hot} \underset{\text{(brown ppt.)}}{2Ag\downarrow} + 2NO_2 + O_2$$

This characteristic property of silver nitrate is used to prepare indelible ink which is used to mark nail and skin of voters after casting vote during election.

Fig: Use of $AgNO_3$ as Indelible ink

4. Action with potassium cyanide:

When silver nitrate is treated with potassium cyanide, a white precipitate of silver cyanide is obtained.

$$AgNO_3 + KCN \rightarrow \underset{\text{(white ppt.)}}{AgCN\downarrow} + 2KNO_3$$

5. Precipitation reaction:

Silver nitrate reacts with aqueous solution of halides, sulphate, phosphate, sulphide, chromate to produce precipitate of corresponding silver salt with nitrate solution. For example,

$$AgNO_3 + Cl^- \rightarrow \underset{\text{(white ppt.)}}{AgCl\downarrow} + NO_3^-$$

$$2AgNO_3 + SO_4^{--} \rightarrow \underset{\text{(white ppt.)}}{Ag_2SO_4\downarrow} + 2NO_3^-$$

$$3AgNO_3 + PO_4^{---} \rightarrow Ag_3PO_4\downarrow + 3NO_3^-$$

(yellow ppt.)

Test yourself:

Q. How would you test the presence of Br^- and I^- in lab?

6. Displacement reaction:

Metals such as Na, Al, Cu, etc. lying above silver in electrochemical series can displace silver from its salt. For example,

$$Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$$

Fig: Cu displacing Ag from $AgNO_3$

Test yourself:

Q. Can you store silver nitrate solution in a vessel made up of lead?

Uses of silver nitrate:

i. Silver nitrate is used as laboratory reagent.
ii. It is used to prepare indelible ink.
iii. It is used to prepare Tollen's reagent.
iv. It is used in the preparation of photographic film.
v. It is used in silvering mirror.
vi. It is used as laboratory reagent.

B. Horn silver (AgCl) :

4. Activity:

Fig: Silver chloride

Observe the given picture of silver chloride and answer the following questions-

a. Give a test reaction to confirm this salt contain chloride ion.

b. What happens when you add silver chloride to water and ammonia solution?

c. Why is this salt commonly called horn silver?

a.	....
b.	....
c.	....

Introduction :

Silver chloride is white crystalline solid sparingly soluble in water, having molecular formula AgCl. It is commonly known as "Horn silver".

Preparation of silver chloride :

Silver chloride can be prepared by the action of silver nitrate on soluble chloride salt. For example,

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

Physical properties of silver chloride:

i. It is crystalline white colored solid sparingly soluble in water.
ii. It turns grey or violet when exposed to sunlight.
iii. It is soluble in ammonia solution.

Chemical properties of silver chloride:

1. Action of light:

When silver chloride is exposed to sunlight, it decomposes to produce silver metal and chlorine gas.

$$2AgCl \xrightarrow{\text{Light}} 2Ag + Cl_2$$

Due to this reaction, silver chloride turns grey or violet when exposed to light.

2. Action with ammonia:

Silver chloride dissolves in excess of ammonia solution forming a soluble complex called diamminesilver(I)chloride.

$$AgCl + 2NH_4OH \rightarrow \underset{\text{Diamminesilver(I)nitrate}}{2[Ag(NH_3)_2Cl]} + 2H_2O$$

When nitric acid is added to this complex precipitate of silver chloride is obtained.

Test yourself:

Q. How would you test the presence of Cl^- in lab?

Uses of silver chloride:

i. Silver chloride is used in photography due to its light senstivity.
ii. It is used as antimicrobial agent.
iii. It is used in photochemical lenses that darken in sunlight.
iv. It is used to prepare silver-silver chloride electrode.

Exercise

A. Multiple choice questions

1. Which of the following is a chief ore of silver?

a. Argentite b. Horn silver c. Ruby silver d. Silver copper glance

2. Which of the following ore is subjected to cyanide process?

a. Galena b. Haematite c. Silver glance d. Bauxite

3. Which gas is released when silver nitrate is heated strongly?

a) Oxygen b) Nitrogen c) Nitric oxide d) Nitrogen dioxide

4. Which of the following is lunar caustic?

a. Silver bromide b. Silver nitrate
c. Silver chloride d. Daimmine silver(I) chloride

5. Which of the following is photosensitive?

a. $AgNO_3$ b. $CuSO_4$ c. Ag_2S d. PbS

6. Which of the following is used to prepare indelible ink?

a.AgBr b. Ag_2S c. $AgNO_3$ d. AgCl

7. Which of the following metal is extracted by Mac-Arthur Forrest process?

a.Zn b. Cu c. Fe d.Ag

8. What is the molecular formula of horn silver?

a. Ag_2S b. AgBr c. AgCl d. $AgNO_3$

9. Which of the following compound is used in silvering mirror?

a. Silver nitrate b. Silver chloride c. Silver bromide d. Silver sulphide

10. Which of the following metal cannot displace silver from silver nitrate?

a. Ca b. Au c. Na d. Cu

B. Short answers questions:

11. Give reason,
    - a. Silver coin turns black when exposed to air.
    - b. Silver chloride turns grey when exposed to light.
    - c. Silver nitrate is stored in dark colored bottle.

12. What is Mac-Arthur-Forrest process? What type of element is extracted by this method?

13. Write the chemistry of lunar caustic.

14. Write a note on- Horn silver.

15. A student mistakenly put a piece of copper wire in a vessel containing silver nitrate solution. Predict and explain the likely outcome, including relevant chemical equations and observations. How would you modify the procedure to prevent this error?

16. Silver nitrate is called lunar caustic.
    - a. Write a method of preparation of lunar caustic.
    - b. How does lunar caustic produce black stain on skin?
    - c. What happens when silver nitrate is heated?

17. Write the balanced chemical equation for-
    - a. Action of sodium cyanide on argentite.
    - b. Action of ammonia solution on silver chloride.
    - c. Action of alkali on silver nitrate.

18. Describe the extraction of silver from its chief ore with necessary balanced chemical equation. What is frosting of silver?

C. Long answer question:

19. A coinage metal 'Q' having atomic number 47 lies in group 11 of periodic table. It is most commonly used in jewelry and photgraphy.
- a. Identify the metal 'Q'.
- b. Write the formula of the chief ore of 'Q'.
- c. How would you extract 'Q' starting from its chief ore?
- d. What happens when 'Q' is exposed to air?
- e. What happens when 'Q' is heated**?**
- f. Write any two uses of 'Q'.

PROJECT WORK

1. Prepare a project on, " Electrolytic refining of silver".
2. Take a chart paper and write the steps involved in extraction of silver from its chief ore along with necessary diagrams".
3. Many of utility items used in home are made or contain silver. Take a chart paper and prepare the list of those items that contain silver as one of the main component.
4. Take a chart paper to prepare a presentation analyzing the importance of silver nitrate in various field .

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UNIT 8
HALOALKANES

Activity 1: Identify the following compounds, relate them as isomers and write IUPAC name.

i) $CH_3CH_2CH_2Cl$ ii) $CH_3CH(Cl)CH_3$ ii) $CH_3C(Cl)(CH_3)CH_3$

Know Your Capacity (KYC) 1: Fill in the blank cells of the table

IUPAC Name	Common Name	Molecular Formula	Type of Haloalkane
Chloromethane	Methyl chloride		
	Ethyl bromide	C_2H_5Br	
1-Chloropropane			**Primary haloalkane**
	Isopropyl chloride		
1-Bromo-2-methylpropane			**Primary haloalkane**
	sec-Butyl iodide		
2-Bromo-2-methylpropane			Tertiary haloalkane
1,2-Dichloroethane			

8.1 Introduction

Halogen derivatives of hydrocarbons are called haloalkanes or haloarenes. Halogen derivatives of aliphatic hydrocarbons are called haloalkanes.

$$R - H \xrightarrow{+X,\ -H} R - X$$

In a haloalkane molecule halogen atom is bonded with carbon via covalent bond, it is a polar covalent bond because of the higher electronegativity of halogens than carbon and higher electronegativity difference creat partial charges on carbon and halogen.

The general formula of monohaloalkane is $C_nH_{2n+1}X$, where X represents halogen atom.

Example: CH_3Cl, C_2H_5Br, C_3H_7I

8.2. Nomenclature, Isomerism and classification of monohaloalkanes

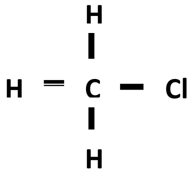
8.2.1. Classification:

Haloalkanes are classified on the basis of

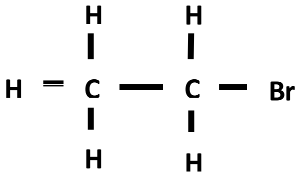
1. Number of halogen atoms:

a) Monohaloalkanes: These are the derivatives of hydrocarbons which contain one halogen atom in place of a hydrogen.

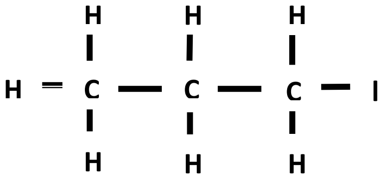
For example: CH_3Cl, C_2H_5Br. C_3H_7I etc.



$$\begin{array}{ccc} & H & \\ & | & \\ H - & C & - Cl \\ & | & \\ & H & \end{array}$$



$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H - & C - & C & - Br \\ & | & | & \\ & H & H & \end{array}$$



$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H - & C - & C - & C & - I \\ & | & | & | & \\ & H & H & H & \end{array}$$

b) Dihaloalkanes: These are the derivatives of hydrocarbons which contain two halogen atoms in place of two hydrogen atoms. Based on the position of these halogen atom, they are classified in to two types-

i) Vicinal dihalides- The dihalides in which two halogen atoms are attached with adjacent carbon atoms in a carbon chain, called vicinal dihalides or vic-dihalides.

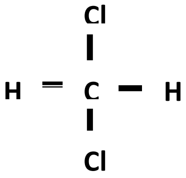
It has general formula- $R\text{-}CHX\text{-}CHX\text{-}R'$

For example- CH_2Cl_2, $C_2H_4Br_2$ etc.

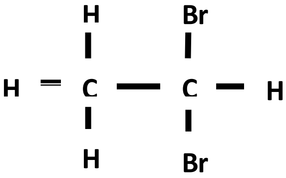
i) Geminal dihalides- The dihalides in which two halogen atoms are attached with same carbon atom in a carbon chain, called geminal dihalides or gem-dihalides.

It has general formula- $R\text{-}CH_2\text{-}CX_2\text{-}R'$

For example- CH_3CHBr_2, CH_2Cl_2, $CH_3CH_2CCl_2CH_3$



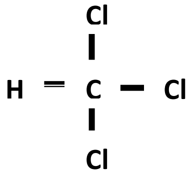
$$\begin{array}{ccc} & Cl & \\ & | & \\ H - & C & - H \\ & | & \\ & Cl & \end{array}$$



$$\begin{array}{cccc} & H & Br & \\ & | & | & \\ H - & C - & C & - H \\ & | & | & \\ & H & Br & \end{array}$$

c) Polyhaloalkanes: These are the derivatives of hydrocarbons which contain more than two halogen atoms in place of hydrogen atoms.

For example: $CHCl_3$, CHI_3 etc.

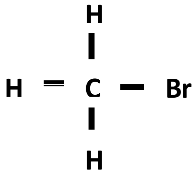


$$\begin{array}{ccc} & Cl & \\ & | & \\ H - & C & - Cl \\ & | & \\ & Cl & \end{array}$$

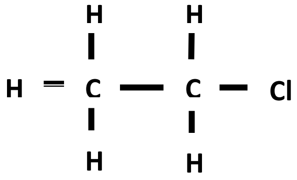
2. Classification on the basis of type of carbon attached to the halogen

a) Primary (1°) haloalkane : The haloalkanes in which halogen attached with primary carbon (carbon bonded with only one or no other carbon atoms) of the compound are called primary (1°) haloalkanes. For example,

$$CH_3Br, CH_3CH_2Cl, \ CH_3CH_2CH_2I \ etc.$$



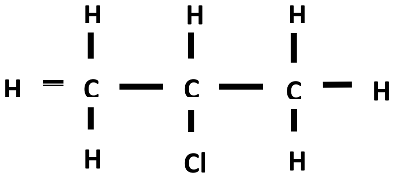
$$\begin{array}{ccc} & H & \\ & | & \\ H - & C & - Br \\ & | & \\ & H & \end{array}$$



$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H - & C & - C & - Cl \\ & | & | & \\ & H & H & \end{array}$$

b) Secondary (2°) haloalkane: The halogen derivatives of hydrocarbons which contain halogen bonded with secondary carbon (carbon bended with two other carbon atoms) of the compound are called secondary (2°) haloalkanes. For example,

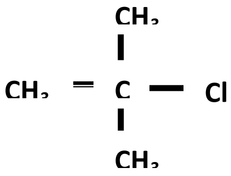
$CH_3CH(Cl)CH_3$



$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H - & C & - C & - C & - H \\ & | & | & | & \\ & H & Cl & H & \end{array}$$

c) Tertiary (3°) haloalkane: The halogen derivatives of hydrocarbons which contain halogen bonded with tertiary carbon (carbon bended with three other carbon atoms) of the compound are called tertiary (3°) haloalkanes. For example,

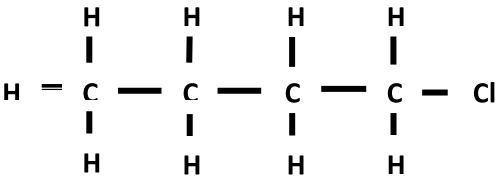
$(CH_3)_3-C-Cl$



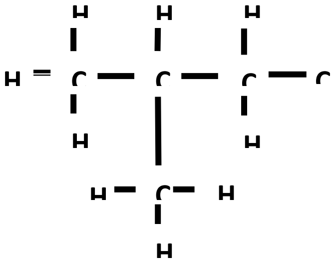
$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3 - & C & - Cl \\ & | & \\ & CH_3 & \end{array}$$

2-Chloro-2-methylpropane

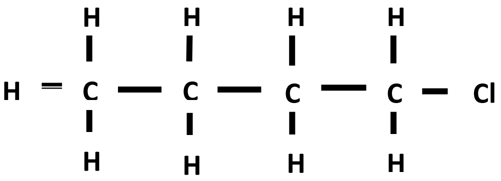
8.2.2. Isomerism:



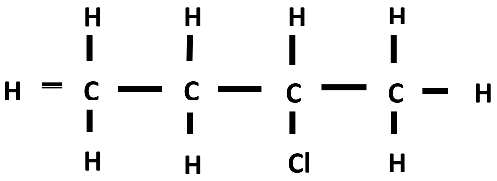
1-Chlorobutane



1-Chloro-2-



1-Chlorobutane

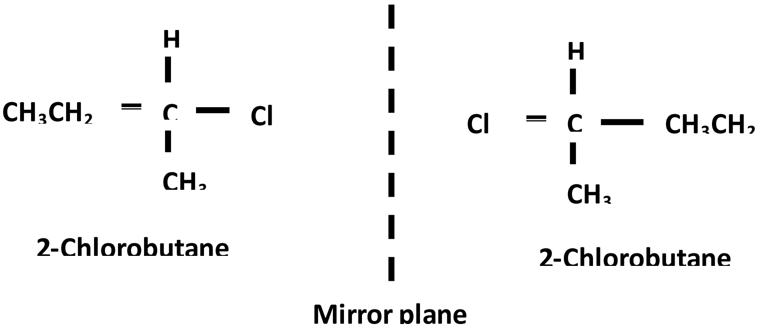


2-Chlorobutane

Haloalkanes exhibit two types of isomerism:

1) Structural Isomerism: The compounds with same molecular formula but different structural arrangement are called structural isomers. Generally haloalkanes exhibit two types of structural isomers;
   i) Chain isomers: The haloalkanes which have same molecular formula but different arrangement of chain are called chain isomers.
   For example: C_4H_9Cl
   ii) Positional isomerism: The haloalkanes which have same molecular formula but different position of halogen in carbon chain are called positional isomers.
   For example: C_4H_9Cl

2) **Stereoisomerism:**



2-Chlorobutane

2-Chlorobutane

Mirror plane

Enantiomers

The compounds having same molecular formula but differ in orientation in space are called stereo isomers. In terms of stereoisomerism halogens with chiral carbon atom shows optical isomerism. In such isomers atoms, their numbers and bonds are same with different special arrangement. These isomers are non-superimposable mirror images and are called enantiomers. For example: $CH_3CH_2CH(CH_3)Cl$

Try yourself: *Express the possible isomers of molecular formula* $C_5H_{11}Cl$ *and write their IUPAC names.*

8.2.3. Nomenclature:

These compounds can be named in two ways:

1. Common naming system
   In this system the name of these compounds is expressed as the name of alkyl group first and followed by the name of halogen as halide; written in two separate words. For example: $CHCl_3$ – Methyl chloride, CH_3CH_2Br – Ethyl bromide.

2. IUPAC Naming System: In this system alkyl halides are called haloalkanes. By choosing longest carbon chain and number the chain to give lowest number to the carbon containing halogen. Follow the rules for other priority orders. The name is written as. one word**.** For example:

   CH_3Cl: Chloromethane, $CH_3CH(CH_3)CH_2Cl$: 1-chloro-2-methylpropane

Compound with formula	**Common Name**	**IUPAC Name**
CH_3-Cl	Methyl Chloride	Chloromethane
CH_3-CH_2-I	Ethyl Iodide	Iodoethane
CH_3-$C(CH_3)_2$-Cl	tert-Butyl Chloride	2-Chloro-2-methylpropane
$CHCl_3$	Chloroform	1,1,1-Trichloromethane

Activity 3:

Objective: To prepare a flow chart for the preparation of haloalkanes from alkane (free radical halogenation), alkene (electrophilic addition) and alcohols (nucleophilic substitution)

Conclusion: Students will understand methods of preparing haloalkanes and the conditions required for each reaction.

8.3 Preparation of monohaloalkanes from alkanes, alkenes and alcohols:

There are varieties of methods for the preparation of haloalkanes, some of them are as follows.

a) From alkanes: Alkanes are saturated simple organic compounds which undergo very few reactions, one of the important reaction is free radical (free radical substitution mechanism) halogenation reaction. It produces haloalkanes but not in pure form, it contains many polyhalogen derivatives..

For example:

$$CH_4 + Cl_2 \xrightarrow{Sun\ light/h\nu} CH_3Cl + HCl$$

If halogen is used in excess

$$\underset{\text{(excess)}}{CH_4 + Cl_2} \xrightarrow[-\,HCl]{h\nu} \underset{\text{(methy chloride)}}{CH_3Cl} \xrightarrow[-\,HCl]{h\nu} \underset{\text{(methylene chloride)}}{CH_2Cl_2} \xrightarrow[-\,HCl]{h\nu} \underset{\text{(chloroform)}}{CHCl_3} \xrightarrow[-\,HCl]{h\nu} \underset{\text{(carbon tetrachloride)}}{CCl_4}$$

This reaction not stops here and the product is contaminated with poly haloalkanes like CH_2Cl_2, $CHCl_3$ and CCl_4. In some extent formation of polyhaloalkanes is controlled by using excess alkane.

Direct iodination of alkanes to produce iodoalkane is not commonly used because iodine is less reactive compared to chlorine and bromine and the reaction tends to be reversible. However it can be carried out in the presence of an oxidizing agent like HIO_3 or HgO to drive the reaction forward.

$$R - H + I_2 \xrightarrow{Oxidizing\ agent} R - I + HI$$

Since HI reacts with iodoalkane to give alkane back, so HIO_3 or HgO is used which removes HI to shift reaction in forward direction.

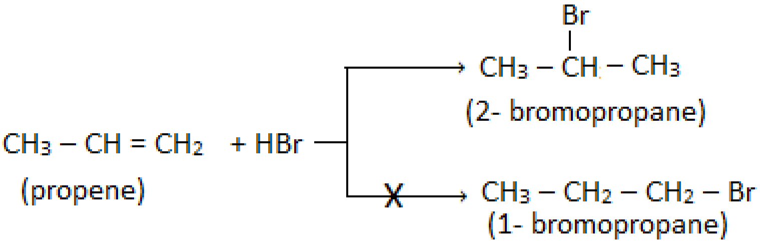
$$5H - I + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

b) From alkenes: When alkenes are treated with halogen acids (HX) respective haloalkanes are obtained. The reactivity order of halogen acids is HI > HBr > HCl > HF.

$$CH_2 = CH_2 + HX \longrightarrow CH_3 - CH_2X$$

But in unsymmetrical alkenes addition of HX follow Markovnicoff’s rule,

Markovnicov's rule



Markovnikov's rule was formulated by Russian chemist **Vladimir Markovnikov** in 1870. This rule describes the outcome of some addition reactions,

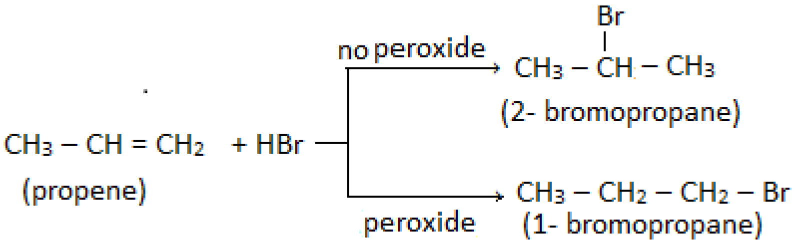
It states that,"When a protic acid (HX) is added to an asymmetric alkene, the hydrogen from the acid bonds to the carbon with more hydrogen atoms, while the halide bonds to the carbon with more alkyl groups (or lesser number of hydrogen atoms).

Markovnikov's rule follow ragioselectivity as positive part of the reagent goes to the double bonded carbon having more hydrogen atoms . It follows electrophilic addition reaction mechanism. It is due to the higher stability of secondary carbocation.

$$CH_2 = CH_2 \ + \ HBr \quad \rightarrow \quad CH_3\text{-}CH_2Br$$

$$CH_3CH{=}CH_2 \ + \ HBr \quad \rightarrow \quad CH_3 \text{ - } CH\ (Br)\text{-}CH_3$$

Anti-Markonikov's addition:



It is also known as **Peroxide Effect or Kharasch Effect.** This is a type of addition reaction (in organic chemistry) where the product forms in the opposite manner to that predicted by Markovnikov;s rule. This reaction do not occur through formation of carbocation but through the formation of free radicals (due to the presence of organic peroxide, which is a free radical ionizing substance).

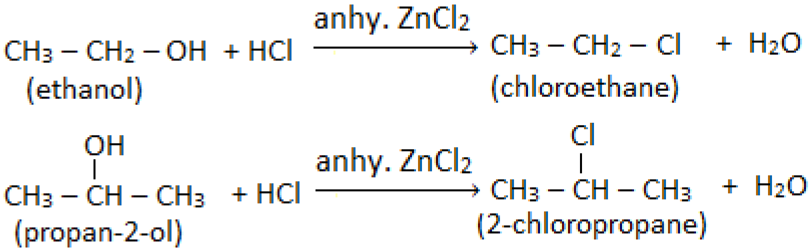
According to this effect," when HBr is added to an unsymmetrical alkene in presence of organic peroxide then hydrogen goes to the more substituted carbon having double bond". It is the product opposite that of Markonikov's addition.

Do you know: Peroxide effect follows free radical mechanism and occurs only in case of HBr but not in HCl and HI. In HCl it is difficult for homogeneous cleavage to produce free radical while in case of HI, iodine free radical combined together to produce I_2

C. From Alcohols:

Generally alkyl halides are prepared from alcohols by displacement of —OH group by an halogen ion. This is usually by using Lucas reagent, HX or PX_3 or PX_5

(i) Use of Lucas reagent- It is a mixture of conc. HCl and anhy. $ZnCl_2$ It is used to convert alcohols into haloalkanes through substitution reaction.



$$\underset{\text{(ethanol)}}{CH_3-CH_2-OH} + HCl \xrightarrow{\text{anhy. } ZnCl_2} \underset{\text{(chloroethane)}}{CH_3-CH_2-Cl} + H_2O$$

$$\underset{\text{(propan-2-ol)}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3} + HCl \xrightarrow{\text{anhy. } ZnCl_2} \underset{\text{(2-chloropropane)}}{CH_3-\overset{\overset{Cl}{|}}{C}H-CH_3} + H_2O$$

As anhy. $ZnCl_2$ is a Lewis acid it coordinates with the oxygen of alcohol and in this reaction anhy. $ZnCl_2$ helps to break C-O bond.

(ii) Similarly phosphorous halides reacts with alcohols to give alkyl halide which gives more than 80% yield.

With PX_3:

$$\underset{\text{(alcohol)}}{3R-OH} + PX_3 \xrightarrow{\Delta} \underset{\text{(haloaklane)}}{3R-X} + \underset{\text{(phosphorus acid)}}{H_3PO_3}$$

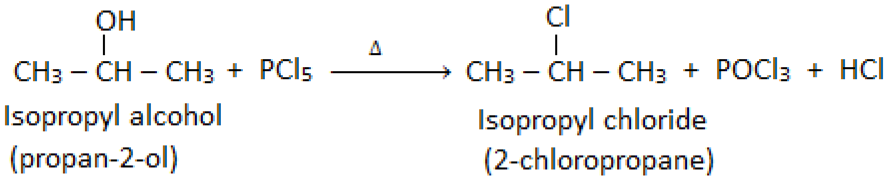
$$3\,CH_3OH + PCl_3 \xrightarrow{\Delta} 3CH_3Cl + H_3PO_3$$

$$3CH_3CH_2CH_2OH + PCl_3 \xrightarrow{\Delta} 3CH_3CH_2CH_2Cl + H_3PO_3$$

With PX_5 :

$$R-OH + PX_5 \xrightarrow{\Delta} R-X + POX_3 + HX$$

$$CH_3CH_2OH + PCl_5 \xrightarrow{\Delta} CH_3CH_2Cl + POCl_3 + HCl$$



$$\underset{\substack{\text{Isopropyl alcohol}\\ \text{(propan-2-ol)}}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3} + PCl_5 \xrightarrow{\Delta} \underset{\substack{\text{Isopropyl chloride}\\ \text{(2-chloropropane)}}}{CH_3-\overset{\overset{Cl}{|}}{C}H-CH_3} + POCl_3 + HCl$$

With thionyl chloride ($SOCl_2$):

When alcohol is refluxed with SOCl2 in presence of pyridine chloroalkane is obtained.

$$R-OH+SOCl_2\xrightarrow{Reflux,\ Pyridin}R-Cl+SO_2\uparrow+HCl\uparrow$$

$$CH_3CH_2-OH+SOCl_2\xrightarrow{Reflux,\ Pyridin}CH_3CH_2-Cl+SO_2\uparrow+HCl\uparrow$$

Since SO2 and HCl are gases .so haloalkane produced is pure.

Activity 3:

Objective: To compare the boiling point of chloroethane, bromoethane and iodoethane with the reason behind it.

Conclusion: Students will understand the effect of size of halogen in boiling point.

8.4 Physical properties of monohaloalkanes:

Lower members of haloalkanes (monohaloalkanes) like CH_3X, C_2H_5X are colourless gases but higher members are colourless liquids up to the alcohols of 18 carbons while, the higher members are colourless solids.

Density and boiling point of alcohols depend upon molecular mass i.e. density and boiling point increases with increasing molecular mass. For example b.p. and density of some compounds on increasing order is

$$CH_3Cl < C_2H_5Cl < C_3H_7Cl < C_4H_9Cl$$

Increased branching in haloalkanes decreases their boling point. As branching increases in a haloalkane, the surface area decreases which reduces Van der Waals forces and leading to a lower boiling point.

Try yourself: How would you suggest the reason behind less solubility of haloalkanes in water?

Activity 4

Objective: To compare the reactivity towards nucleophilic substitution reaction of chloroethane, bromoethane and iodoethane.

Conclusion: Students will understand the effect of size of halogen on reactivity and bond strength.

Know Your Capacity (KYC) 2: Match the following

Column A (Properties/Concepts)	**Column B (Descriptions/Reactions)**
1. Boiling point in haloalkanes	A .Reaction of haloalkane with **Mg in dry ether** to form RMgX
2. SN1 reaction	B. Undergoes **β-elimination** to form alkenes
3. SN2 reaction	C. Wurtz reaction, forms **alkanes** (R-R)
4. C-X bond polarity	D Forms **alcohols** through nucleophilic substitution.
5. Grignard reagent formation	E Increases as the size of the halogen increases (RI > RBr > RCl)
6. Reaction with aqueous NaOH	F. Carbon is **partially positive (δ^+)**, and halogen is **partially negative (δ^-)**
7. Reaction with Na in dry ether	G. AgCl (white ppt), AgBr (cream ppt), AgI (yellow ppt) forms
8. Reaction with alcoholic KOH	H. Favors **tertiary haloalkanes** and forms a carbocation intermediate
9. Silver nitrate test for halides	I. Favors **primary haloalkanes** and occurs via a single-step mechanism

8.5 Chemical properties, Substitution reactions SN1 and SN2 reactions.:

Activity 5:

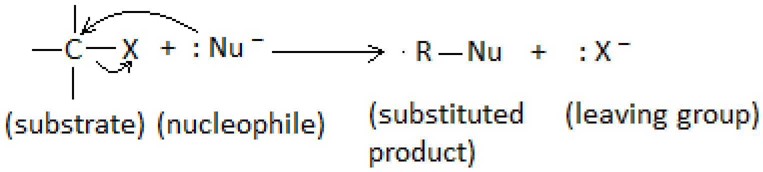
Objective: To write the following reactions

i) React tert. Butyl bromide with aq.KOH.
ii) React methyl bromide with aq. KOH.

Compare the reaction rates and product formed.

Conclusion: Students will understand the difference between SN1 and SN2 mechanism, including the role of substrate (alkyl halides).

8.5.1. Nucleophilic substitution reactions:



In alkyl halide halogen is attached as a nucleophile, when any other nucleophile which is stronger than halogen attack on alkyl halide, halogen get replaced (or substituted) from alkyl halide. Such reaction is called nucleophilic substitution reaction. Halogen which is detached from haloalkane is called leaving group.

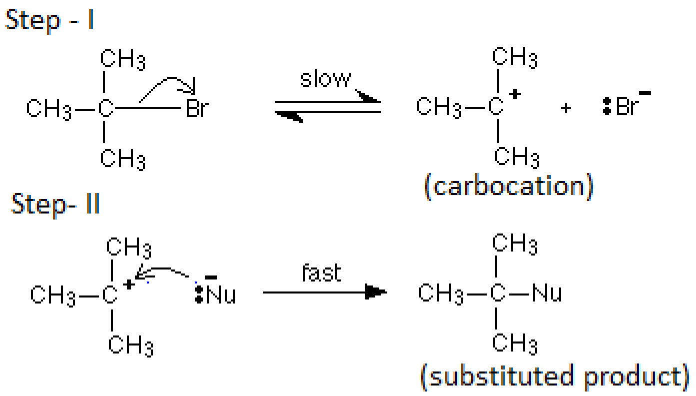
Nucleophilic substitution reaction occur mainly through two ways i.e. SN1 and SN2 reactions.Main difference in these two types is the bond formation and bond breaking steps.

SN1 Reaction: This is the nucleophilic substitution reaction which occurs through two steps. The first step involves in breaking of bond between carbon and halogen to form carbocation which is a slow rate determining step.In ther second step there is fast addition of nucleophile to the carbocation to give the substitution product. The rate of reaction depends upon concentration of substrate i.e.

show first order kinetics. In SN1 reaction Racemization occurs due to the formation of carbocation intermediate. The nucleophile can attack from either the front or the back of the planner carbocation with equal probability which leads to the formation of both R and S enantiomers. Complete racemization occurs only if the nucleophile attacks with equal probability from both sides. However, sometimes slight retention of configuration is seen due to ion-pair interaction with leaving group.

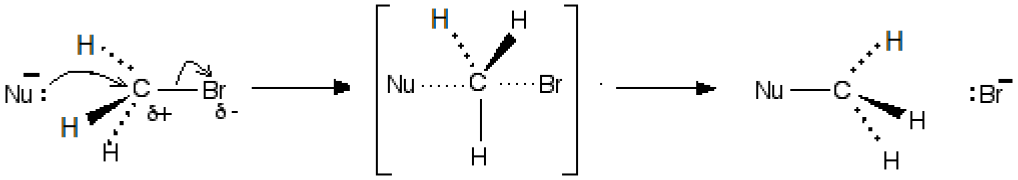
$$Rate \propto [substrate]$$

$$Rate = K[substrate]$$



On the basis of stability of carbocation reactivity follows the order $3^o > 2^o > 1^o >$ methyl carbocation

SN2 reaction:



(transition state)

This is the nucleophilic substitution reaction which completes in single step by forming intermediate transition state. In this reaction incoming nucleophile attack on carbon containing halogen from back side to form unstable five- membered transition state. Breaking and formation of bond with leaving group and incoming nucleophile occur simultaneously to give stable substituted product. The important characteristic feature of SN2 reaction is inversion of configuration at the center of reaction as nucleophile attack from opposite side of the leaving group.

The rate of reaction depend upon the concentration of both substrate and nucleophile. So it follow second order kinetics. Presence of bulky group (Steric hindrance) affect the rate of reaction, so reactivity of haloalkane towards SN2 reaction follow the order,

Methyl halide $>1^o > 2^o > 3^o$

8.6 . Formation of alcohol, nitrile, amine, ether, thioether, carbylamines, nitrite and nitro alkane using haloalkanes.

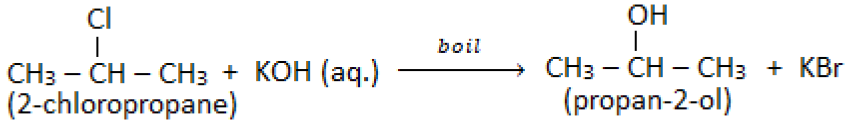
8.6.1: Formation of alcohol:

Alcohol is obtained from haloalkane by a substitution reaction, in which haloalkane is boiled with aqueous solution of KOH.

$$RX + KOH_{(aq)} \xrightarrow{boil} ROH + KX$$

e.g.

$$CH_3CH_2Cl + KOH_{(aq)} \xrightarrow{boil} CH_3CH_2OH + KCl$$



$$\underset{\text{(2-chloropropane)}}{CH_3-\overset{\overset{Cl}{|}}{C}H-CH_3} + KOH\,(aq.) \xrightarrow{boil} \underset{\text{(propan-2-ol)}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3} + KBr$$

There is another method for the preparation of alcohol from haloalkane (substitution of halogen by –OH), in which haloalkane is boiled with moist silver oxide.

$$Ag_2O + H_2O \quad \rightarrow \quad 2AgOH$$

$$CH_3CH_2Cl + AgOH \xrightarrow{boil} CH_3CH_2OH + AgCl$$

8.6.2. Formation of nitrile:

Alcoholic solution of KCN produces alkane nitrile (alkyl cyanide) as major product when treated with haloalkane.

$$RX + KCN_{(alc.)} \quad \rightarrow \quad RCN + KX$$

e.g.

$$CH_3CH_2Cl + \text{alc. KCN} \quad \rightarrow \quad CH_3CH_2-C \equiv N \ + KCl$$

Propane nitrile

(Ethyl cyanide)

But when haloalkane is treated with AgCN it produces iso cyanide.

$$R-X + \text{alc. AgCN} \longrightarrow \underset{\text{(Alkyl isocyanide)}}{R-N \overset{\rightarrow}{\equiv} C} + AgX$$

eg.

$$CH_3CH_2Br + \text{alc. AgCN} \longrightarrow \underset{\text{(ethyl isocyanide)}}{CH_3CH_2NC} + AgBr$$

In KCN, there is an ionic bond between K^+ and CN^- . The CN^- acts as a nucleophile and forms a bond with alkyl group through carbon of cyanide ion resulting in the formation of alkyl cyanide (R-CN).

However in AgCN, the Ag-CN bond is covalent, preventing the free release of CN^- ion. As a result, the nucleophilic attack occurs through lone pair on nitrogen leading to the formation of alkyl isocyanide (R-NC). This behavior shows that the cyanide ion is an ambident nucleophile. Therefore it can attack from either the carbon or nitrogen, depending on the reaction condition.

If the reaction is followed by hydrolysis then different organic compounds can be obtained.

a) Partial hydrolysis produces amide.

$$R-C\equiv N + H_2O \xrightarrow[\text{or alkaline } H_2O_2]{\text{conc. HCl}} \underset{\text{(amide)}}{RCONH_2}$$

b) Complete hydrolysis in presence of acid and alkaline H_2O_2 produces acid.

$$R-C\equiv N + H_2O \xrightarrow{H^+} \underset{\text{(acid)}}{RCOOH} + NH_3$$

c) Reduction of alkyl cyanide by reducing agent like $LiAlH_4$ or Na/ C_2H_5OH or H_2/Ni produces primary amine.

$$R-C\equiv N + 4[H] \xrightarrow[\text{Na}/C_2H_5OH \text{ or } H_2/\text{Ni}]{LiAlH_4 \text{ or}} \underset{(1^0 \text{ amine})}{RCH_2NH_2}$$

eg.

$$\underset{\text{(propanenitrile)}}{CH_3CH_2-C\equiv N} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{(propanamine)}}{CH_3CH_2CH_2NH_2}$$

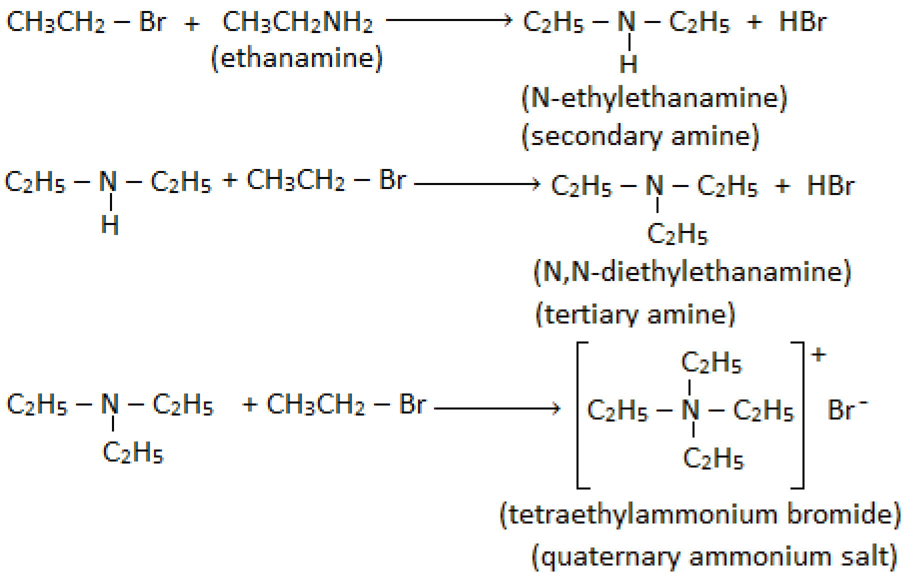
Formation of Amine:

When alkyl halide is heated with alcoholic solution of ammonia in a sealed tube primary amines are obtained

$$R-X + NH_3\text{ (alc.)} \longrightarrow RNH_2 + HBr$$

$$CH_3CH_2-Br + NH_3 \longrightarrow \underset{\substack{\text{(ethanamine)}\\ \text{(primary amine)}}}{CH_3CH_2NH_2} + HBr$$

If haloalkane is used in excess, this process involves series of reactions. On adding excess haloalkane it reacts with primary amine produced in the reaction to give secondary amine. Similarly it gives tertiary and quaternary ammonium salt.



$$CH_3CH_2-Br + \underset{\text{(ethanamine)}}{CH_3CH_2NH_2} \longrightarrow C_2H_5-\underset{\underset{H}{|}}{N}-C_2H_5 + HBr$$

(N-ethylethanamine)
(secondary amine)

$$C_2H_5-\underset{\underset{H}{|}}{N}-C_2H_5 + CH_3CH_2-Br \longrightarrow C_2H_5-\underset{\underset{C_2H_5}{|}}{N}-C_2H_5 + HBr$$

(N,N-diethylethanamine)
(tertiary amine)

$$C_2H_5-\underset{\underset{C_2H_5}{|}}{N}-C_2H_5 + CH_3CH_2-Br \longrightarrow \left[C_2H_5-\overset{\overset{C_2H_5}{|}}{\underset{\underset{C_2H_5}{|}}{N}}-C_2H_5 \right]^+ Br^-$$

(tetraethylammonium bromide)
(quaternary ammonium salt)

Formation of ether: (Williamson's ether synthesis)

When haloalkane is treated with sodium alkoxide it produces ether. The process is known as Williamson's ether synthesis. Both symmetrical and unsymmetrical ethers can be prepared by this method

$$R-X + R'ONa \longrightarrow \underset{\text{(ether)}}{R-O-R'} + NaX$$

eg.

$$CH_3CH_2-Br + \underset{\text{(sod. methoxide)}}{CH_3-ONa} \longrightarrow \underset{\text{(methoxy ethane)}}{CH_3CH_2-O-CH_3} + NaBr$$

$$CH_3CH_2-Br + \underset{\text{(sod. ethoxide)}}{CH_3-CH_2-ONa} \longrightarrow \underset{\text{(ethoxy ethane)}}{CH_3CH_2-O-CH_2-CH_3} + NaBr$$

Formation of Thioether:

When alkyl halide is heated with Sodium or potassium sulphide in presence of aqueous ethanol thioether is produced.

$$RX + Na_2S \xrightarrow{\Delta, C_2H_5OH/H_2O} R-S-R + 2NaX$$

$$CH_3CH_2Br + Na_2S \xrightarrow{\Delta, C_2H_5OH/H_2O} CH_3-S-CH_3 + 2NaBr$$

Formation of carbylamine:

When trihaloalkane is treated with primary amine in presence of alcoholic solution of alkali like KOH, isocyanide or carbylamine is produced. This reaction is called carbylamine reaction.

$$R\text{-}NH_2 + CHCl_3 + 3KOH_{(alc)} \xrightarrow{\Delta} R\text{-}NC + 3KCl + 3H_20$$

$$CH_3\text{-}NH_2 + CHCl_3 + 3KOH_{(alc)} \xrightarrow{\Delta} CH_3\text{-}NC + 3KCl + 3H_2O$$

Formation of nitroalkane and nitrite:

Reaction with $AgNO_2$

In $AgNO_2$, Ag to O bond is covalent and lone pairs of electrons are available in both oxygen and nitrogen. Since nitrogen is less electronegative than oxygen, so lone pair on nitrogen is easily available for bonding. Thus the reaction between haloalkane and silver nitrite produces nitroalkane.

$$\underset{}{R-X + AgNO_2\ (alc.)} \longrightarrow \underset{(nitroalkane)}{R-NO_2} + AgX$$

eg.

$$CH_3CH_2-Br + AgNO_2\ (alc.) \longrightarrow \underset{(nitroethane)}{CH_3CH_2NO_2} + AgBr$$

Reaction with KNO_2

In KNO_2 , K to O bond is ionic in nature and one of the oxygen bear negative charge. Thus during the reaction between haloalkane and KNO_2, negatively charged oxygen is easily available for bonding and product will be alkyl nitrite.

$$R-X + KNO_2 \longrightarrow R-O-N=O + KX$$

eg.

$$CH_3CH_2-Br + KNO_2 \longrightarrow \underset{(Ethyl\ nitrite)}{CH_3CH_2-O-N=O} + KBr$$

Do you know: -NO_2 is an ambident nucleophile as it has two binding sites. . Nitrogen and oxygen both in KNO_2t are able hrough which attack can take place. This can be observed from above reactions.

8.7 Elimination reaction (dehydrohalogenation-saytzeff's rule), Reduction reactions, Wurtz reaction:

8.7.1. Elimination reaction (dehydrohalogenation-saytzeff's rule)

It is also known as α, β-elimination reaction because it involves elimination of halogen from α-carbon and hydrogen from β- carbon in presence of alcoholic KOH or NaOH. Thus, on treating haloalkane in presence of alcoholic KOH or NaOH, hydrogen and a halogen are eliminated from haloalkane to produce alkene, known as dehydrohalogenation reaction or α, β-elimination reaction.

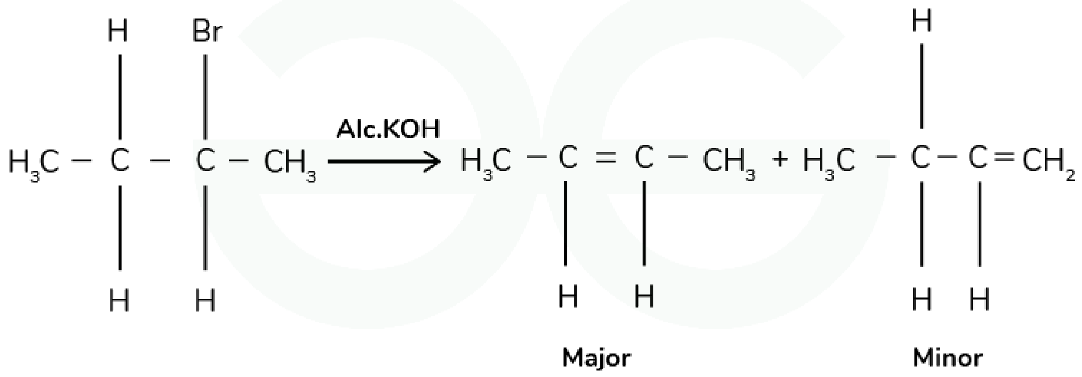
$$CH_3 - CH_2Cl + KOH_{(alc)} \longrightarrow CH_2 = CH_2 + KCl + H_2O$$

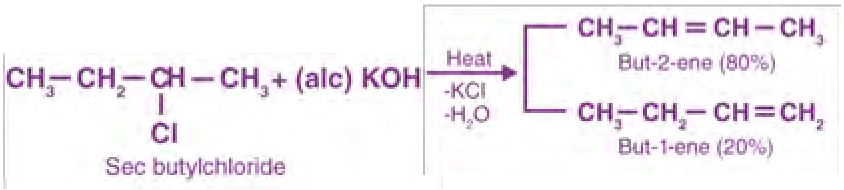
$$CH_3 - CH_2 - CH_2Br + KOH_{(alc)} \longrightarrow CH_3 - CH = CH_2 + KBr + H_2O$$

8.7.2. Saytzeff's rule

Saytzeff's rule explains that, removal of- β-Hydrogen atom from haloalkane takes place from more substituted β -carbon atom (having more number of alkyl groups), therefore more stable alkene is formed. e.g.,

$$CH_3-CH_2-CHBr-CH_3+KOH_{(alc)} \longrightarrow CH_3-CH=\mathrm{CH}-CH_2+KBr+\ H_2O$$





Reduction reaction:

Haloalkanes are reduced in presence of reducing agent like $LiAlH_4$, H_2/Ni, Na/ethanol, Zn/HCl, HI/Red phosphorus etc.,

$$R-X\ +\ 2[H] \xrightarrow[\text{or LiAlH}_4]{\text{Zn/HCl or Na/ethanol}} R-H\ +\ HX$$

eg.

$$CH_3CH_2Br + 2[H] \xrightarrow{''} \underset{\text{(ethane)}}{CH_3-CH_3} + HBr$$

$$\underset{\text{(chloroethane)}}{CH_3CH_2-Cl} + H_2 \xrightarrow{Ni} \underset{\text{(ethane)}}{CH_3-CH_3} + HBr$$

8.7.3. Wurtz Reaction:

The reaction of haloalkane with sodium metal in presence of dry ether to produce a new alkane with higher number of carbon atoms is called wurtz reaction.

$$R\boxed{-X+2Na+X}-R \xrightarrow{Dry\ ether} \underset{\text{Alkane}}{R-R}+2\ NaX$$

$$CH_3 - \boxed{Br + 2Na + Br} - CH_3 \xrightarrow{Dry\ ether} CH_3 - CH_3 + 2\ NaBr$$

Ethane

$$CH_3 - \boxed{I + 2Na + I} - CH_3 \xrightarrow{Dry\ ether} 2NaI + CH_3 - CH_3$$

Ethane

$$CH_3CH_2 - \boxed{I + 2Na + I} - CH_2CH_3 \xrightarrow{Dry\ ether} 2NaI + CH_3CH_2 - CH_2CH_3$$

Butane

8.7.4. Reaction with magnesium (Mg).

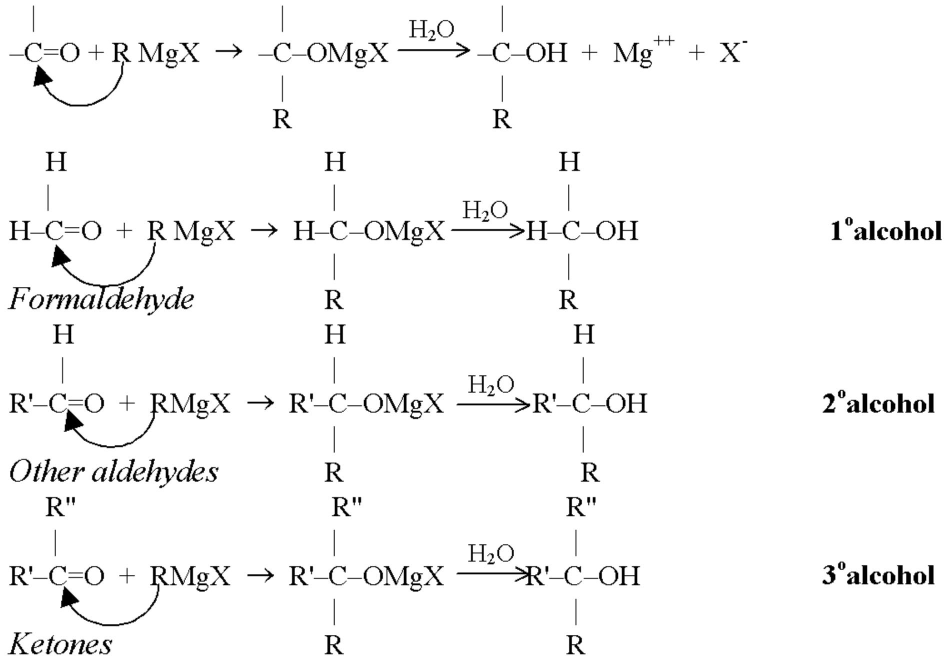
When an alkyl halide/aryl halide is treated with magnesium in presemce of dry ether, alkyl/aryl magnesium halide is obtained through insertion reaction (Mg get inserted between carbon (of alkyl/aryl) and halogen. The product obtained from this reaction is called Grignard reagent (R-Mg-X).

$$R - X + Mg \xrightarrow{Dry\ ether} R - Mg - X$$

$$CH_3 - Br + Mg \xrightarrow{Dry\ ether} CH_3 - Mg - Br$$

Methyl magnesium bromide
(Grignard reagent)

Some reactions of Grignard reagent.



$$-\overset{|}{C}=O + RMgX \rightarrow -\overset{|}{\underset{\underset{R}{|}}{C}}-OMgX \xrightarrow{H_2O} -\overset{|}{\underset{\underset{R}{|}}{C}}-OH + Mg^{++} + X^-$$

$$H-\overset{\overset{H}{|}}{C}=O + RMgX \rightarrow H-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-OMgX \xrightarrow{H_2O} H-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-OH \quad \textbf{1°alcohol}$$

Formaldehyde

$$R'-\overset{\overset{H}{|}}{C}=O + RMgX \rightarrow R'-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-OMgX \xrightarrow{H_2O} R'-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-OH \quad \textbf{2°alcohol}$$

Other aldehydes

$$R'-\overset{\overset{R''}{|}}{C}=O + RMgX \rightarrow R'-\overset{\overset{R''}{|}}{\underset{\underset{R}{|}}{C}}-OMgX \xrightarrow{H_2O} R'-\overset{\overset{R''}{|}}{\underset{\underset{R}{|}}{C}}-OH \quad \textbf{3°alcohol}$$

Ketones

Victor Grignard (1871-1935), a French chemist, discovered the Grignard reagent in 1900, revolutionizing organic synthesis by enabling carbon-carbon bond formation. He earned the Nobel Prize in chemistry in 1912. Grignard also contributed to industrial chemistry during World War I, particularly in pharmaceuticals and explosives. His work remains influential in organic chemistry

8.7.4. Reaction with Lithium (Li).

Treatment of alkyl halide with lithium produces alkyl lithium and lithium halide.

$$R-X+2Li \longrightarrow \mathrm{R-LI + Li\text{-}X}$$

$$CH_3-Br+2Li \longrightarrow CH_3Li+Li-Br$$

Activity: Fill in the blank cells

Object: It gives the idea about reaction with reagent and conditions.

Reactant	Reagent	Conditions	Product
Methane (CH_4)	______	UV light	**Chloromethane (CH_3Cl)**
Ethene (C_2H_4)	HBr	______	______
Alcohol (ROH)	**PCl_5**	Room temperature	______
1-Propanol (C_3H_7OH)	$SOCl_2$	**Pyridine**	______
______	NaBr + H_2SO_4	Heat	**Bromoethane (C_2H_5Br)**
Toluene ($C_6H_5CH_3$)	Cl_2	______	Benzyl chloride ($C_6H_5CH_2Cl$)
Propene (C_3H_6)	**HCl**	**Peroxide absent**	______
Acetone (CH_3COCH_3)	PCl_5	______	**Trichloromethane ($CHCl_3$)**

Know Your Capacity (KYC) 3:

In equal volumes of 1-bromopropane, 2-bromopropane and 2-bromo-2-methylpropane, small amount of $AgNO_3$ (in ethanol) is added. After observing the precipitation of AgBr, answer the following questions.

i) Which compound gives precipitate fastest?

ii) What does this indicate about reaction mechanism?

iii) Arrange the haloalkanes in order of reactivity.

8.8. Tri-chloromethane or Chloroform ($CHCl_3$)

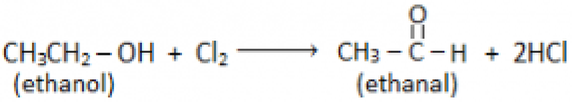
It is a tri-halogen compound with molecular formula ($CHCl_3$) in which three chlorine atoms are covalently bonded with carbon.

8.8.1. Preparation: In the laboratory chloroform is prepared by heating ethyl alcohol (ethanol) or acetone (propanone) with the paste of bleaching powder.

$$CaOCl_2 + H_2O \longrightarrow \underset{\text{(bleaching powder paste)}}{Ca(OH)_2 + Cl_2}$$

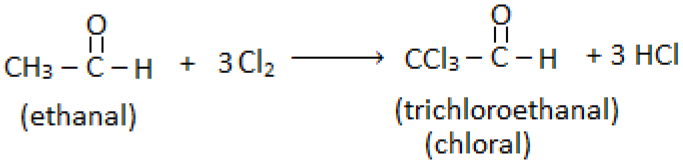
(i) From ethanol:

Step I: Oxidation: In this step ethanol is oxidized by chlorine obtained from bleaching powder.



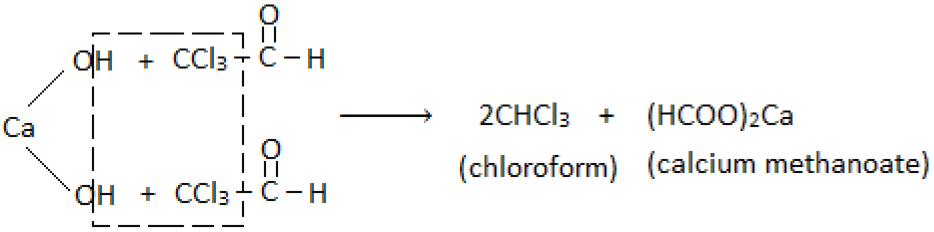
$$\underset{\text{(ethanol)}}{CH_3CH_2-OH} + Cl_2 \longrightarrow \underset{\text{(ethanal)}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H} + 2HCl$$

Step II: Chlorination: Nascent chlorine obtained from the paste of bleaching powder reacts with ethanal to produce trichloroethanal (Chloral).



$$\underset{\text{(ethanal)}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H} + 3Cl_2 \longrightarrow \underset{\substack{\text{(trichloroethanal)}\\ \text{(chloral)}}}{CCl_3-\overset{\overset{\displaystyle O}{||}}{C}-H} + 3HCl$$

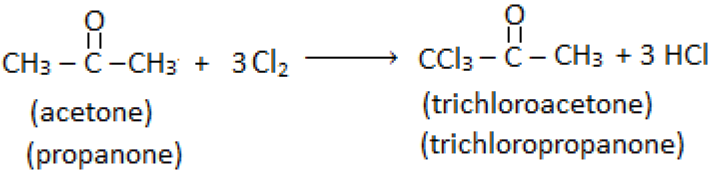
Step III: Hydrolysis: In this step Chloral is hydrolysed by $Ca(OH)_2$ to produce chloroform.



$$Ca(OH)_2 + 2\,CCl_3-\overset{\overset{\displaystyle O}{||}}{C}-H \longrightarrow \underset{\text{(chloroform)}}{2CHCl_3} + \underset{\text{(calcium methanoate)}}{(HCOO)_2Ca}$$

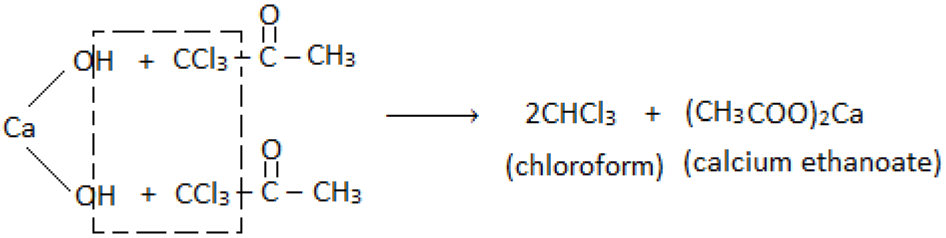
ii) From Acetone:

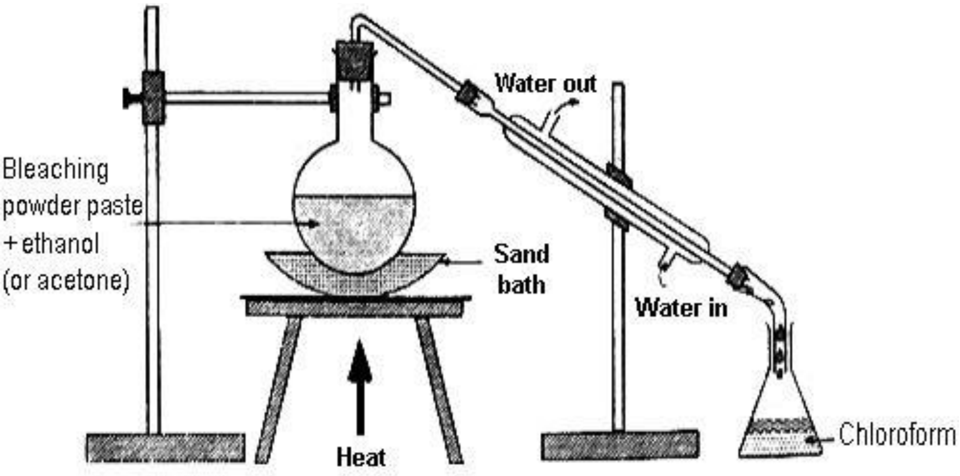
Step I: When chlorine, obtained from paste of bleaching powder, reacts with acetone, trichloroacetone (or chloretone) is formed.



$$\underset{\substack{\text{(acetone)}\\ \text{(propanone)}}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3} + 3Cl_2 \longrightarrow \underset{\substack{\text{(trichloroacetone)}\\ \text{(trichloropropanone)}}}{CCl_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3} + 3HCl$$

Step II: In this step chloretone is hydrolyzed by $Ca(OH)_2$ to produce chloroform.





8.9. Properties of chloroform

8.9.1. Physical properties.

i) Chloroform is a colorless liquid with sweet smell

ii) It has boiling point 61°C and freezing point -63°C.

iii) It is heavier than water

iv) It dissolves well in organic solvent but slightly soluble in water

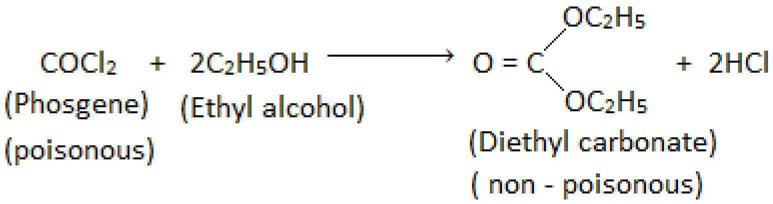
v) Its vapor induce unconsciousness, making it useful as anesthetic in surgery

Chemical properties of chloroform

8.9.1. Oxidation: Chloroform reacts with air and sunlight to form a toxic gas phosgene.

$$2\,CHCl_3 + O_2 \xrightarrow{h\upsilon} \underset{\substack{\text{(phosgene)}\\ \text{(carbonyl chloride)}}}{2COCl_2} + 2HCl$$

To prevent chloroform from oxidation, it is stored in a brown coloured bottle filled to the brim, with a small amount of ethanol to convert phosgene in to the non-toxic diethyl carbonate.



8.9.2. Reduction of Chloroform

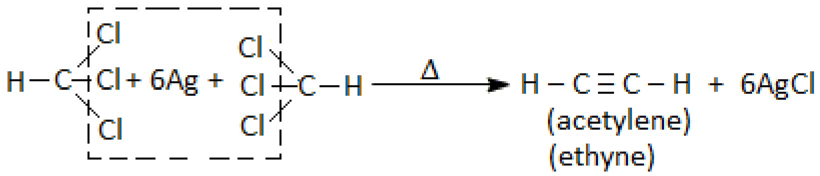
When chloroform undergoes reduction in acidic medium (Zn / HCl), it forms methylene chloride where as in neutral medium (Zn / H_2O), it produces methane.

$$CHCl_3 + 2[H] \xrightarrow{Zn/HCl} \underset{\substack{\text{(methylene chloride)}\\\text{(dichloromethane)}}}{CH_2Cl_2} + HCl$$

$$CHCl_3 + 6[H] \xrightarrow{Zn/H_2O} \underset{\text{(methane)}}{CH_4} + 3HCl$$

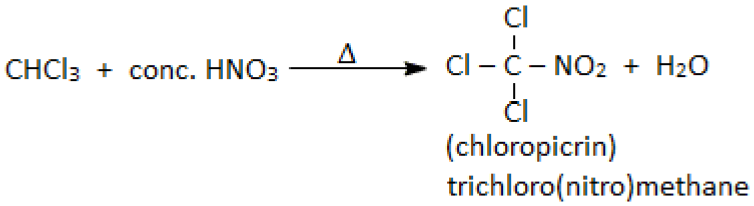
8.9.3. Action of chloroform on silver powder

On heating chloroform with silver powder produces acetylene (or ethyne).



8.9.4. Reaction with conc. Nitric acid:

On heating with conc. Nitric acid, chloroform produces chloropicrin



$$CHCl_3 + \text{conc. } HNO_3 \xrightarrow{\Delta} Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-NO_2 + H_2O$$

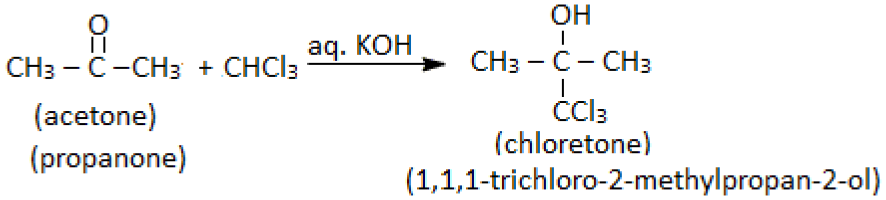
(chloropicrin)

trichloro(nitro)methane

Do you know: *Chloropicrin is a strong tear gas and toxic in nature which is widely used during First World War*

8.9.5. Reaction with propanone (acetone)

Chloroform reacts with propanone in the presence of alkali, such as aq. KOH, to produce chloretone. It is used as hypnotic (sleep inducing) drug.



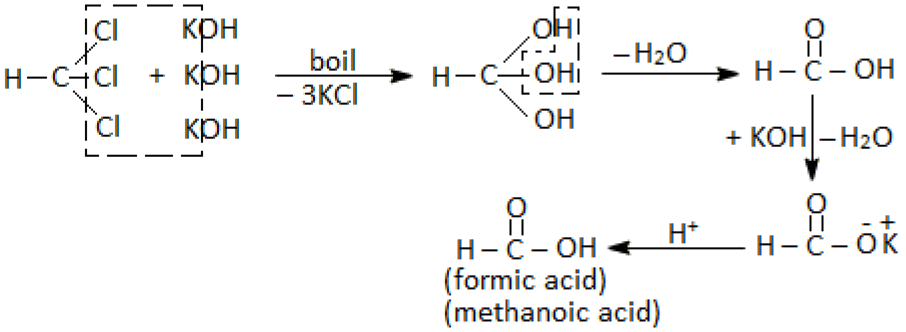
$$CH_3-\overset{\overset{O}{||}}{C}-CH_3 + CHCl_3 \xrightarrow{\text{aq. KOH}} CH_3-\underset{\underset{CCl_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

(acetone)
(propanone)

(chloretone)
(1,1,1-trichloro-2-methylpropan-2-ol)

8.9.6. Reaction with aqueous alkali

Boiling chloroform with aq.KOH hydrolyses it to form potassium formate, which, on acidification, yields formic acid.



(formic acid)
(methanoic acid)

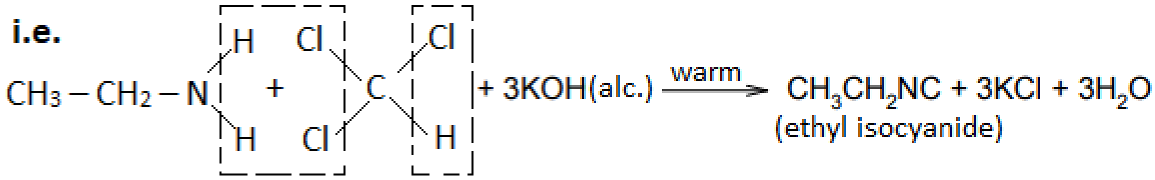
8.9.7. Reaction with primary amine in presence of aqueous alkali:

When chloroform is heated with primary amine in presence of alcoholic KOH or NaOH, it produces isocyanide or carbylamines, so it is also known as **Carbylamine reaction**.

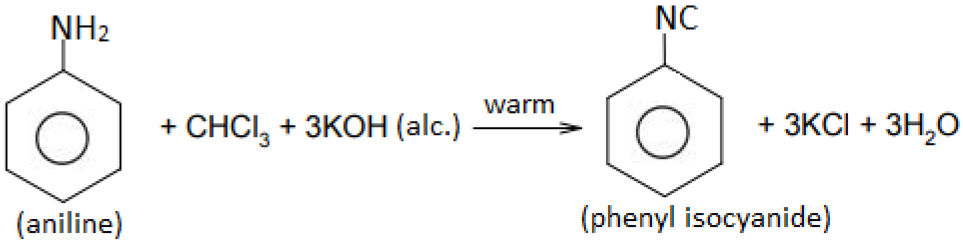
$$CH_3CH_2NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\text{warm}} CH_3CH_2NC + 3KCl + 3H_2O$$

(ethanamine) (ethyl isocyanide)

i.e.



(ethyl isocyanide)

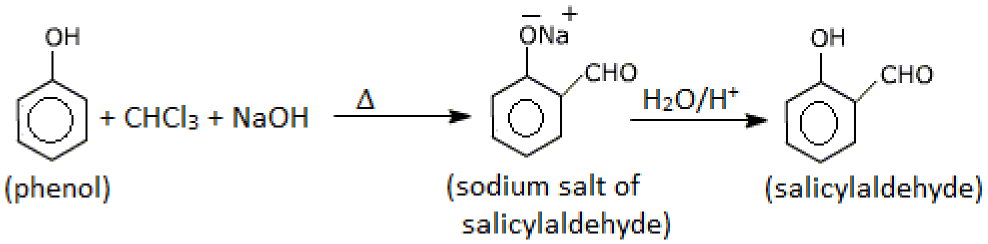


(aniline)

(phenyl isocyanide)

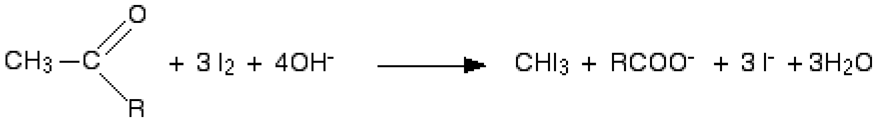
8.9.7. Reaction with phenol in presence of aqueous alkali: (**Riemer-Tiemann reaction.)**

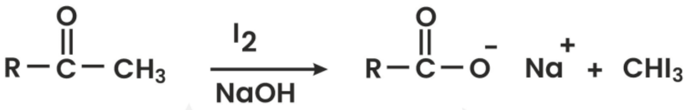
When phenol is treated with chloroform in presence of alkali at about 70^oC, it produces salicylaldehyde. This reaction is known as **Riemer-Tiemann reaction.**



Iodoform (CHI_3)

It is a tri-iodo methane and has properties like that of chloroform. Iodoform is widely used for a special test called Iodoform test. This test is positive for the compounds having $CH_3C\text{-}O$ group. E.g.





$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[NaOH]{I_2} R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\ \overset{+}{Na} + CHI_3$$

$$R-\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[NaOH]{I_2} R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\ \overset{+}{Na} + CHI_3$$

Exercise 8.1

Multiple Choice Questions:

1. The general molecular formula of haloalkane is

a. $a. C_nH_{2n+2}X$ b. $C_nH_{2n-2}X$ c. $C_nH_{2n+1}X$ d. $C_nH_{2n-1}X$

2. The bond between carbon and halogen in haloalkanes is-

a. $Ionic$ b. $Normal\ Covalent$ c. $Polar\ covalent$ d. $Coordinate\ covalent$

3. IUPAC name of $CH_3C(CH_3)_2CH_2I$ is-

a. $Iodopentane$ b. $2-methyl-1-chlorobutane$

c. $2-methyl-2-chloropropane$ d. $2-chloro-2-methylpropane$

4. Total number of structural isomers formed from $C_4H_{11}Cl$ are-

a. 3 b. 4 c. 5 d. 6

5. Among the isomers of $C_4H_{11}Cl$ which one has chiral carbon atom.

a. $1-chlorobutan$ b. $2-chlorobutane$

c. $1-chloro-2-methylpropane$ d. $2-chloro-2-methylpropane$

6. Haloalkanes have higher boiling points than alkanes with simila molecular weight due to-

a. $Hydrogen\ bonding$ b. $diopole-dipole\ interaction$

c. Van der waal's force d. Ionic bonding

7. Which reagent is commonly used to convert alkanes to haloalkanes

a. $HCl/ZnCl_2$ b. Cl_2 $in\ presence\ of\ UV\ light$

c. $SOCl_2$ d. PCl_3

7. Which of the following halides undergo hydrolysis most rapidly?

a. CH_3Cl b. CH_3Br c. CH_3I d. CH_3F

8. Which reaction mechanism is followed by primary haloalkane in nucleophilic substitution?

a. SN^1 b. SN^2 c. E^1 d. E^2

9. The expected product of the reaction between ethyl bromide and aq. KOH is-

b. $Ethene$ b. $Ethanol$ c. $Potassium\ ethoxide$ d. $Ethane$

10. The statement that differentiate SN^1 and SN^2 reaction

a. $SN^1 involves\ one\ step\ while\ SN^2 involves\ two\ steps$

b. $SN^1 involves\ 1^{st} order\ kinetics\ while\ SN^2 involves\ 2^{nd} order\ kinetics.$

c. $SN^1 prefers\ primary\ halides\ while\ SN^2 preferss\ secondary\ halides$

d. SN^1 and SN^2 $mechanisms\ are\ identical$

11. A compound C_3H_7Cl undergoes a reaction with alcoholic KOH. The major product is propene. What type of reaction is this?

a. $Substitution$ b. $Elimination$ c.$Reduction$ d. $Oxidation$

12. What is the major product when 2-bromobutane undergoes elimination reaction?

a. $1 - butene$ b. $2 - butene$ c. $1 - bomo - 2 - butene$ d. $Butane$

13. Which statement is true regarding Saytzeff's rule?

a. $The\ least\ substituted\ alkene\ is\ the\ major\ product.$

b. $The\ most\ substituted\ alkene\ is\ the\ major\ product.$

c. $It\ is\ applicable\ only\ in\ case\ of\ nucleophilic\ substitution$

d. $It\ is\ applied\ only\ to\ primary\ haloalkanes.$

14. The correct arrangement of $CH_3Cl, CH_3Br\ and\ CH_3I$ on increasing order of reactivity in SN^2 reactions is

a. $CH_3Cl < CH_3Br < CH_3I$ b. $CH_3I < CH_3Br < CH_3Cl$

c. $CH_3Br < CH_3I\ and\ CH_3Cl$ d. $CH_3Cl < CH_3I < CH_3Br$

15. Tertiary butyl alcohol undergoes hydrolysis with water to give tertiary alcohol.

a. The reaction followaSN^2 mechanism

b. The reaction followaSN^1 mechanism

c. Water acts as an electrophile

d. The reaction follows Elimination mechanism

16. Which of the following reagent is responsible for the reduction of haloalkanes?

a. Zn/HCl b. $Na/$dry ether c. $AgNO_2$ d. $Aq.KOH$

17. A mixture of ethyl bromide and sodium in dry ether gives butane. The reaction is called

a. Fittig reaction b. Wurtz – Fittig reaction

c. Wurtz reaction d. Saytzeff′sreaction

18. Which statement is true about Wurtz reaction?

a. It forms alkenes b. It gives symmetrical alkanes

c. It gives unsymmetrical alkanes d. It gives ether as major product

19. On treating chloroform with silver powder, the hydrocarbon obtained is-

a. Methane b. Ethane c. Ethene d. Ethyne

Exercise 8.2

1. Haloalkanes are hydroxyl derivative of hydrocarbons. There is covalent bond between carbon and halogen but due to electronegativity difference it is polar in nature.

a) Why do haloalkanes have higher boiling points compared to their parent hydrocarbon?

b) Arrange the following in the order of decreasing boiling point.

$$CH_3CH_2CH_2CH_2Cl, \quad CH_3CH(CH_3)CH_2Cl, \quad CH_3C(CH_3)_2Cl$$

2. If a compound has same molecular formula but different structural arrangement then these are called isomers.

a) Write possible isomers of the compound with molecular formula C_4H_9Cl.

b) Write IUPAC names of all isomers and identify their types.

c) Identify the chiral carbons in isomers.

4. Alcohols can be classified as the nature of carbon to which -OH group is attached.

(i) Write structural formula and classify the following alcohols:

a) 1-chloropropane

b) 2-chloropropane

c) 1-chlorobutane

c) 2.chloro-2-methylpropane

5. Complete the following reactions:

a) $CH_3CH_2OH \xrightarrow{?} ? + POCl_3 + ?$

b) $CH_3CH_2OH \xrightarrow{?} ? + H_3PO_3$

c) $CH_3CH_2OH \xrightarrow{?} ? + SO_2 + ?$

d) $CH_2 = CH_2 + HCl \xrightarrow{?} ? + KCl + ?$

6. Boiling point of haloalkanes is affected by different factors. How would you explain the effect of following factors-

a) Molecular mass

b) Strength of C-X bond

c) Intermolecular forces

d) Branching

7. The reaction in which a stronger nucleophile substitutes the weaker nucleophile from a compound is called nucleophilic substitution. This reaction can proceeds through two mechanisms i.e. unimolecular (SN1) or bimolecular (SN2).Identify the type of reaction with explanation for following cases-

a) $CH_3C(CH_3)_2Cl + aq.KOH \longrightarrow CH_3C(CH_3)_2OH + KBr$

b) $CH_3CH_2Br + aq.KOH \longrightarrow CH_3CH_2OH + KBr$

8. Arrange the following compounds in decreasing order of reactivity towards SN^2 reaction.

$$CH_3Cl,\ CH_3CH_2Cl, (CH_3)_2CHCl$$

9. Chloroethane is a primary haloalkane and can show nucleophilic substitution reaction. Write the reaction of it with following reagents.

a) aq. KOH b) alc. KCN c) NH_3 d) alc. AgCN

10. Complete the following reactions.

a) $CH_3CH_2Br + CH_3ONa \xrightarrow{dry\ ether}$

b) $CH_3CH_2Br + NH_3 \xrightarrow{\Delta}$

c) $CH_3CH_2Br + alc.KCN \longrightarrow$

d) $CH_3CH_2Br + alc.AgNO_2 \longrightarrow$

e) $CH_3CH_2Br + aq.KNO_2 \longrightarrow$

11. Elimination reaction is the reaction in which certain group is eliminated from the compound in presence of particular reagent and major product is determined on the basis of Saytzeff rule.

a) State Saytzeff rule.

b) Explain α, β – elimination reaction with example.

c) Identify the major product of the reaction between $CH_3C(CH_3)_2CCl(CH_3)CH_3$ $and\ alc.$ KOH.

12. When propene reacts with HCl, it produces 2-chloropropane but not 1-chloro propane as major product. It follows a principle to form this product.

a) Name and state the rule with suitable example.

b) When HCl is replaced by HBr and organic peroxide is present, it produces just opposite product. Explain.

13. When haloalkane is treated with sodium metal, dry ether is used as solvent because of the air and moisture sensitivity of sodium. It connects carbons of two molecules of haloalkane by removing halogens.

a) Name this reaction and write statement with suitable example.

b) What will be the major product when 2-chloropropane is treated with Na metal in presence of dry ether.

14. Chloroform, a tri halogen compound, was previously used as an anesthetic however, its use has been discontinued due to its toxic effects.

    i) Discuss the principle behind laboratory preparation of chloroform using-

    a) Ethanol and b) Acetone. How is it purified?

    ii) Chloroform is stored in a dark colored bottle filled up to brim with the addition of some ethanol. Explain with reason.

    iii) How could you conform the presence of phosgene in a sample of chloroform? Give a detection method.

15. Chloroform shows different type of reactions. It is more reactive than carbon tetrachloride towards nucleophilic substitution reaction. Show the reaction of chloroform with following reagents.

    i) Conc. HNO3 ii) aq. KOH iii) Ag powder iv) Acetone

    v) C_6H_5OH/ KOH vi) $C_6H_5NH_2$/ KOH

16. Take a small amount of bromoethane in a test tube. Add aq. NaOH and warm the mixture. On the basis of observation.

    i) What type of reaction occurs?

    ii) Write a balanced chemical equation for the reaction.

    iii) What is the functional group present in the product formed?

Exercise 8.3

Comprehensive questions

1. An alcohol "X" reacts with HCl in presence of anhydrous $ZnCl_2$ to form "Y". "Y" undergoes dehydrohalogenation with alc. KOH to form "Z". On ozonolysis, "Z" gives only acetaldehyde as the product. Identify X, Y and Z.
2. Take 2-bromopropane in two separate test tubes. Add aq. KOH to one and alc. KOH to the other. Heat both. Use Bayer's reagent (Alkaline $KMnO_4$) for test the unsaturation.
   i) What difference in the product formation do you observe?
   ii) How does Bayer's test help identify the reaction type?
   iii) Write the reactions involved in both cases.
3. React ethanol with bleaching powder ($CaOCl_2$) and heat gently. Observe the reaction and identify the product. Answer the following questions:
   i) What is the role of bleaching powder in the reaction?
   ii) Write the balanced equation for the formation of chloroform.
   iii) How can you conform the presence of chloroform in the product?

4. Convert following:
    a) Bromoethane to methane
    b) Chloroethanr to 1-chloropropane
    c) Iodoethane to ethoxyethane
    d) 1-bromopropane to butanoic acid
    e) Chloromethane to Acetyl Chloride

Activity (Bingo-Game)

Instruction

1. A 5 × 5 bingo card is provided to you or draw in your notebook
2. A word bank comprising 25 terms is provided below. You should select the appropriate term that corresponds to the clue provided by the teacher.
3. The box at the center is your FREE space, which may be marked automatically.
4. Only one term should be filled per box on your Bingo card.
5. Listen carefully as your teacher reads out clues or definitions related to the terms.
6. When a clue matches a term on word bank, fill the term in that box randomly.
7. The first student to fill a full row, column, or diagonal shouts "BINGO!" and wins!

Bingo Card

		Free space		

Word Bank (Fill in the bingo card)

Alkyl halide, SN1 reaction, SN2 reaction, Lucas Test, Iodoform test, C–X bond, Saytzeff rule, Wurtz reaction, C_2H_5Br, Hydrolysis, Grignard reagent, CH_3I, Elimination, Primary alkyl halide, Reactivity order, Silver nitrate test, Polar solvent, Aqueous KOH, Nucleophile, Isomerism, Boiling point, Secondary halide, Methyl chloride, Nitrile, Alcohol to halide

Teacher clue sheet (Read Aloud)

1. This reaction proceeds via a carbocation intermediate.

2. This test gives cloudiness with tertiary alcohols.

3. Yellow precipitate in presence of $CH_3CO–$ group.

4. Predicts more substituted alkene in elimination reactions.

5. Bond that becomes polarized due to electronegative halogen.

6. Used to form alkyl cyanide from haloalkane.

7. A haloalkane that reacts fastest with Lucas reagent.

8. Used to make Grignard reagent.

9. Reaction that joins two alkyl halides using sodium metal.

10. Reagent that gives alcohol from haloalkane on hydrolysis.

11. A nucleophile with a lone pair to donate electrons.

12. Has a partial double bond character due to resonance.

13. Used in the silver nitrate test for halide ions.

14. A common test to distinguish methyl ketones.

15. A type of substitution reaction proceeding via inversion.

16. A molecule containing a halogen bonded to a saturated carbon atom.

17. A substitution reaction that occurs in a single concerted step.

18. Reagent that forms haloalkane from alcohol in the presence of ZnCl2.

19. Test used to detect the presence of iodine in methyl ketones.

20. Indicates the boiling range of a haloalkane compound.

21. Structural difference due to same molecular formula in haloalkanes.

22. The part of the molecule where the halogen is directly bonded.

23. A common primary haloalkane used in lab preparations.

24. A property that increases with increasing molecular weight in haloalkanes.

25. Group that replaces halide during aqueous KOH reaction.

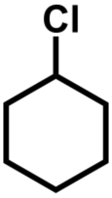
Project work-

1. To compare the reactivity among primary, secondary and tertiary haloalkanes.

2. To explain the role of haloalkanes in organic sybthesis.

UNIT 9
HALOARENES

Activity 9.1: Observe the following compounds and identify haloarene with suitable reason



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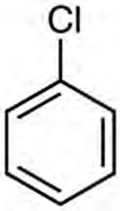

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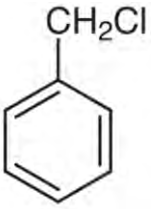

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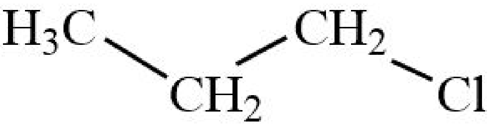
III

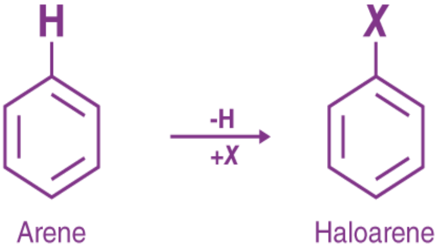


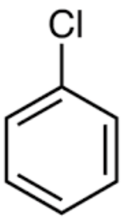
IV

9.1 Introduction:

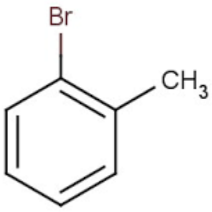
Haloarenes (Aryl halides) are compounds containing one or more halogen attached directly to sp2 hybridised carbon atom(s) of an aromatic ring by substituting hydrogen. They have general formula ArX ,Where Ar is phenyl or substituted phenyl or any other aryl group.

Ar-H + X ——---------> Ar - X + H

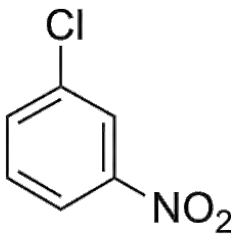




Chlorobenzene,



o-bromotoluene

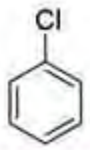


m-Chloronitrobenzene

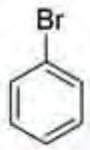
9.2 Nomenclature and isomerism of haloarenes:

On the basis of IUPAC system nomenclature of haloarenes are performed by adding prefix halo with the name of aromatic hydrocarbon.

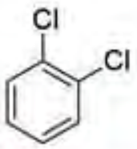
For substituted compounds Position is indicated by Ortho (1,2), meta (1,3) and para (1,4).



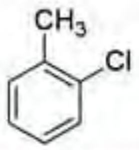
Chlorobenzene



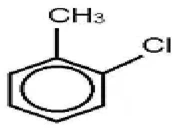
Bromobenzene



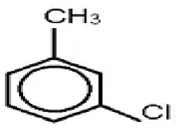
1,2-dichlorobenzene



2-chlorotoluene



2-Chlorotoluene
(o-Chlorotoluene)



3-Chlorotoluene
(m-Chlorotoluene)

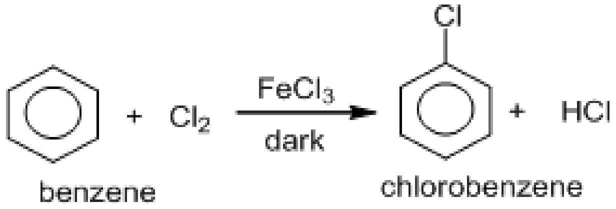
Activity 9.2:

Column A – Term or Reaction	Column B – Match
C_6H_5Cl	Sandmeyer reaction
$C_6H_4Cl_2$ (1,2-position)	Chlorobenzene
$C_6H_4Cl_2$ (1,3-position)	Laboratory method of chlorobenzene
$C_6H_4Cl_2$ (1,4-position)	Indirect method to obtain phenol, but can form haloarene
Electrophilic substitution of benzene with Cl_2 in presence of $FeCl_3$	p-Dichlorobenzene
Hydrolysis of benzene diazonium salt	Dichlorobenzene
Reaction of benzene sulphonic acid with NaOH followed by HCl	Bromobenzene
IUPAC name of C_6H_5Br	o-Dichlorobenzene
IUPAC name of C_6H_5I	Preparation using CuCl (Sandmeyer reaction)
$Ar–N_2^+ + CuCl \rightarrow Ar–Cl + N_2$	Iodobenzene

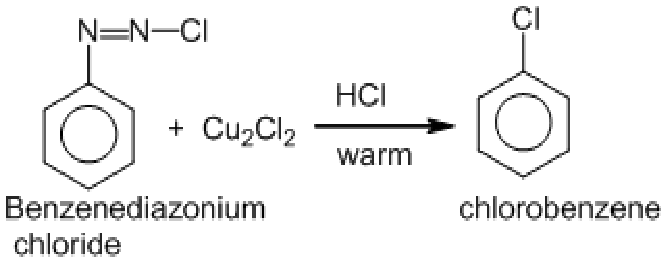
9.3 Preparation of chlorobenzene:

There are different methods for preparation of chlorobenzene.

1. **By direct chlorination of benzene:**
   When dry chlorine is passed through Benzene at in presence of FeCl3 as halogen carrier, chlorobenzene is obtained. It is an example of electrophilic aromatic substitution reaction.

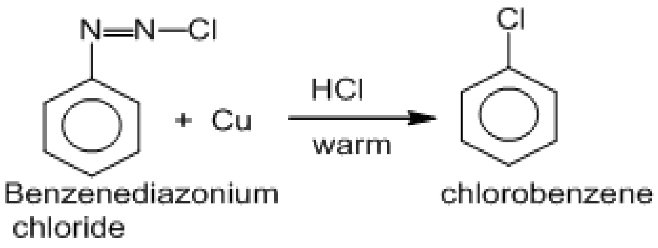


2. **By using Benzene diazonium chloride:**
   a) sandmeyer reaction : When Benzene diazonium Chloride is treated with cuprous chloride / cuprous bromide in presence of HCl / HBr chlorobenzene is obtained due to replacement of diazonium group by -Cl , known as **sandmeyer reaction.**



When Aniline, dissolved or suspended in cold aqueous mineral acid,, is treated with sodium nitrite, a diazonium salt is formed.

   b) **Gattermann reaction:** When Benzene diazonium Chloride is treated with copper powder in presence of HCl chlorobenzene is obtained, known as Gattermann reaction. Thos is the modification of sand-meyer reaction



Activity: Fill in the blanks.

Reactant	Reagent	Conditions	Product
	Chlorine (Cl_2)	Presence of anhy.**$AlCl_3$ catalyst**	Chlorobenzene (C_6H_5Cl)
Aniline ($C_6H_5NH_2$)		**Sandmeyer Reaction**	
Benzene Sulfonic Acid ($C_6H_5SO_3H$)		**Heat with NaCl & H_2SO_4**	Chlorobenzene (C_6H_5Cl)
Benzene diazonium chloride	Cu / HCl		

9.4 Physical properties:

1. It is a colourless volatile liquid with boiling point 132 degree centigrade.
   Boiling point of heloarenes follow the order:

   Iodobenzene> Bromobenzene> chlorobenzene

2. In case of dihaloarenes , .o-, m- and p-dichlorobenzene,melting point of para isomer is greater than others because of its symmetrical structure.
3. It has almond-like odour.
4. It is insoluble in water but soluble in organic solvents.
5. It is heavier than water (Density= 1.11 g / c.c.)

9.5 Chemical properties:

9.5.1 Nucleophilic substitution in haloarene:

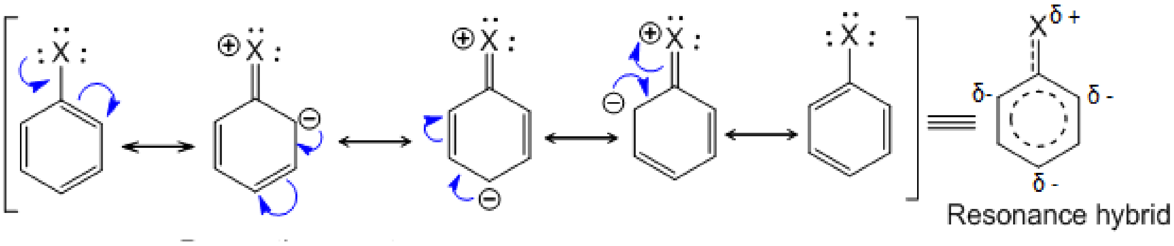


Fig 9.1 : Resonating structures of Chlorobenzene

In the above structures, structures III, IV and V show that Chlorine is bonded with the carbon of the ring through a double bond. It means that chlorine is strongly bonded to carbon.of the ring. Here chlorine is attached as a nucleophile and due to the strong attachment with carbon it is very hard to replace chlorine by another nucleophile. Therefore nucleophilic substitution in chlorobenzene (haloarene) is very difficult.

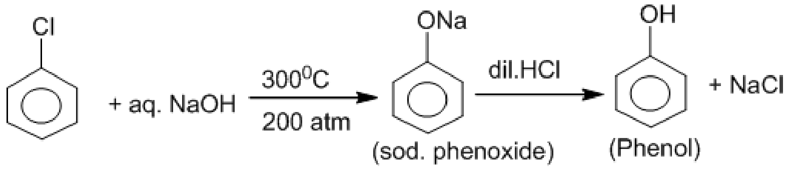
Towards nucleophilic substitution reactions halo-arenes are extremely less reactive than haloalkanes due to the effect of different factors. some of which are-

a) **Resonance effect**:From above resonating structures it is clear that replacement of halogen from haloarene is very difficult while such a condition does not exist in case of haloalkane.
b) Aryl groups are electron rich and they can create a repulsion for incoming nucleophiles.
c) **.Hybridization:** in haloarene halogen is attached with SP2 hybridised carbon. It has more electronegative character so it will form strong bond with halogen then the carbon with SP3 hybridization.

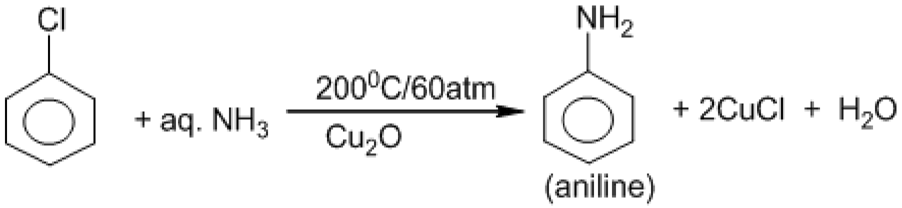
In this way haloarene Is very less reactive towards nucleophilic substitution reaction then haloalkanes.

Under some special conditions, nucleophilic substitution may occur in haloarenes. For example:

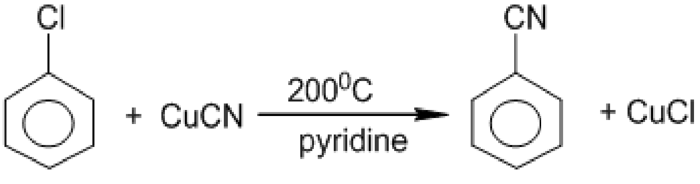
a) **Reaction with NaOH:** When chlorobenzene is treated with NaOH at 623 K temperature and 300 atm. Pressure. It is also known as Dow's process.



b) **Reaction with aq. NH3:** When chlorobenzene is treated with aq. ammonia or Ammonia solution at 200^oC temperature and 60 atmosphere pressure in presence of cuprous oxide (Cu_2O), aniline is obtained.



c) **Reaction with cuprous cyanide:** When chlorobenzene is treated with anhydrous cyanide at 200°c degree temperature in presence of pyridine Phenyl cyanide or cyanobenzene is obtained



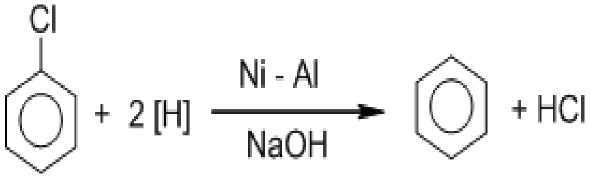
(phenyl cyanide)
(benzonitrile)
(benzenenitrile)

But in haloalkanes the condition is different

R-X + :Nu —> R-Nu + X-

In case of haloalkanes there is no possibility of such resonating structures to provide strong bonding between halogen and carbon so it is more reactive than haloarenes towards nucleophilic substitution

9.5.2. **Reduction of chlorobenzene**: In presence of metallic alloy and alkali, chlorobenzene can be reduced by nascent hydrogen into Benzene.

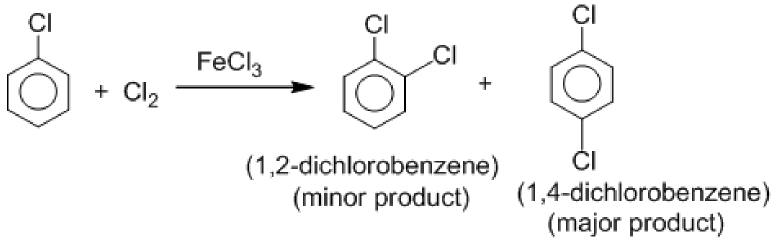


(Benzene)

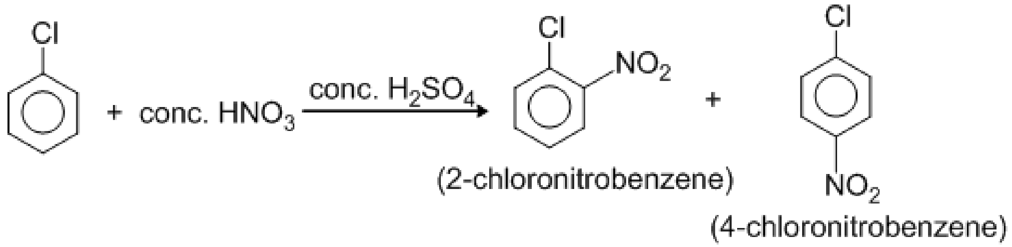
9.5.3. Electrophilic substitution reactions

In haloarenes, the halogen atom exhibits +M (mesomeric) effect by donating its lone pair of electrons into the aromatic ring through resonance, which increases electron density at the ortho and para positions. This makes these positions more reactive towards electrophilic substitution reactions, fig 9.1 shows the reactivity of ortho and para positions. However, due to the strong –I (Inductive) effect of halogen, it withdraws electrons through the sigma bond, the ring as a whole becomes less reactive than benzene, resulting in slower reactions. Thus haloarenes undergo electrophilic substitution at ortho and para positions but the reactions occur at a slower rate compared to unsubstituted benzene.

a)

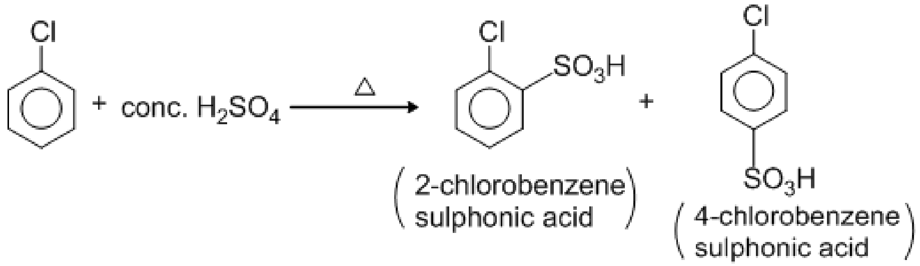

Cl
+ Cl_2
$FeCl_3$
Cl
Cl
+
Cl
Cl
(1,2-dichlorobenzene)
(minor product)
(1,4-dichlorobenzene)
(major product)

b)

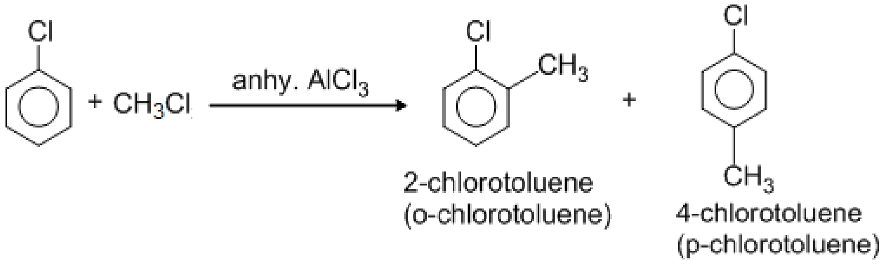

Cl
+ conc. HNO_3
conc. H_2SO_4
Cl
NO_2
+
Cl
NO_2
(2-chloronitrobenzene)
(4-chloronitrobenzene)

c)

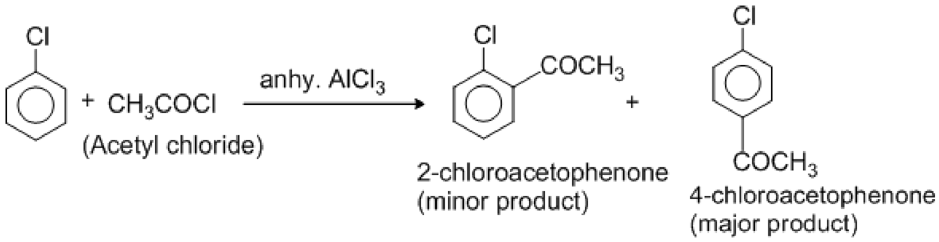
d)


Cl
+ conc. H_2SO_4
△
Cl
SO_3H
+
Cl
SO_3H
(2-chlorobenzene sulphonic acid)
(4-chlorobenzene sulphonic acid)

e)

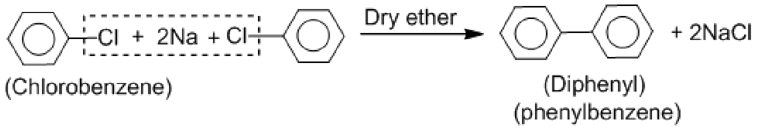

Cl
+ CH_3Cl
anhy. $AlCl_3$
Cl
CH_3
+
Cl
CH_3
2-chlorotoluene
(o-chlorotoluene)
4-chlorotoluene
(p-chlorotoluene)

f)

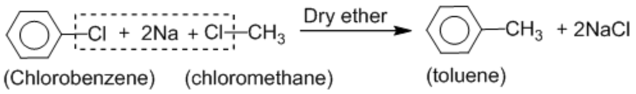

Cl
+ CH_3COCl
(Acetyl chloride)
anhy. $AlCl_3$
Cl
$COCH_3$
+
Cl
$COCH_3$
2-chloroacetophenone
(minor product)
4-chloroacetophenone
(major product)

9.5.4. Action with Na (fittig and Wurtz- fittig reactions)

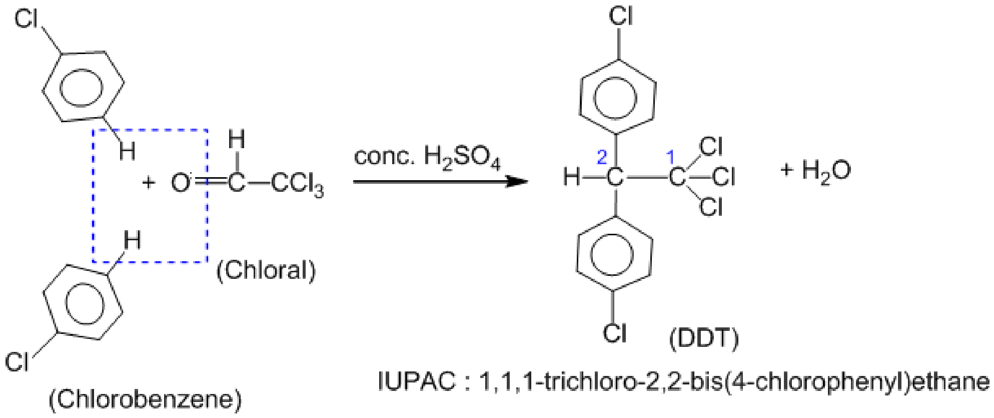
Fittig reaction : Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction



Wurtz-Fittig reaction: A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.



9.5.5. Action with chloral:



9.6. Uses of haloarenes:

Exercise 9.1

Multiple Choice questions:

1. Chlorobenzene has higher boiling point than that of benzene, the reason behind it is:

   a. *It has higher molecular weight* b. *It forms hydrogen bonds*

   c. *It has hydrogen bonds* d. *It is more reactive than benzene*

2. The order of increasing boiling point of isomers of chlorobenzene is:

   a. $para > ortho > meta$ b. $Meta > ortho > para$

   c. $ortho > meta > para$ d. $para > meta > ortho$

3. To prepare chlorobenzene in the lab from benzene diazonium chloride, which reagent to be should be used-

   a. Zn/HCl b. $CuCl$ *and* HCl c. $NaOH$ *and* Br_2 d. $SOCl_2$

4. If a chemist find that a compound is not showing nucleophilic substitution even in the presence of a strong nucleophile. If it contains halogen the compound may be:

   a. CH_3Cl b. C_6H_5Cl c. $C_6H_5CH_2Cl$ d. CH_3I

5. Why are haloarenes less reactive than haloalkanes towards nucleophilic substitution reaction?

   a. *The carbon hydrogen bond in haloarenes is weaker than haloalkanes.*

   b. *The carbon in haloarenes have* sp^3 *hybridization*

   c. *Resonance stabilization in haloarenes makes* $C - X$ *bond stronger.*

   d. *The halogen in haloarenes is more reactive than in haloalkanes.*

6. The effect of halogen on the electron density of benzene ring is:

   a. It increases electron density at all positions

   b. *It decreases electron density at ortho and para positions.*

   c. It decreases electron density at meta position.

   d. *It increases electron density at ortho and para position.*

7. Halogen is an electron withdrawing group but ortho-para director due to:

   a. +I effect of halogen. b. $-I$ *and* $+M$ *effect respectively*

   c. Only –I effect of halogen. d. *Only* $+M$ *effect of halogens.*

8. DDT is an insecticide, if it is to be prepared in the lab the two compounds required are

a. *Chlorobenzene and benzene.* b. *Chlorobenzene and chloral*

c. *Benzene and chloral.* d.*Chlorobenzene and chloritone*

9. Why does Friedel-Crafts alkylation of chlorobenzene give a poor yield?

a. *The chlorine atom activates the ring for substitution.*

b. *The chlorine atom deactivates the ring and makes it less reactive.*

c. *The chlorine atom undergoes nucleophilic substitution.*

d. *The chlorine atom doesnot affect the reaction.*

10. Which of the following is used for the preparation of haloarene.

a. *Wurtz reaction.* b. *Friedel − Crafts alkylation*

c. *Sandmeyer reaction.* d. Williamson’s ether synthesis

11. In Fittig reaction chlorobenzene reacts with sodium in dry ether to form:

a. *Toluene.* b. *Biphenyl* c. *Benzophenone.* d. Benzyl chloride

12. The major product obtained when chlorobenzene undergoes nitration with conc.HNO_3 and conc. H_2SO_4:

a. *o − nitrochlorobenzene.* b. *m − nitrochlorobenzene*

c. *p − nitrochlorobenzene.* d. Both o-and p- nitrochlorobenzene

13. Which of the following will not undergo nucleophilic substitution easily?

a. *Benzyl chloride.* b. *Chlorobenzene* c. *Methyl chloride.* d. Allyl chloride

14. Which of the following reactions involves both nucleophilic and electrophilic substitution steps?

a. *Kolbe'sreaction.* b. *Fittig reaction*

c. *Reimer − Teimann reaction.* d. Wurtz reaction

15. Which of the following best explains why Fittig reaction requires dry ether as a solvent?

a. *Water helps in stabilizing the product.*

b. *Dry ether prevents oxidation of sodium*

c. *Sodium reacts violently with water and can demolish the reaction.*

d. Ether acts as an oxidizing agent.

Exercise 9.2

1. Write possible isomers of $C_6H_4Cl_2$. Draw structures and name them.

2. There are different methods for the preparation of chlorrobenzene.
   - i) What happens when benzene is treated with chlorine
   - ii) How will you prepare chlorobenzene from benzene diazonium chloride? Name the reaction.
   - iii) What is the use of CuCl in the preparation chlorobenzene from diazoniumchloride?

3. Chlorobenzene is an aromatic compound in which chlorine is bonded with carbon of the ring.
   - i) Compare the solubility of chlorobenzene in water and organic solvent.
   - ii) Arrange the following in the increasing order of boiling point.
     Chlorobenzene, Bromobenzene and Iodobenzene
   - iii) What is the reason behind higher boiling point of cholrobenzene than that of benzene?

4. Nucleophilic substitution reaction is the replacement of a nucleophile by another stronger one to give new compound.
   - i) Explain the reason behind less reactivity of haloarene towards nucleophilic substitution reaction.
   - ii) Compare the bond strength of C-Cl bond and reactivity of haloarene and haloalkane towards nucleophilic substitution reaction.

5. In chlorobenzene electronegative chlorine is attached with carbon of the ring.
   - i) How could you prove that –Cl is ortho and para director in chlorobenzene?
   - ii) In spite of being ortho-para director –Cl is deactivator of aromatic ring. Explain.

6. Complete the following reactions and identify the major product.

i) $C_6H_5Cl + Conc.H_2SO_4 \xrightarrow{Conc.HNO_3}$

ii) $C_6H_5Cl + Conc.H_2SO_4 \xrightarrow{\Delta}$

iii) $C_6H_5Cl + CH_3COCl \xrightarrow{anhy.AlCl_3}$

iv) $C_6H_5Cl + CH_3Cl \xrightarrow{anhy.AlCl_3}$

v) $C_6H_5Cl + Cl_4 \xrightarrow{FeCl_3}$

7. Complete the following reaction.

i) $C_6H_5Cl + H_2 \xrightarrow{Ni,\ \Delta}$

ii) $C_6H_5Cl \xrightarrow{Na,\ C_2H_5OH}$

iii) $C_6H_5Cl \xrightarrow{Zn,\ NaOH}$

iv) $C_6H_5Cl \xrightarrow{Na,\ dry\ ether}$

v) $C_6H_5Cl + CH_3Cl \xrightarrow{Na,\ dry\ ether}$

8. There are different name reactions in which halogen derivatives are treated with sodium metal in presence of dry ether.

i) What happens when chlorobenzene is treated with chloroethane in presence of sodium and dry ether. Name the reaction.

ii) Compare Fittig and Wurtz-Fittig reactions with suitable examples.

9. Chlorobenzene is used for the manufacture of insecticides.

i) What is the full form of DDT? Write structure and IUPAC name of the compound.

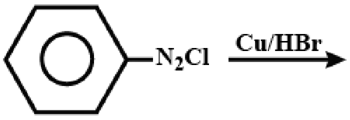
ii) What happens when chlorobenzene is treated with chloral in presence of H_2SO_4 .

iii) Why the product of above reaction is used as an insecticide?

10. Polychlorinated biphenyls have extensive use in the past but are banned currently. Explain the reason.

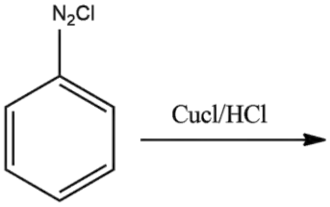
11. Complete the following reaction

i)



Benzene diazonium chloride

ii)



12. Why does the reaction of chlorobenzene with aqueous NaOH occur only at high temperature and pressure, while benzyl chloride reacts readily under mild conditions? Explain based on reaction mechanisms.

13. Explain why chlorobenzene behaves differently from trichloromethane ($CHCl_3$) in reactions with reducing agents such as Zn/HCl.

14. Complete the following conversions.

    i) Nitrobenzene to Chlorobenzene
    ii) Chlorobenzene to Aniline
    iii) Chlorobenzene to Benzoic acid
    iv) Chlorobenzene to Phenol

Bingo-Game

Instruction

1. A 5 × 5 bingo card is provided to you or draw in your notebook
2. A word bank comprising 25 terms is provided below. You should select the appropriate term that corresponds to the clue provided by the teacher.
3. The box at the center is your FREE space, which may be marked automatically.
4. Only one term should be filled per box on your Bingo card.
5. Listen carefully as your teacher reads out clues or definitions related to the terms.
6. When a clue matches a term on word bank, fill the term in that box randomly.
7. The first student to fill a full row, column, or diagonal shouts “BINGO!” and wins!

Bingo-Card

		🎯FREE		

Word Bank (Use to fill the Bingo Card)

Chlorobenzene, Electrophilic substitution, Nitration, Sulphonation, Friedel-Crafts reaction, Ortho product, Meta product, Para product, Halogenation, Resonance, C–Cl bond, Aryl halide, Dow’s process, Sandmeyer reaction, Reimer-Tiemann reaction, Kolbe's reaction, Acylation, Bromobenzene, Fluorobenzene, Iodobenzene, Phenyl group, Activating group, Deactivating group, Boiling point, Uses of haloarenes

Teacher Clue Sheet (Read aloud)

1. Benzene ring with a chlorine atom attached.

2. General type of reaction haloarenes undergo with aromatic ring.

3. Substitution of NO_2 group on benzene ring.

4. Substitution of SO_3H group in aromatic ring.

5. Reaction involving alkyl or acyl halides in presence of $AlCl_3$.

6. Position adjacent to the substituent on benzene.

7. Position one carbon away from substituent on benzene.

8. Position opposite to the substituent on benzene.

9. Reaction with halogen in presence of Lewis acid catalyst.

10. Delocalization of electrons in benzene ring.

11. Bond partially double due to resonance in haloarenes.

12. General name for halogen-substituted aromatic compounds.

13. Preparation of chlorobenzene using NaOH at high temp & pressure.

14. Reaction involving diazonium salt and CuCl or CuBr.

15. Reaction producing salicylaldehyde using chloroform and alkali.

16. Reaction that introduces COOH group on phenol ring.

17. Reaction of benzene with acid chloride in presence of $AlCl_3$.

18. A benzene ring with a bromine substituent.

19. Haloarene that contains fluorine atom.

20. Haloarene that contains iodine atom.

21. C_6H_5- group often used as a substituent.

22. Group that increases electron density on aromatic ring.

23. Group that withdraws electron density from aromatic ring.

24. Property that increases with molecular mass in haloarenes.

25. Applications like solvents, pesticides, and pharmaceuticals.

Project work:

1. To study the role of halogen substitution in aromatic substitution reaction.

2. To study the uses and environmental impact of haloarenes.

Unit 10

Alcohols

Activity: 10.1

i) Can you name some common things around you that have alcohol in them?

ii) Why do you think alcohols are important in our daily life and in chemistry

10.1 Introduction

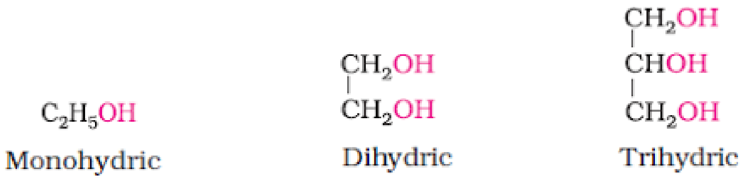
Hydrocarbons, in which one or more hydrogen(s) are replaced by -OH group, are called alcohols.-OH (hydroxyl) group in alcohol is attached with alkyl group (R). General formula of alcohol is represented by R-OH.

$$\text{R-H} \xrightarrow[\text{-H}]{\text{+-OH}} \text{R- OH}$$

R-OH	Alkyl alcohol	(Alkanol)
CH_3-OH	$Methyl\ alcohol$	$(Methanol)$
CH_3-CH_2-OH	Ethyl alcohol	Ethanol
$CH_2(OH)-CH_2(OH)$	$Ethyleneglycol$	$(Ethan-1{,}2-diol)$
$CH_2(OH)-CH(OH)-CH_2(OH)$	$Glycerol$	$(Propan-1{,}2{,}3-triol)$

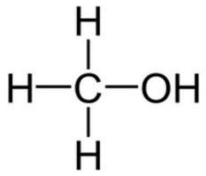
10.2 Nomenclature isomerism and classification of monohydric alcohols

10.2.1 Classification:



Generally alcohols are classified on the basis of the number of -OH groups attached to the hydrocarbon as-

a) Monohydric alcohols: Hydrocarbons in which only one hydrogen is substituted by -OH group are called monohydric alcohols.
For example: CH_3-OH , CH_3-CH_2-OH etc.



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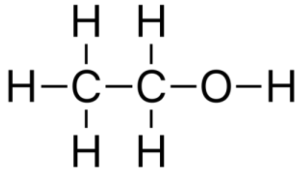
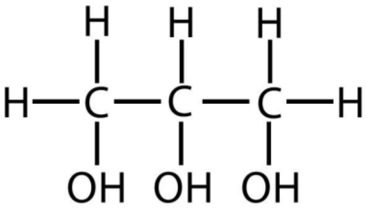


b) Dihydric alcohols: Hydrocarbons in which two hydrogen atoms are substituted by -OH group are called monohydric alcohols.
For example

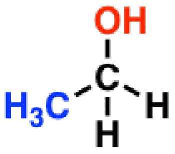
Ethylene Glycol (Ethan-1,2-diol)

c) Trihydric alcohols:Hydrocarbons in which three hydrogen atoms are substituted by -OH group are called monohydric alcohols.
For example:



Glycerol (Propan-1,2,3-triol)

Monohydric alcohols can also be classified in the basis of the nature of carbon with which -OH group is attached as-



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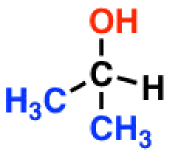

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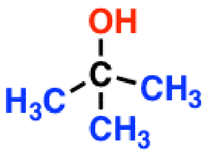
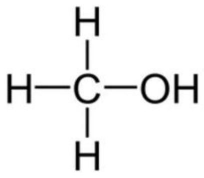


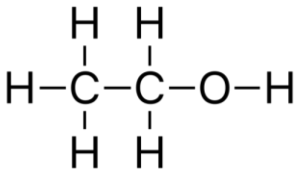
(1^o) **(2^o)** **(3^o)**

a) **Primary (1^o) alcohol**:



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH$$

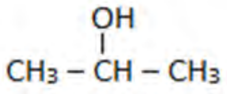
,



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-H$$

The alcohols in which -OH group is attached to the 1^o $(primary)$ carbon atom,which is further attached with one or no other carbon atoms, are called primary (1^o) alcohol.

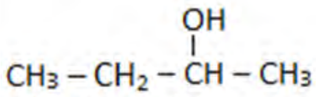
b) **Secondary (2^o) alcohol**:



$$CH_3-\overset{\displaystyle OH}{CH}-CH_3$$

(propan-2-ol)

,

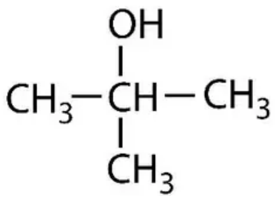


$$CH_3-CH_2-\overset{\displaystyle OH}{CH}-CH_3$$

(butan-2-ol)

The alcohols in which -OH group is attached to the 2^o $(secondary)$ carbon atom,which is further attached with two other carbon atoms, are called secondary (2^o) alcohol.

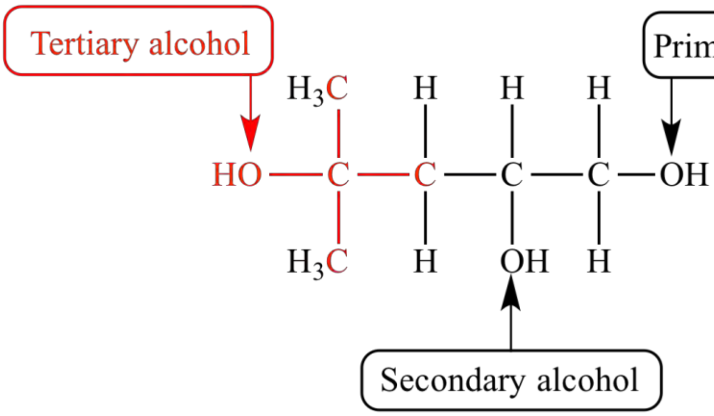
c) **Tertiary (3^o) alcohol**:



$$CH_3-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{CH}}-CH_3$$

(2-Methylpropan-2-ol)

The alcohols in which -OH group is attached to the 3^o $(tertiary)$ carbon atom,which is further attached with three other carbon atoms, are called secondary (2^o) alcohol.



10.2.2. Nomenclature:

CH_3-OH	(Methyl alcohol)	(Methanol)
$CH_3CH_2CH_2-OH$	(n-propyl alcohol)	(Propan-1-ol)
$CH_3CH\ (OH)CH_3$	(Isopropyl alcohol)	(Propan-2-ol)
$CH_3CH_2CH_2CH_2-OH$	(n-butyl alcohol)	(Butan-1-ol)
$CH_3CH_2CH\ (OH)\ CH_3$	(Sec. butyl alcohol)	(Butan-2-ol)
$CH_3\ CH\ (CH_3)\ CH_2-OH$	$(Isobutyl\ alcohol)$	$(2-Methylpropan-1-ol)$
$CH_3\ C\ (CH_3)_2\quad -OH$	(tert. Butyl alcohol)	(2-Methylpropan-2-ol)
$CH_3\ C\ (CH_3)_2\ CH_2-OH$	(Neopentyl alcohol)	(2,2-dimethylpropan-1-ol)
$CH_2(OH)-CH_2(OH)$	$Ethyleneglycol$	$(Ethan-1,2-diol)$
$CH_2(OH)-CH(OH)-CH_2(OH)$	$Glycerol$	$(Propan-1,2,3-triol)$

There are mainly two systems of naming alcohols:

1. Common system :- In common system alcohols are named as alkyl alcohol followed by prefixes n-, iso- and neo-. n- represents straight chain,iso- represents chain where second carbon bears a methyl group as a side chain and neo- represents carbon chain where second carbon bears two methyl groups as side chains.
2. IUPAC system:- in IUPAC system alcohols are named as alkanols. In this system, the longest carbon chain containing the -OH group is considered as the main chain. Numbering of carbon is started from that side, from which the carbon containing -OH group gets the lowest number. In the name alkane, -e is replaced by suffix -ol and substituent groups are written as prefixes with the number of positions.

10.2.3. Isomerism

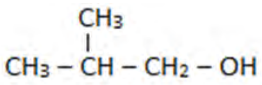
Alcohols exhibits following types of structural isomerism:

1. **Chain isomerism:** chain isomerism is shown by the alcohols having four or more carbon atoms, where the main carbon chain has a different number of carbon atoms. For example-

$CH_3-CH_2-CH_2-CH_2-OH$

(butan-1-ol)

and



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-OH$

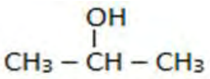
(2-methylpropan-1-ol)

2. **Position isomerism**: In this isomerism -OH group of alcohol is attached with different carbon atoms of the compound, position isomerism is shown by the alcohol having three or more carbon atoms.

$CH_3-CH_2-CH_2-OH$

(1-propanol)

and



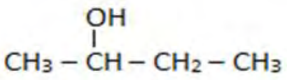
$CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3$

(2-propanol)

$CH_3-CH_2-CH_2-CH_2-OH$

(1-butanol)

and



$CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-CH_3$

(2-butanol)

3. **Functional isomerism**: In functional isomerism compounds have same molecular formula but different functional groups. Alcohols and ethers are functional isomers. It is shown by the compounds having two or more carbon atoms.

CH_3-CH_2-OH and CH_3-O-CH_3

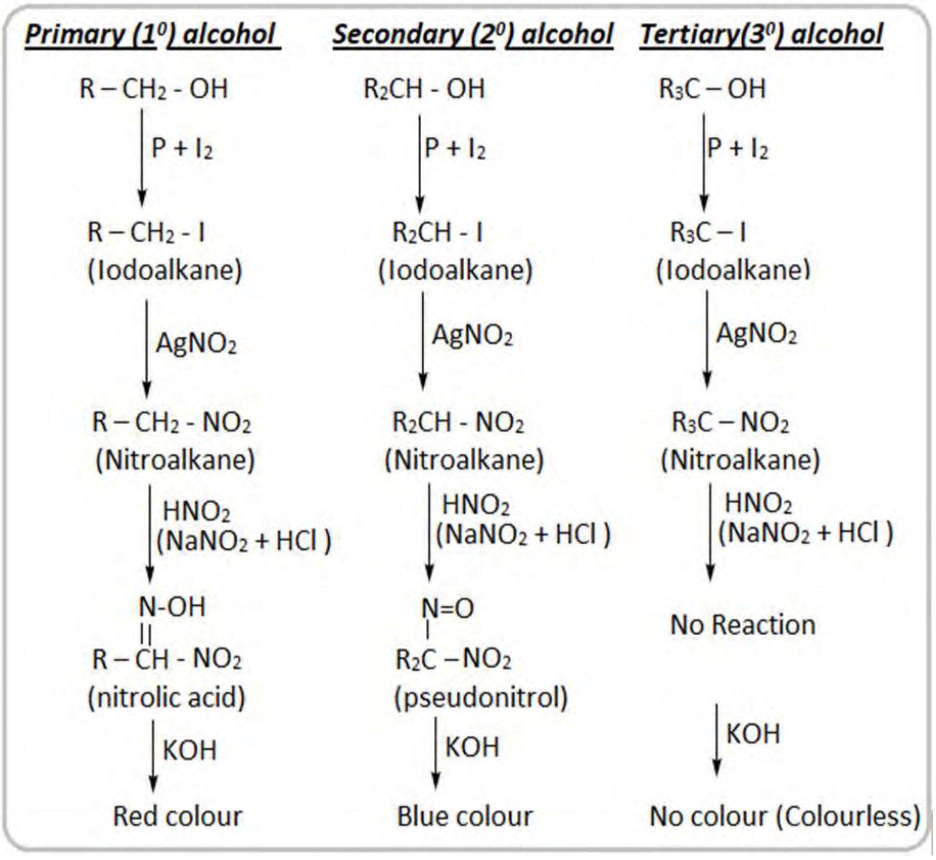
(1-ethanol) (methoxymethane)

$CH_3-CH_2-CH_2-OH$ and $CH_3-CH_2-O-CH_3$

(1-propanol) (methoxyethane)

Try yourself: *Express the possible isomers of molecular formula* $C_5H_{11}Cl$ *and write their IUPAC names. Classify these isomeric alcohols.*

10.3. Distinction of Primary secondary and tertiary alcohols by Victor meyer's method



Victor mayer's method is one of the important method for the separation of alcohols. In this method different reagents are used to treat with alcohols and by observing the final result, alcohol can be separated. the reagents are (i) $P + I_2$ (ii) $AgNO_2$ (iii) $HNO_2 \; or \; (NaNO_2 + HCl)$

(iv) KOH, Finally the color observed on adding KOH separates the alcohols as-

a) Red colour - primary alcohol
b) Blue colour - secondary alcohol
c) No colour (colourless) - tertiary alcohols

Try yourself: There are three isomeric alcohols A, B and C of C_4H_9OH. On subjecting to the victor mayer's method B gives red colour, C gives blue colour and A remains colourless. Write the structures of A, B and C.

10.4. Preparation of monohydric alcohols from haloalkanes Primary amines and esters.

There are different methods for the preparation of alcohol. Some of the important methods are-

a) By the hydrolysis of haloalkanes:

When haloalkanes are treated with aqueous solution of strong alkali (NaOH or KOH) alcohols are obtained.

$$R-Cl \; + \; aq.NaOH/KOH \quad \rightarrow \quad R-OH \; + NaCl \,/\, KCl$$

$$CH_3\,CH_2-Cl \; + \; aq.NaOH \quad \rightarrow \quad CH_3\,CH_2-OH \; + NaCl$$

b) By hydrolysis of Easter:

On hydrolysis, in presence of dilute acid or alkali, ester produces alcohol.

$$RCOO\,R' + H_2O \rightarrow RCOOH + R'OH$$

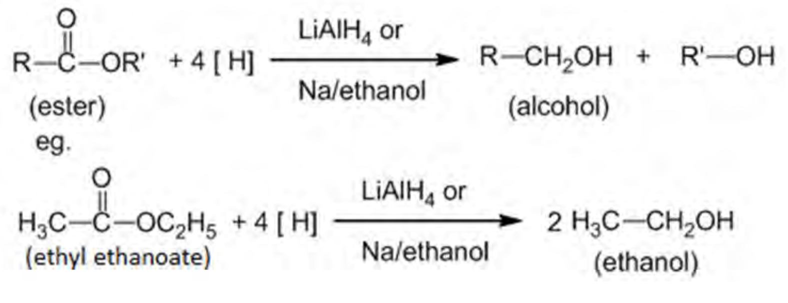
$$CH_3CH_2COO\,CH_3 + H_2O \rightarrow CH_3CH_2COOH + CH_3OH$$

c) By the reduction of Ester with $\boldsymbol{LiAlH_4}$ or $\boldsymbol{Na/Ethanol}$.

$\boldsymbol{LiAlH_4\ in\ ether}$**(or $\boldsymbol{Na/Ethanol}$.)** Is a reducing agent produces nascent hydrogen and this nascent hydrogen reduces ester into primary alcohols. During the reduction of ester two alcohols are formed in which at least one is primary alcohol.

$$RCOO\,R' + 4\,[H] \rightarrow RCH_2OH + R'OH$$

$$CH_3CH_2COO\,CH_3 + H_2O \rightarrow CH_3CH_2CH_2OH + CH_3OH$$



d) From primary amines:

When primary amine is treated with nitrous acid (HNO_2) at $0^o - 5^oC$ alcohol is produced. It is taken as test of alcohol where nitrogen gas is evolved.

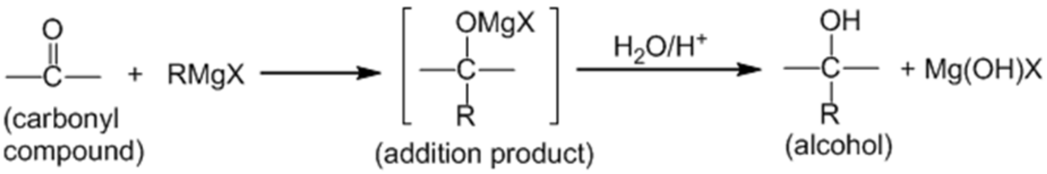
$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

$$RNH_2 + HNO_2 \rightarrow R-OH + N_2 + H_2O$$

$$CH_3NH_2 + HNO_2 \rightarrow CH_3-OH + N_2 + H_2O$$

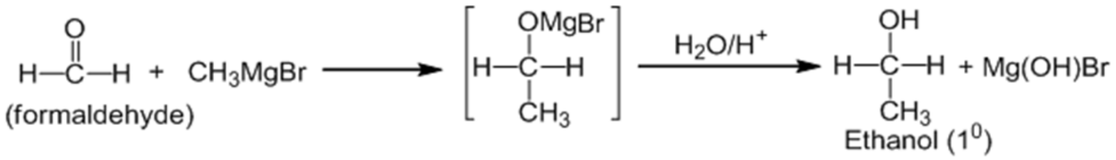
e) By the use of Grignard reagent:

Grignard reagent is an organometallic compound having general formula R-Mg-X, when it is treated with carbonyl compounds, it produces alcohols.

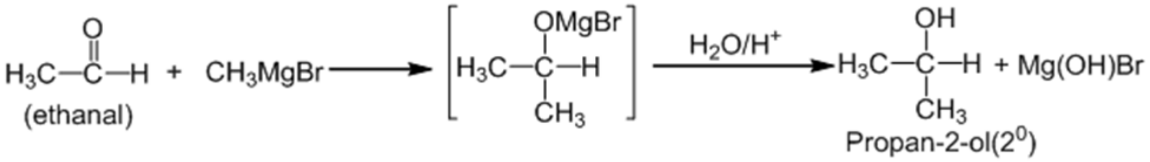


According to the nature of carbonyl compound the alcohol produced may be $1^o, 2^o$ and 3^o. Formaldehyde produces 1^o , $Other\ aldehydes\ produces$ 2^o and ketones produces 3^o alcohols. For example;

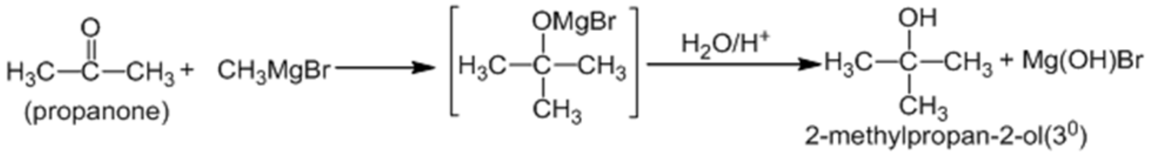
Preparation of 1^o alcohol:



Preparation of 2^o alcohol:



Preparation of 3^o alcohol:



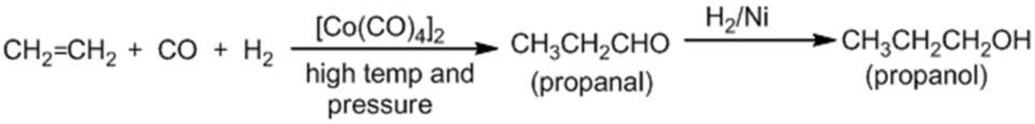
Try yourself: How will you obtain following compounds using Grignard's reagent-

(i) ***CH3 CH2 (CH3)OH*** ***(ii) CH3C(CH3)2CH2OH***
(ii) ***CH3C(CH3)3OH***

10.5. Industrial manufacture of alcohols from: oxo process ,Hydroboration oxidation of ethene and fermentation of sugar

10.5.1. Oxo process:

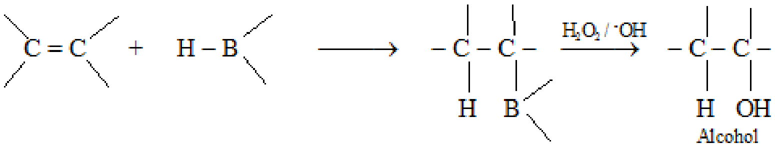
When alkene is treated with carbon monoxide and hydrogen in presence of catalyst like cobalt carbonyl (Actually dicobalt octacarbonyl) $[Co(CO)_4]_2$, it produces carbonyl compounds and on reduction of carbonyl compounds alcohols are obtained. It is also known as hydroformylation reaction.



$$CH_2{=}CH_2 + CO + H_2 \xrightarrow[\text{high temp and pressure}]{[Co(CO)_4]_2} \underset{\text{(propanal)}}{CH_3CH_2CHO} \xrightarrow{H_2/Ni} \underset{\text{(propanol)}}{CH_3CH_2CH_2OH}$$

10.5.2. **Hydroboration oxidation of ethene:**

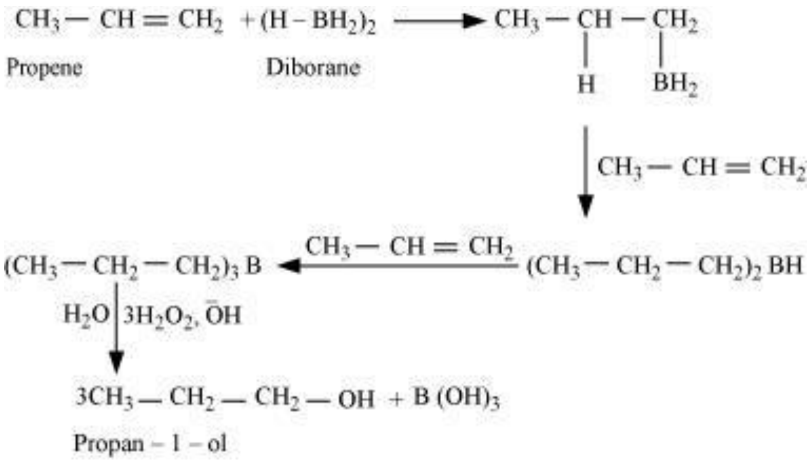
The reaction of alkenes with boron hydride (diborane, B_2H_6) in which hydrogen from borane attaches to the more substituted carbon and boron attaches to the least substituted carbon having double bond. Thus it follows anti-Markovnikov's addition. The addition product (trialkyl boron) reacts with H_2O_2 in the presence of alkali to produce alcohol.



$$\boldsymbol{CH_2 = CH_2 + \frac{1}{2}B_2H_6 \rightarrow (CH_3 - CH_2)_3B \rightarrow CH_3 - CH_2OH}$$

For propene:

Step wise process:



10.5.3. Fermentation:

Activity:

Fermentation is a common process in local areas of Nepal.

i) Why do people in Nepal still use fermentation in traditional drink preparation?

ii) What are the advantages and disadvantages of this practice?

Tongba

Fermentation is a biochemical process in which larger organic compounds like starch,sugar etc.are broken down with the help of enzyme catalysts (Generally obtained from yeast) in absence of oxygen (anaerobic process) to produce smaller compounds like alcohol.In Nepal fermentation is widely used in local level for the production of alcohol and other fermented foods e.g. pickle. There are mainly two raw materials which are widely used in the fermentation process for the production of alcohol.

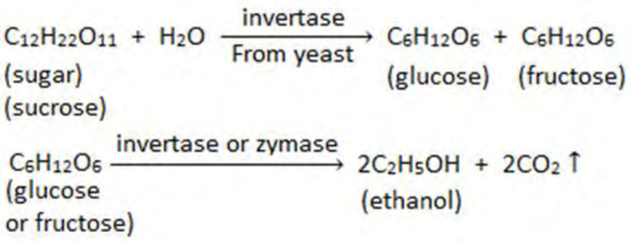
i) Molasses

ii) Starch

Ethyl alcohol from fermentation of molasses:

Molasses is the thick brown syrup left behind after the formation of crystals of sugar from juice of sugar cane. It contains sucrose (table sugar) which can be fermented to produce ethyl alcohol.

During fermentation when enzyme invertase (from yeast) is added in aqueous solution of molasses containing sucrose, glucose and fructose are produced which on further treating with enzyme invertase or zymase (from yeast), ethyl alcohol is obtained.

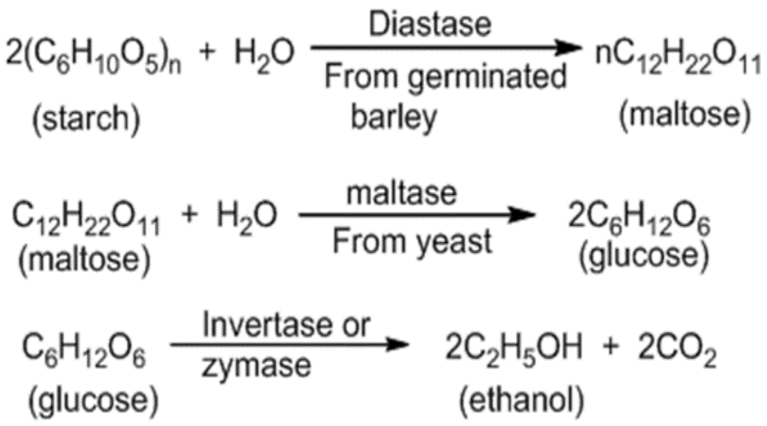


$$\underset{\substack{\text{(sugar)}\\\text{(sucrose)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{From yeast}]{\text{invertase}} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

$$\underset{\substack{\text{(glucose}\\\text{or fructose)}}}{C_6H_{12}O_6} \xrightarrow{\text{invertase or zymase}} \underset{\text{(ethanol)}}{2C_2H_5OH} + 2CO_2\uparrow$$

Ethyl alcohol from fermentation of starch:

Starch is contained in different plants,fruits, vegetables etc. When it is subjected to fermentation ethyl alcohol is obtained. Enzyme diastase (from barley) converter it in to maltose, maltase converts maltose into glucose and invertase converts glucose into ethyl alcohol.



Know Your Capacity (KYC):

i) How can science help to improve traditional fermentation method to make them safer and more efficient?

10.6. Definition of common terms: absolute alcohol, power alcohol, denatured alcohol (methylated spirit), Alcoholic beverage

10.6.1. Absolute alcohol:

Absolute alcohol is pure (about 100%) ethanol(ethyl alcohol) that contains less than 1% water. This type of alcohol is prepared from azeotropic distillation of rectified spirit and Is found in alcoholic beverages.

10.6.2. power alcohol (Gasohol)

Power alcohol is a liquid mixture Composed of Petrol (80%), ethanol (20%) and small amount of benzene.It is commonly used in the automotive industry as a fuel to generate energy for various operations. In addition to being more cost-effective than petroleum,Power alcohol serves as a fuel with excellent anti knocking properties, having an octane rating of 90.

10.6.3 denatured alcohol (methylated spirit),

Denatured alcohol is Ethanol that has been mixed with harmful substances to make it unsafe to drink. Poisonous substances such as pyridine Copper sulphate and methanol are commonly used in this process. When ethanol is mixed with methanol, it is called methylated spirit, which is commonly used as cleaner, fuel or solvent.

10.6.4 Alcoholic beverage:

An alcoholic beverage is a drink that contains ethanol(generally known as alcohol) produced by the fermentation of sugars by yeast.Alcoholic beverages are classified based on their alcohol content and production process in to three main categories

On the basis of production alcoholic baverages are classified as-

i) Undistilled alcoholic baverages- These are alcoholic drinks made by fermentation only and are not distilled after fermentation. They usually have lower alcohol content(about 4% to 15%). For example- Jaand, Tongba, Chhyang (traditional), Beer, Wine.

Beer: Generally made by the fermentation of grains like barley, wheat or maize.

Alcohol content is about 3-8%.

Wine: It is generally made by the fermentation of fruits like grapes. Alcohol content is about 8-15%.

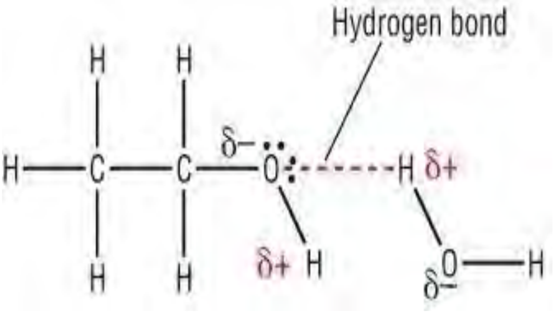
ii) Distilled alcoholic baverages- These are alcoholic drinks made by fermentation followed by distillation to increase alcohol content. They have a higher alcohol content about 20% to 50% or more. For example- Raksi (traditional), whisky, vodka, rum, brandy.

Spirits (or distilled beverage): It is produced by the distillation to concentrate alcohol. Alcohol content is about 20-40% or more.

10.7. Physical properties of monohydric alcohols

1. Lower members of alcohols are colourless liquid with characteristic alcoholic odour but higher members are waxy solids without colour and odour.
2. Lower members are highly soluble in water due to the formation of intermolecular hydrogen bonds but solubility decreases with increasing carbon number. On increasing carbon

number the size of hydrophobic group increases, which resists mixing of the compound with water and decreases solubility.



3. Melting point and boiling point of alcohols are higher than corresponding hydrocarbons but lower than that of water. Melting point and boiling point increases with increasing molecular weight of alcohols. On increasing branching surface area decreases and boiling point and melting point decreases. The higher boiling point of alcohol is due to hydrogen bonding but in ether there is no hydrogen bond, so ether has lower boiling and melting points than alcohol.

Try yourself: Compare the boiling point of –

$CH_3CH_2CH_2CH_2OH$, $CH_3CH(CH3)CH_2OH$, CH3CH2CH(OH)CH3 and CH3C(CH3)2OH

10.8. Chemical properties of Monohydric alcohols

10.8.1. Reaction with HX px3 PCl5, SOCl2

These are the reactions of alcohols involving cleavage of C-OH bond, nucleophilic substitution reaction, to produce alkyl halide

a) Reaction with HX: here X^- substitutes the OH^- showing nucleophilic substitution reaction

$$CH_3CH_2OH + HCl \xrightarrow[\text{or conc. } H_2SO_4]{\text{anhy. } ZnCl_2} CH_3CH_2Cl + H_2O$$

$$CH_3CH_2OH + HBr \xrightarrow[\text{or conc. } H_2SO_4]{\text{anhy. } ZnCl_2} CH_3CH_2Br + H_2O$$

b) Reaction with PX_3 and PX_5: In this reaction X from PX_3 and PX_5 substitutes -OH from alcohol to produce alkyl halide. For example

$$\underset{\text{(alcohol)}}{3R-OH} + PX_3 \xrightarrow{\Delta} \underset{\text{(haloaklane)}}{3R-X} + \underset{\text{(phosphorus acid)}}{H_3PO_3}$$

eg.

$$3\ CH_3OH + PCl_3 \xrightarrow{\Delta} 3CH_3Cl + H_3PO_3$$

$$R-OH + PX_5 \xrightarrow{\Delta} R-X + POX_3 + HX$$

e.g.

$$3CH_3CH_2CH_2OH + PCl_3 \xrightarrow{\Delta} 3CH_3CH_2CH_2Cl + H_3PO_3$$

c) Reaction with $SOCl_2$: In this reaction alcohols produce alkyl halide. This reaction is known as Darzen's reaction.

$$ROH + SOCl_2 \xrightarrow[pyridine]{reflux} RCl + SO_2 + HCl$$

eg.

$$CH_3CH_2OH + SOCl_2 \xrightarrow[pyridine]{reflux} CH_3CH_2Cl + SO_2 + HCl$$

10.8.2. Action with reactive metals like Na, K ,Li. Acidic and basic nature of alcohol

When alcohol is treated with reactive metals like Na, K and Li, metal alkoxide is produced with the release of hydrogen gas.

$$R-OH \quad + \quad M \rightarrow \quad RO^- + M^+ + H_2$$

Example:

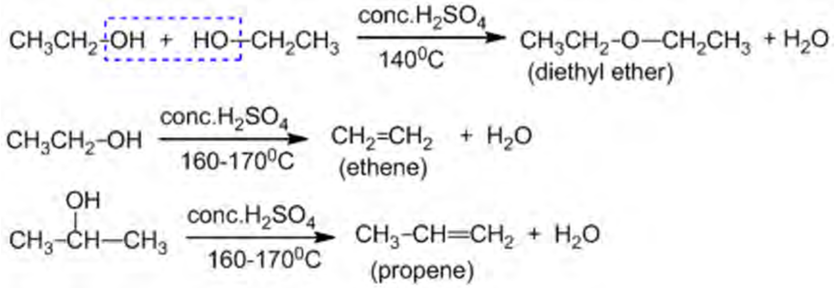
$$CH_3CH_2OH + Na \rightarrow CH_3CH_2O^- + Na^+ + H_2$$

Alcohol behaves like an acid because it can release hydrogen gas with the formation of alkoxide ion when it reacts with active metals. Methanol and ethanol, the simplest alcohol, have acidity level similar to that of water while most other alcohols are slightly less acidic than water
It also **acts as a Lewis base** because the oxygen atom in the –OH group has lone pairs of electrons that it can donate or it can accept H^+ ion.

10.8.3. Dehydration of alcohols

a) **Dehydration of alcohols using conc.H_2SO_4**: Conc. H_2SO_4 is a strong dehydrating agent. During dehydration of alcohols, products are formed on the basis of temperature. Below 100^oC alkyl hydrogen sulphate is produced (if excess alcohol is used, dalkyl sulphate is produced), at 140^oC ether is produced due to intermolecular dehydration and at 170^oC alkene is produced due to intramolecular dehydration.

$$CH_3CH_2-OH \quad \rightarrow CH_3CH_2-OSO_3H$$

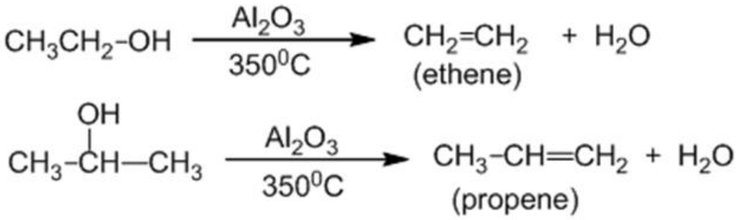


$$CH_3CH_2\boxed{OH + HO}CH_2CH_3 \xrightarrow[140^0C]{conc.H_2SO_4} \underset{\text{(diethyl ether)}}{CH_3CH_2\text{-}O-CH_2CH_3} + H_2O$$

$$CH_3CH_2\text{-}OH \xrightarrow[160\text{-}170^0C]{conc.H_2SO_4} \underset{\text{(ethene)}}{CH_2{=}CH_2} + H_2O$$

$$CH_3\text{-}\overset{OH}{\overset{|}{C}}H-CH_3 \xrightarrow[160\text{-}170^0C]{conc.H_2SO_4} \underset{\text{(propene)}}{CH_3\text{-}CH{=}CH_2} + H_2O$$

b) Dehydration of alcohols using Al_2O_3: The dehydration of alcohol can also be done by passing vapour of alcohol over heated alumina (Al_2O_3) produces ether at 250^oC and alkene 350^oC.



$$CH_3CH_2\text{-}OH \xrightarrow[350^0C]{Al_2O_3} \underset{\text{(ethene)}}{CH_2{=}CH_2} + H_2O$$

$$CH_3\text{-}\overset{OH}{\overset{|}{C}}H-CH_3 \xrightarrow[350^0C]{Al_2O_3} \underset{\text{(propene)}}{CH_3\text{-}CH{=}CH_2} + H_2O$$

Oxidation of alcohols follow the order-

$$3^o > 2^o > 1^o$$

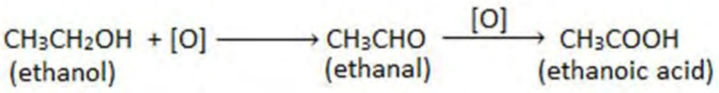
Try yourself: Predict the major product of dehydration of Butan-1-ol, if the reaction is acid catalysed.

10.8.4. Oxidation of Primary secondary and tertiary alcohols with Mild oxidizing agent like $KmnO_4$ or $K_2Cr_2O_7$.

General steps of oxidation of alcohols can be represented as-

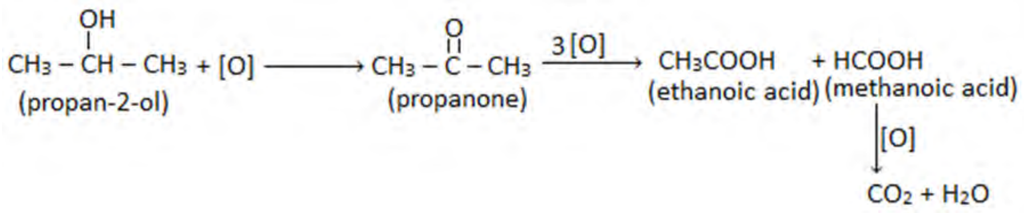
$$R-CH_2-OH + [O] \rightarrow R-CHO \xrightarrow{[O]} R-COOH$$

Primary alcohols:



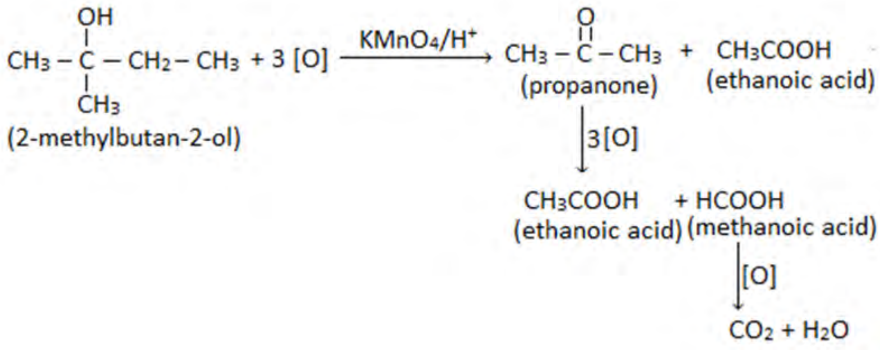
$$\underset{\text{(ethanol)}}{CH_3CH_2OH} + [O] \longrightarrow \underset{\text{(ethanal)}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{(ethanoic acid)}}{CH_3COOH}$$

Secondary alcohols:



Tertiary alcohols:

Due to the lack of alpha hydrogen tertiary alcohols cant be oxidized in normal conditions. Tertiary alcohols require drastic conditions to oxidize because it needs breaking of C - C bond.

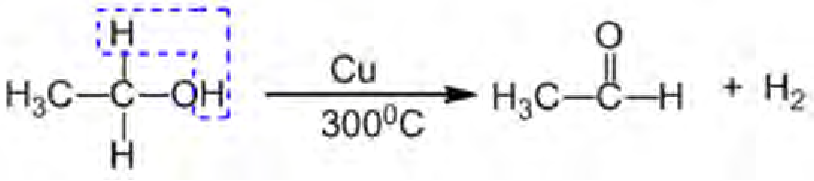


Oxidation of alcohols is also known as oxidative degradation. Common oxidizing agents are K2CrO4, KmnO4, H2CrO4 and PCC (Pyridinium chlorochromate for mild oxidation).

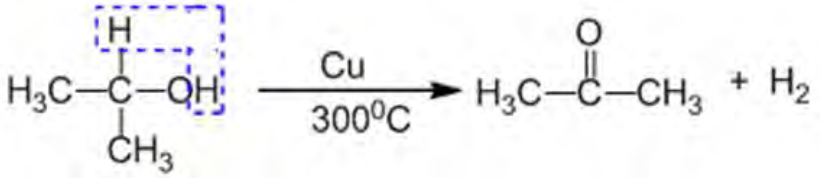
10.8.5. Catalytic Dehydrogenation of $1^o$and 2^o alcohols and dehydration of 3^o alcohol.

The chemical reaction to extract hydrogen from alcohol in the presence of a catalyst is called dehydrogenation. Different alcohols give different products during dehydration.

a) Dehydrogenation of 1^o alcohol: When vapour 1^oalcohol is passed over hot copper at $300^o C$aldehyde is produced.

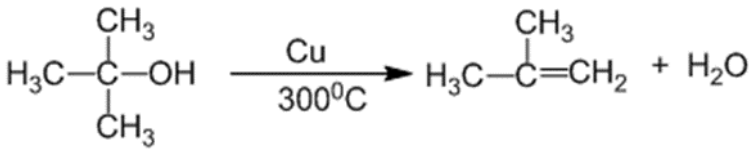


b) Dehydrogenation of 2^o alcohol: When vapour of 2^o alcohol is passed over hot copper at 300^oC ketone is produced.



c) Dehydration of 3^o alcohol: Due to the lack of alpha hydrogen, 3^o alcohol can't get dehydrogenated but on passing over hot copper at 300^oC, It undergoes dehydration to produce alkene.

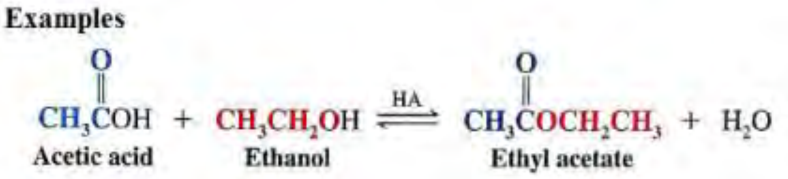
Reaction



Try yourself: How is 2,2-dimethylpropan-1-ol behaves in catalytic dehydrogenation ($Cu, 300^oC$) of alcohols.

10.8.6. Esterification reaction.

It is the reaction for the preparation of esters.Thus, the reaction in which alcohol is treated with carboxylic acid in presence of dehydrating agent like conc.H_2SO_4 to produce pleasant fruity smell of easter is known as esterification reaction .



10.8.7. **Test of ethanol.**

Chemical test for ethanol can be performed in different ways-

a) Dichromate test:

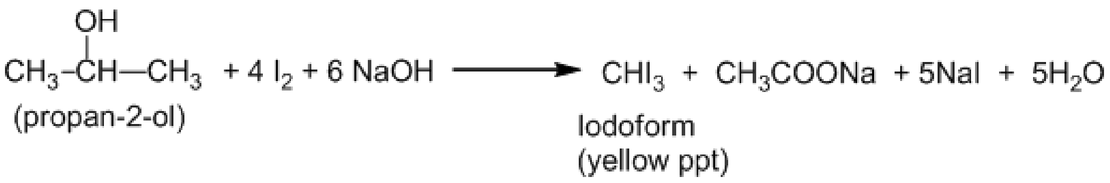
When ethanol is treated with sodium dichromate solution in acidic medium, ethanol get oxidized to acetaldehyde which further get oxidized to produce ethanoic acid and colour of dichromate changes to green due to the formation of chromic sulphate. (In the primary and secondary alcohols, the orange color of the solution changes to green but in tertiary alcohol there is no change in colour.)

$$\text{ethanol} + \underset{\textit{from the oxidising agent}}{\text{oxygen}} \xrightarrow[\text{sulphuric acid}]{\text{sodium dichromate}} \text{ethanal} + \text{water}$$

$$CH_3CH_2OH + [O] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} CH_3CHO + H_2O$$

b) Iodoform test:

When ethanol is heated with iodine and aqueous solution of NaOH, iodoform having a hospital smell is obtained.



$$\underset{\text{(propan-2-ol)}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_3} + 4\,I_2 + 6\,NaOH \longrightarrow \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + CH_3COONa + 5NaI + 5H_2O$$

c) Ceric ammonium nitrate test:

This test detects the presence of alcohol in the solution. When Orange- yellow coloured ceric Ammonium Nitrate is treated with alcohol, it produces red coloured complex.

$$\underset{\substack{\text{Ceric Ammonium}\\ \text{Nitrate}}}{(NH_4)_2[Ce(NO_3)_6]} + 3\,ROH \longrightarrow \underset{\text{Red Complex}}{[Ce(NO_3)_4(ROH)_3]} + 2\,NH_4NO_3$$

Exercise 10.1

Multiple Choice questions:

1. The general formula of alcohol is

a. $C_nH_{2n}O$.   b. $C_nH_{2n+2}O$ c. $C_nH_{2n-2}O$.   d. $C_nH_{2n+1}O$

2. The IUPAC name of $CH_3CH(CH_3)CH_2OH$.

a. $Propan-1-ol$.   b. $Butan-1-ol$

c. $Propan-2-ol$.   d. $Butan-2-ol$

3. Absolute alcohol is

a. $100\%\ ethanol$.   b. $95\%\ ethanol\ and\ 5\%\ ater$

c. $100\%\ methanol$.   d. $Rectified\ spirit$

4. Alcohol has higher boiling point than that of alkene with similar molecular weight, because:

a. $Alcohols\ are\ more\ reactive$.

b. $Alcohols\ form\ hydrogen\ bonds$.

c. $Alcohols\ have\ weaker\ van\ der\ Waals\ force$.

d. $BAlcohols\ do\ not\ undergo\ oxidation$.

5. Which if the following method is most suitable for distinguishing primary,secondary and tertiary alcohols.

a. $Lucas\ test$.   b. $Fehling's\ test$

c. $Bromine\ water\ test$.   d. $Iodoform\ test$

6. Alcohols are soluble in water, the property which is responsible for this is:

a. $Dipole-dipole\ interaction$.   b. $Hydrogen\ bonding$

c. $Ionic\ bonding$.   d. $Covalent\ bonding$

7. Which of the following reacts with $FeCl_3$ to give colored complex?

a. $Ethanol$.   b. $Methanol$ c. $Phenol$.   d. $Propanol$

8. During the preparation of ethanol from ethene, which if the following reagent is responsible?

a. $H_2/Ni.$ b. H_2O/H_2SO_4

c. $NaBH_4.$ d. HBr

9. Which of the following alcohol give a positive iodoform test?

a. $1-Propanol.$ b. $2-Butanol$

c. $2-Propanol.$ d. $Methanol$

10. The enzyme used during the fermentation of sugar to ethanol is:

a. $Amylase.$ b. $Invertase$

c. $Zymase.$ d. $Diastase$

11. The most suitable reagent foe dehydration of ethanol to ethene is:

a. $Conc. HCl.$ b. $Conc. H_2SO_4$ c. $NaOH.$ d. $ZnCl_2$

12. Which of the following alcohol produces ketone on oxidation?

a. $Propan-1-ol.$ b. $Butan-1-ol$

c. $Propan-2-ol.$ d. $2-methylpropan-2-ol$

13. To convert a primary alcohol to an aldehyde without further oxidation to a carboxylic acid, most suitable reagent is:

a. $Acidified\ KMn0_4.$ b. $PCC\ (Pyridinium\ chlorochromate)$

c. $conc. H_2SO_4$ d. $Fehling'ssolutionl$

14. Special additives are added in denatured alcohol because of-

a. $to\ enhance\ its\ flavour.$ b. $to\ make\ it\ unfit\ for\ drinking.$

c. $to\ increase\ its\ alcohol\ content.$ d. $to\ improve\ its\ color.$

15. Esterification involves the reaction of alcohol with-

a. An aldehyde b. A ketone c. A carboxylic acid d) Ether

16. Methanol poisoning is dangerous because its metabolism producces-

a. Acetic acid b. Formic acid c. Lactic acid d. Citric acid

17. Which statement best explains the decreasing solubility of higher alcohols in water?

a. $Molecular\ weight\ increases.$

b. $Hydrogen\ bonding\ increases.$

c. $The\ non-polar\ alkyl\ chain\ becomes\ longer.$

d. $The-OH\ group\ becomes\ less\ reactive.$

18. Which alcohol shows optical activity?

a. $Propan-1-ol.$ b. $Propan-2-ol.$

c. $Butan-2-ol.$ d. $2-methylpropan-2-ol.$

19. Which of the following alcohols will undergo oxidation to form a carboxylic acid without passing through the aldehyde stage.

a. $Methanol.$ b. $Propan-2-ol.$

c. $Butan-1-ol.$ d. $2-methylpropan-2-ol.$

Exercise 10.2

1. An alcohol has molecular formula $C_4H_{10}O$, It may have different structural formulas.
   i) Write possible isomers of $C_4H_{10}O$ and write their IUPAC names.
   ii) Classify these isomeric alcohols.
2. Lower alcohols are liquids with characteristic smell but higher alcohols are solid with no smell.
   i) Explain the cause of solubility of alcohols in water.
   ii) Boiling points of alcohols are higher than their parent hydrocarbon. Explain.
   iii) Compare the solubility of $1^o, 2^o\ and\ 3^o$ alcohols in water.
3. Victor- Meyer's method is a well-known method for the separation of alcohols.
   i) What are the reagents used in the Victor- Meyer's method?
   ii) Write the reactions involved in the Victor- Meyer's method for the separation of solutions containing propan-1-ol, propan-2-ol and 2-methylpropan-2-ol.
   iii) Why doesn't $R_3C\text{-}NO_2$, formed during the test of 3^o alcohol, react with HNO_2?
   iv) In victor-Meyer's test, why does a secondary alcohol produce blue solution while primary alcohol produces red solution?

4. In the Nepali culture fermentation is a common process for the preparation of pickle, homemade alcoholic drinks etc. using vegetables, fruits, barley, millet etc.
   i) Define fermentation with examples.

ii) Which enzyme is used for the fermentation of molasses and sucrose? Represent them with pertinent reactions.

5. Complete the following reactions.

i) $CH_3CHO \xrightarrow{LiAlH_4}$

ii) $CH_3COCH_3 \xrightarrow{LiAlH_4}$

iii) $CH_3CH_2I + aq.KOH \longrightarrow$

iv) $CH_3MgBr + CO_2 \longrightarrow A \xrightarrow{H_2O,H^+} B$

v) $CH_3MgBr + CH_3CHO \longrightarrow A \xrightarrow{H_2O,H^+} B$

vi) $CH_3MgBr + CH_3COCH_3 \longrightarrow A \xrightarrow{H_2O,H^+} B$

vii) $CH_3MgBr + HCHO \longrightarrow A \xrightarrow{H_2O,H^+} B$

viii) $C_2H_5OC_2H_5 + H_2O \xrightarrow{dil.H_2SO_4,\ high\ pressure}$

ix) $CH_3COOH \xrightarrow{LiAlH_4\ or\ Na/C_2H_5OH}$

x) $CH_3COOC_2H_5 \xrightarrow{H^+\ or\ OH^-}$

xi) $C_2H_5NH_2 + HNO_2 \xrightarrow{(NaNO_2 + HCl)/o-5^oC}$

6. Alkenes may be the source of alcohol. Catalytic hydration and Hydoboration-oxidation are the main reactions.

i) Describe the steps involved in the hydroboration-oxidation of ethane with pertinent reactions for the preparation of alcohol.

ii) Write the reactions of alkenes to produce propan-2-ol and 2-methylpropan2-ol.

7. Lucas test and $KMnO_4$ test are the tests to identify the types of alcohols.

i) What is the Lucas reagent? Write reactions involved in the Lucas test of 1^o, 2^o and 3^o alcohols.

ii) Why does a tertiary alcohol not undergo oxidation with acidified $KMnO_4$?

iii) Write the reactions involved in the oxidation of ethanol and propan-2-ol with acidified $KMnO_4$.

8. Complete the following reactions.

i) $CH_3CH_2OH + PCl_3 \longrightarrow$

ii) $CH_3CH(OH)CH_3 + PCl_5 \longrightarrow$

iii) $CH_3CH_2OH + SOCl_2 \xrightarrow{Pyridine}$

iv) $CH_3CH_2OH \xrightarrow{Conc.\ H_2SO_4/100^oC}$

v) $CH_3CH_2OH \xrightarrow{Conc.\ H_2SO_4/140^oC}$

vi) $CH_3CH(OH)CH_3 \xrightarrow{Conc.\ H_2SO_4/170^oC}$

vii) $CH_3CH_2OH \xrightarrow{Al_2O_3/250^oC}$

viii) $CH_3CH(OH)CH_3 \xrightarrow{Al_2O_3/350^oC}$

9. Dehydration of tertiary alcohol occur more readily than primary and secondary alcohols. Suggest your answer.

10. Different alcohols, when passed over heated copper, produces different products. Complete the following reactions.

    i) $CH_3CH_2OH \xrightarrow{Cu/\ 300^oC}$

    ii) $CH_3CH(OH)CH_3 \xrightarrow{Cu/\ 300^oC}$

    iii) $CH_3C(OH)(CH_3)_2 \xrightarrow{Cu/\ 300^oC}$

11. An alcohol A ($C_4H_{10}O$) reacts with PCl_5 to form compound B. Compound B undergoes dehydrohalogenation with alc. KOH to form compound C. Compound C reacts with dil. H_2SO_4 to form compound D, which is a tertiary alcohol. Identify A, B, C and D with pertinent reactions.

12. An alcohol M (C3H8O) reacts with metallic sodium to release hydrogen gas. Upon oxidation, M gives an aldehyde N. Identify M and N. Write their structure and explain their reactions.

13. An alcohol X ($C_5H_{12}O$) reacts with Lucas reagent to give turbidity after 5 minutes. Dehydration of X with conc. H_2SO_4 forms compound Y. Ozonolysis of Y gives Z(C_3H_6O) and W (C_2H_4O). Identify X, Y, Z and W and write their structures with pertinent reactions.

14. An alcohol A ($C_4H_{10}O$) is oxidized to ketone B. When B reacts with I_2 and NaOH, it gives a yellow precipitate of iodoform. Dehydration of A gives compound C. Identify A, B and C and write their structures with pertinent reactions.

15. A compound A (C_2H_6O) is a liquid soluble in water and burns with a blue flame. It reacts with Na-metal to produce a gas and forms compound B when heated with concentrated H_2SO_4 at 170^oC. Compound A also gives a yellow precipitate with iodine in alkaline medium.

    i) Identify compound A and write all possible reactions.
    ii) What is the role of H2SO4 in the above reaction?
    iii) Explain how you can distinguish between A and propan-2-ol using chemical test.
    iv) What change would you observe if A is treated with acidified potassium dichromate solution? Write a balanced equation.

Bingo-Game

Instruction

1. A 5 × 5 bingo card is provided to you or draw in your notebook
2. A word bank comprising 25 terms is provided below. You should select the appropriate term that corresponds to the clue provided by the teacher.
3. The box at the center is your FREE space, which may be marked automatically.
4. Only one term should be filled per box on your Bingo card.
5. Listen carefully as your teacher reads out clues or definitions related to the terms.
6. When a clue matches a term on word bank, fill the term in that box randomly.
7. The first student to fill a full row, column, or diagonal shouts "BINGO!" and wins!

Bingo Card:

		FREE		

Word Bank-

Ethanol, Iodoform, Primary alcohol, Fermentation, Methanol, Hydrogen bonding, Sodium, Conc. H_2SO_4, Victor Meyer test, Power alcohol, Absolute alcohol, Secondary alcohol, $ZnCl_2$/HCl, $FeCl_3$ test, Primary, Tertiary alcohol, Distilled beverages, Fermented beverages, Solubility, Nitrous acid test, Dehydration, Acidified $KMnO_4$, Esterification.

Teacher clues (Reads aloud)

1. This alcohol is used in hand sanitizers and drinking beverages.
2. This test gives a yellow precipitate with ethanol.
3. This alcohol does not react with Lucas reagent even after a long time.
4. This process is used to make alcohol from sugar using yeast.
5. This alcohol is poisonous and is used as a solvent and fuel.
6. These forces are responsible for high boiling point of alcohols.
7. Alcohol reacts with this metal to release hydrogen gas.
8. This chemical is used to dehydrate ethanol at 170°C.

9. This reagent helps to distinguish between primary, secondary, and tertiary alcohols.

10. A fuel blend of petrol and ethanol.

11. This is the purest form of ethanol with no water.

12. This alcohol gives a ketone on oxidation.

13. This reagent is used in Lucas test.

14. This test gives violet color with phenol, but not with alcohol.

15. The IUPAC name of CH_3CH_2OH.

16. This group of alcohols has the $–CH_2OH$ functional group.

17. This type of alcohol gives fastest turbidity with Lucas reagent.

18. These beverages are obtained by fermentation and distillation.

19. These beverages are made only by fermentation, not distilled.

20. This property of alcohol decreases with increase in carbon chain.

21. This test shows different colors for 1°, 2°, and 3° alcohols using nitrous acid.

22. This reaction forms an alkene by removing water from alcohol.

23. This is used as an industrial solvent and fuel but is toxic.

24. A common oxidizing agent that converts ethanol to acetic acid.

25. Alcohols undergo this type of reaction with carboxylic acids to form esters.

Project work

1. To study the alcohol as a fuel: Power alcohol and its importance.

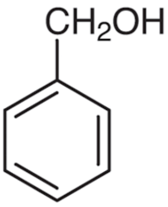
2. To study the Industrial Preparation of Alcohols: Fermentation (in context of Nepal) and Oxo Process.

UNIT 11
PHENOL

11.1.1 ACTIVITY:

Objective: To know the structure and component of phenol

Observe the following structures and identify phenol with reason.



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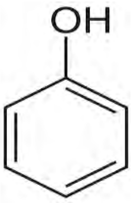

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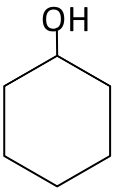
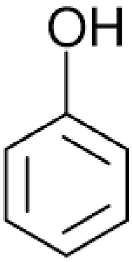


11.1 Introduction and nomenclature: Phenols are naturally occurring Organic compounds which consists of a benzene ring attached with hydroxyl group. They are also known as carbolic acids.



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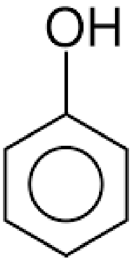

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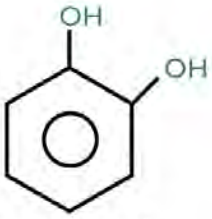
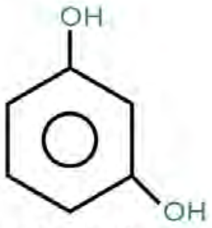
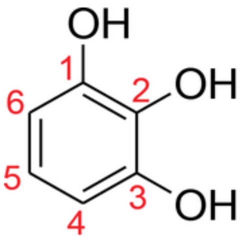


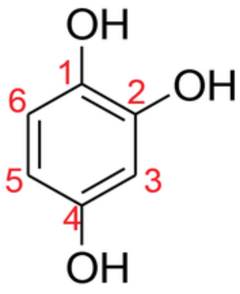
pyrocatechol
(benzene-1,2-diol)



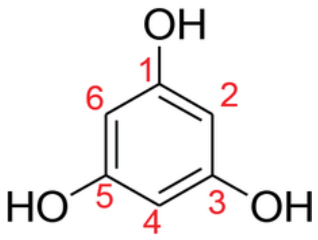
resorcinol
(benzene-1,3-diol)



Pyrogallol



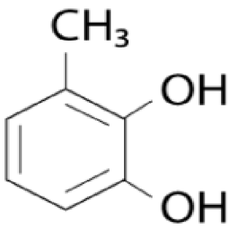
Hydroxyquinol

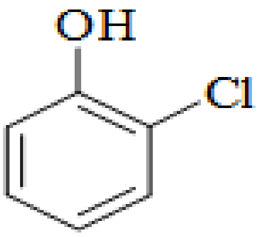


Phloroglucinol

Phenol consists of two components: an aryl group and a hydroxyl group. Depending on the number of aryl groups attached, phenols can be categorized further into mono-, di-, tri-, or polyhydric phenols.

The IUPAC name for phenol is monohydroxybenzene. In case of substituted phenols, the substituent group is written as prefix with the position.





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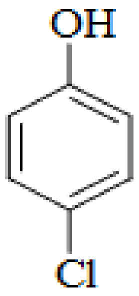

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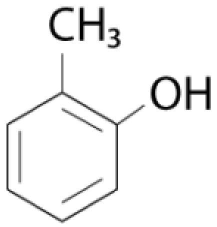

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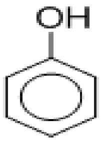
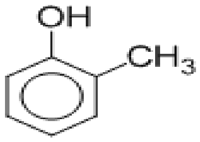
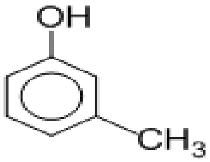
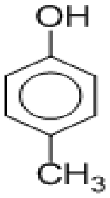
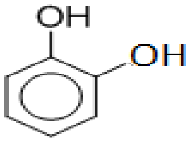
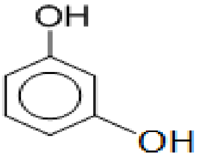
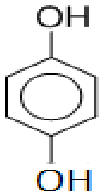
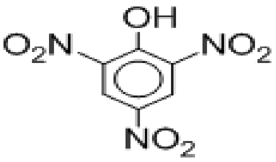
11.1..2. ACTIVITY:

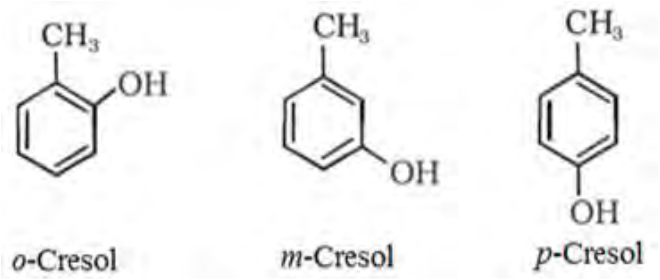
Objective: To know the systematic nomenclature of phenols.

Draw the structural formula of the following compounds.

a) 2-Methylphenol
b) 2,4,6-tribromophenol
c) P -nitrophenol
d) Benzene-1,2-diol.

Conclusion : Students will understand the basics of the structure and nomenclature of phenols. It prepares them to name an identify phenols confidently.

Structure	Common name	IUPAC name
	Phenol	Phenol (Benzenole)
	o-cresol	2-methylphenol
	m-cresol	3-methylphenol
	p-cresol	4-methylphenol
	Catechol	2-hydroxyphenol
	Resorcinol	3-hydroxyphenol
	Quinol	4-hydroxyphenol
	Picric acid	2,4,6-trinitrophenol



11.2 Preparation of phenol:

11.2.1 Activity

Objective: To understand the different processes for the preparation of phenol

a) Prepare a chart showing the complete reaction steps of,

Benzene ⟶ Diazonium salt ⟶ Phenol

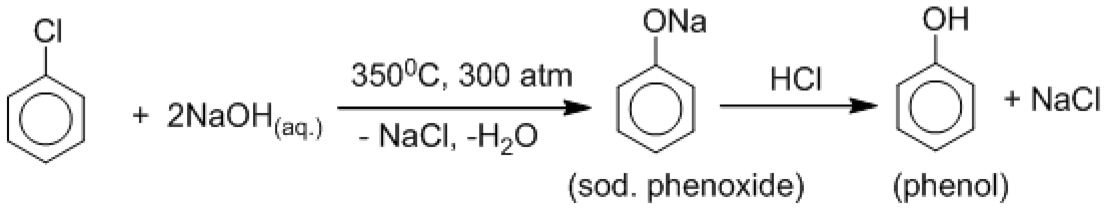
b) Benzene ⟶ Benzenesulfonic acid ⟶ Sodium phenoxide ⟶ Phenol

Write this reaction with complete reagent and suitable conditions.

Conclusion: Students will be confident about the methods of preparation of phenol.

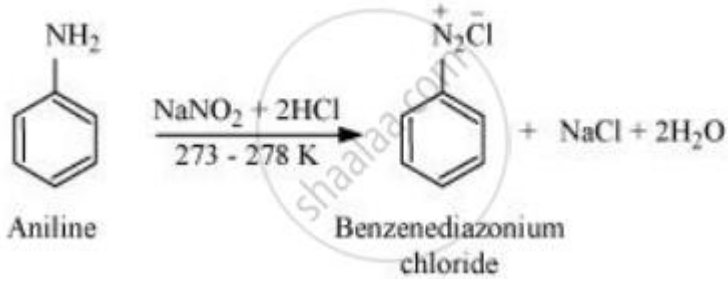
i.From Chlorobenzene (Dow"s process)

Simply nucleophilic substitution in chlorobenzene is very difficult,but with NaOH under drastic conditions (350^oC temperature and 300 atm. pressure) sodium phenoxide is produced, which on acidic hydrolysis produces phenol.

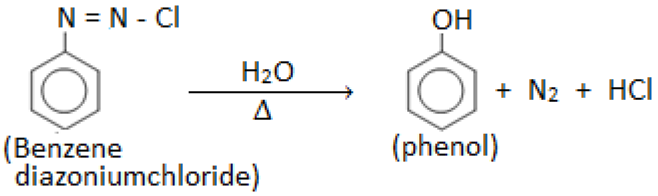


ii. From Diazonium salt:

Diazotization of aniline produces benzene diazonium chloride (BDC)

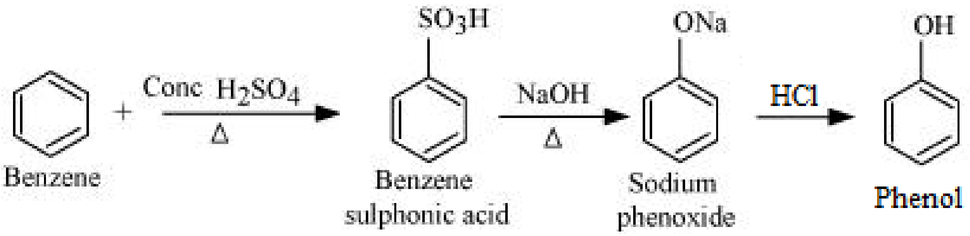


On heating aqueous solution of benzene diazonium chloride (on hydrolysis), phenol is produced.



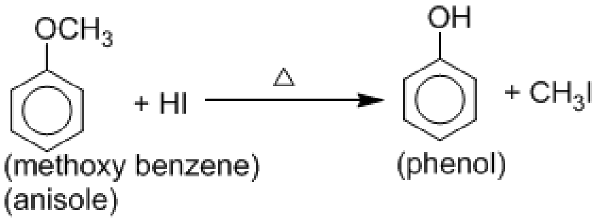
iii. From benzene sulphonic acid:

Electrophilic substitution of benzene with conc.H_2SO_4 , benzene sulphonic acid is produced. On heating with NaOH, it gives sodium phenoxide and which on acidic hydrolysis gives phenol.



Iv. From Anisole:

When anisole is heated with hydrogen iodide (HI), phenol is produced.



11.3 Physical properties of phenol

Phenol is a colourless, hygroscopic, crystalline solid, which is slightly soluble in water but highly soluble in organic solvent. The lower solubility of phenol in water compared to smaller alcohols is mainly due to the presence of its large non-polar benzene ring, which reduces its ability to interact effectively with water molecules.

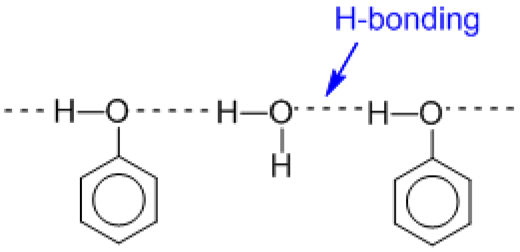


Fig: Hydrogen bonding between phenol and water.

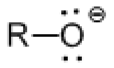
Its melting point is about $42^{o}C$ and boiling point is about $181^{o}C$. It is weakly acidic in nature but more acidic than alcohol, Aqueous solution of phenol containing about 5% water is known as carbolic acid.

11.4 Chemical properties

11.4.1 Activity

Objective: To understand the stability of phenoxide ion.

a) Observe the following two structures and identify that which one is more stable and why.



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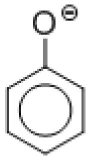
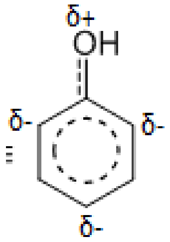


b) Observe the figure below,

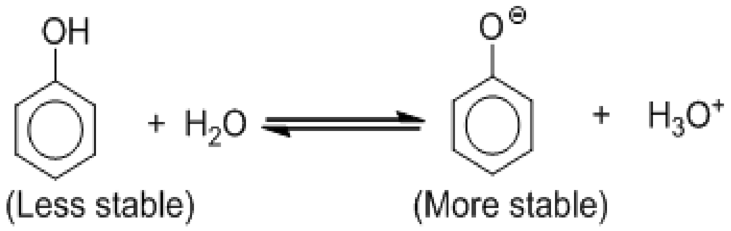


How would you justify the ring activating as well as ortho-para directing nature of phenol?

Conclusion: Student will understand the stability of phenoxide ion and acidic nature of phenol. Similarly activity (b) helps them to understand electrophilic substitution in phenol.

11.4.1 Acidic nature of phenol (comparison with alcohol and water)

The acidic nature of a compound refers to its ability to release protons when dissolved in water. For phenols, dissolving in water results i dissociation to form a phenoxide ion and a proton



The phenoxide ion is highly stable due to resonance.

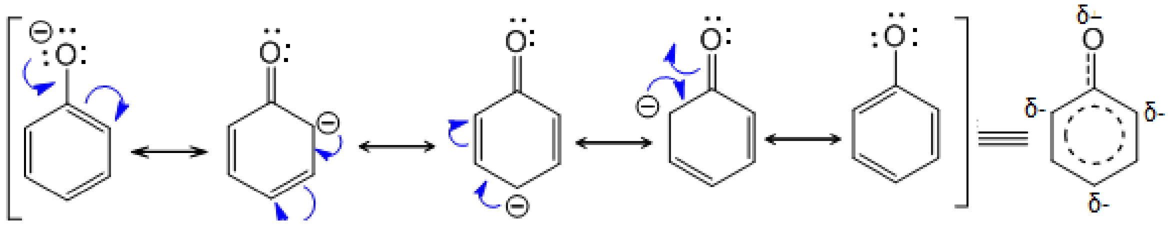


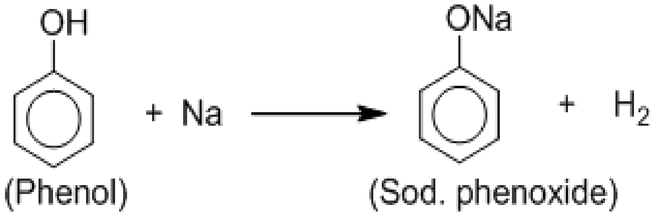
Fig: Resonating structures of phenoxide ion

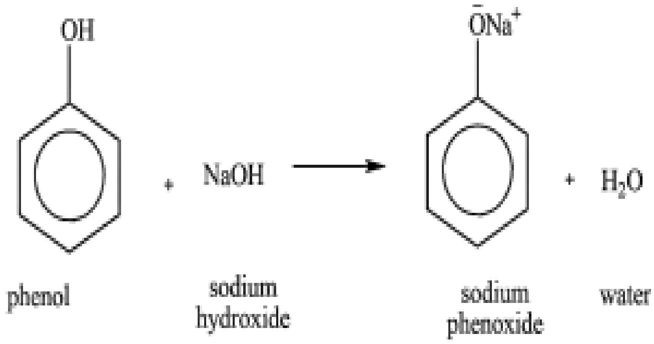
In these structures structure II, III and IV shows that oxygen is bonded with the carbon of the ring through partial double bond which helps to release hydrogen easily from phenol showing acidic nature. Phenol is more acidic than water and alcohol because of the resonance stabilization of phenoxide ion, which is not in case of alcohol and water.

Phenol and phenoxide ion differ significantly in their charge separation. In phenol, the lone pair on the oxygen atom can partially delocalize into the benzene ring, but there is no full negative charge. But In case of, the phenoxide ion, it is formed by the loss of a proton from phenol, carries a full negative charge on the oxygen. This charge is extensively delocalized into the aromatic ring through resonance, resulting in greater charge separation and enhanced stability. This resonance stabilization of the phenoxide ion explains why phenol is more acidic than alcohols.

$$R-O-H \rightleftharpoons R-\ddot{\underset{..}{O}}^{\ominus} + H^{+}$$

Acidic nature of phenol can be shown by following reactions also.





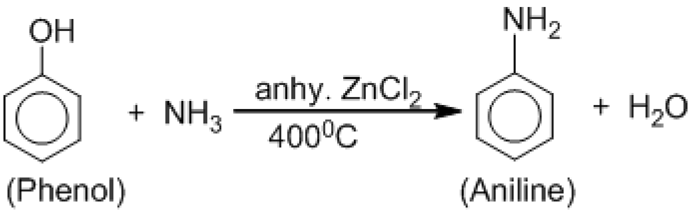
Acidic strength of phenol, alcohol and water follow the order,

Phenol > Water > Alcohol

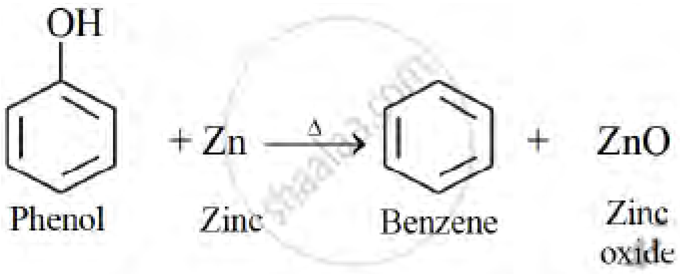
11.4.2 Action with NH3, Zn, Na, benzene diazonium chloride and phthalic anhydride

i) Action of phenol with ammonia (NH_3)

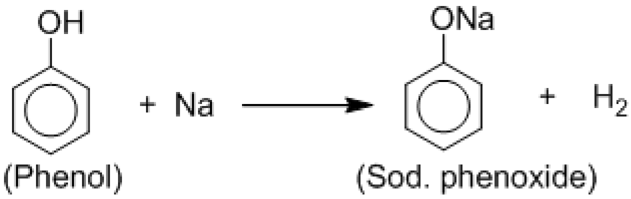
When phenol is treated with ammonia in presence of anhy. $ZnCl_2$ at 400^oC, aniline is produced. It is a nucleophilic substitution reaction.



ii) Action of phenol with zinc (Zn): When phenol is heated with zinc dust, it gets reduced to produce benzene.

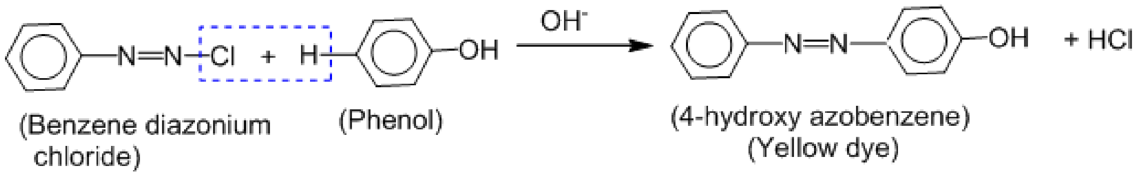


iii) Action of phenol with sodium (Na): When phenol is treated with sodium, hydrogen gas is released with the formation of sodium phenoxide. It shows acidic nature of phenol.



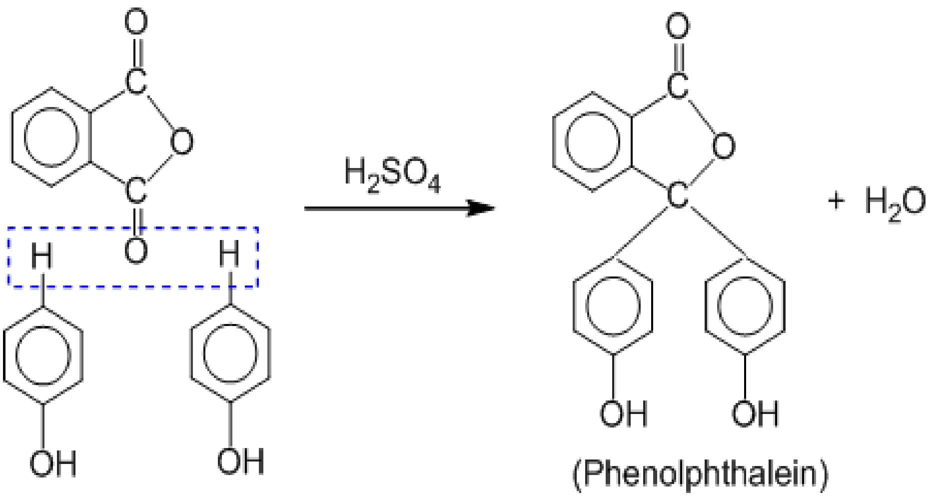
iv) Action of phenol with benzene diazonium chloride ($C_6H_5N_2$Cl):

With benzene diazonium chloride in slightly alkaline medium, phenol gives **coupling reaction** to produce an azo-dye i.e. p-hydroxy azobenzene (4-hydroxy azobenzene).



v) Action of phenol with phthalic anhydride $(C_6H_4(CO)_2O$:

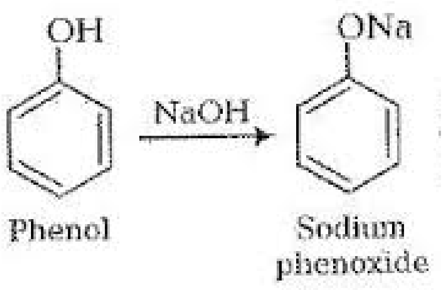
It is a condensation reaction in which phenol is condensed with phthalic anhydride in presence of conc.H_2SO_4, to produce phenolphthalein with release of one molecule of water.

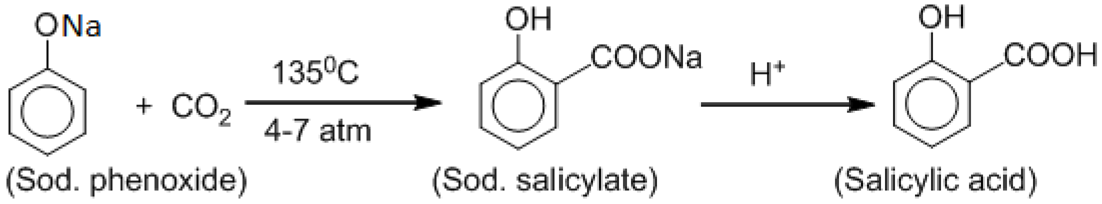


11.4.3 Acylation reaction, Kolbe's reaction, Reimer-Tiemann's reaction

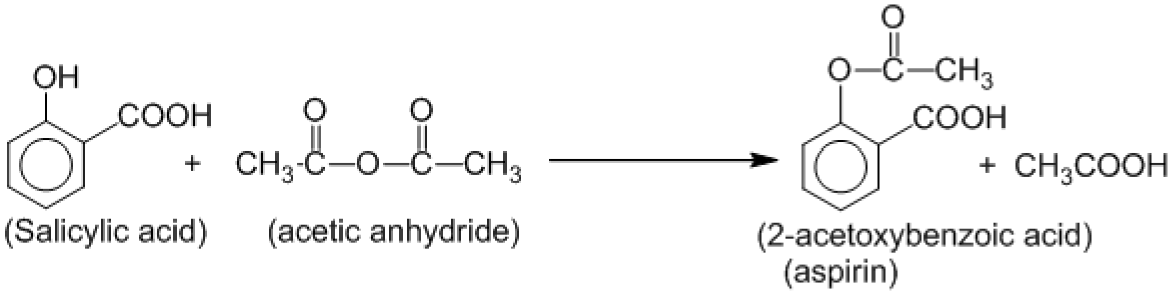
i) Kolbe's reaction: (Carboxylation reaction)

When phenol is treated with sodium hydroxide, sodium phenoxide is produced. When sodium phenoxide is treated with CO_2 at 135^oC temperature and 4-7 atm. Pressure followed by acidic hydrolysis produces salicylic acid (2-hydroxybenzoic acid). This is known as Kolbe’s reaction.



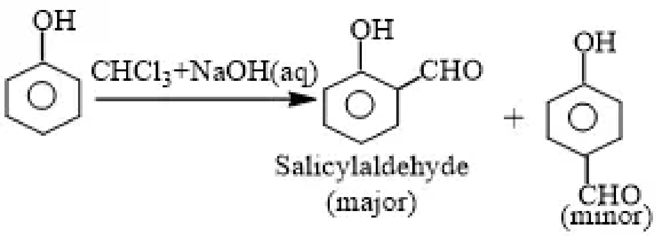


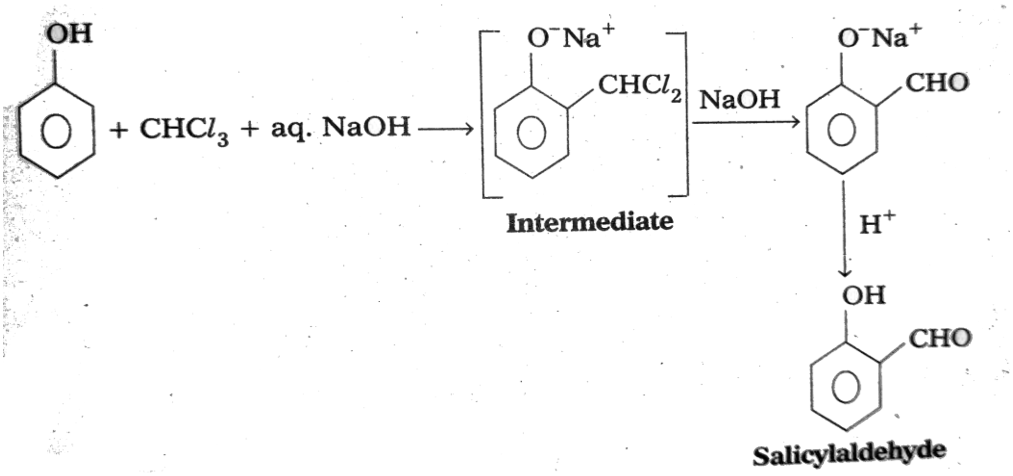
From salicylic acid aspirin can be obtained-



ii) Reimer-Tiemann's reaction:

It is a type of substitution reaction and is used for formylation of phenol at ortho position. Therefore, When phenol is treated with chloroform in presence of aqueous alkali (NaOH or KOH) at about $70^{o}C$ to produce o-hydroxybenzaldehyde as major product, is known as Reimer-Tiemann reaction.

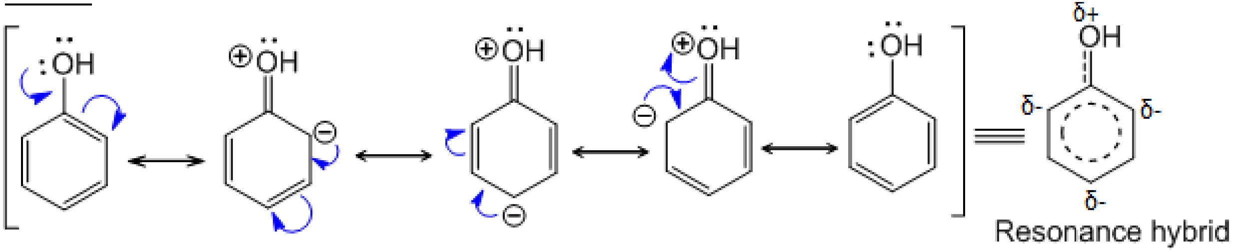




11.4.4 Electrophilic substitution: nitration, sulphonation, bromination and Friedal-Craft's alkylation

i) Electrophilic substitution: In phenol, electrophilic substitution reaction is the reaction in which an incoming electrophile replaces hydrogen, bonded to the carbon of the ring. The position of incoming electrophile in the ring is determined by the functional group i.e. -OH group in the compound, it can be identified by the following resonating structures of phenol.

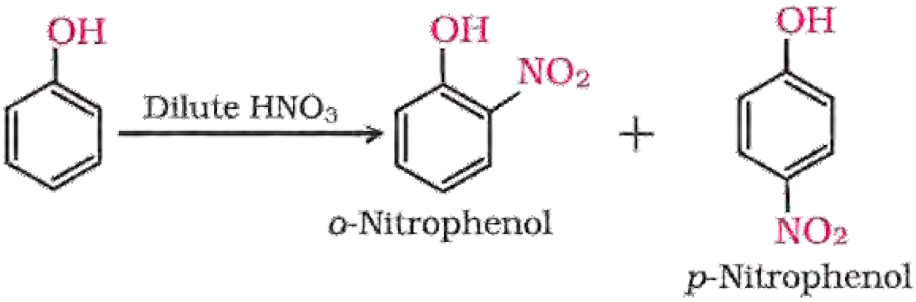
Phenol:



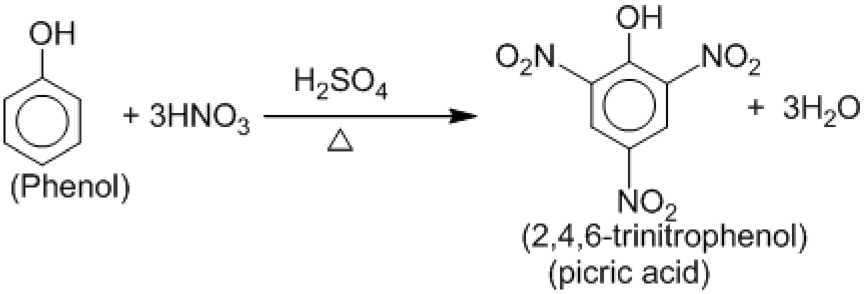
From the resonating structures, it is observed that -OH group is electron releasing group and structure II, III and IV shows that electron density increases on ortho and para position due to which incoming electrophile attack on these positions.

a) Nitration:

Nitration of phenol with dilute nitric acid at 293 K produces 2-nitrophenol as major and 4-nitrophenol as minor product (or o-nitrophenol and p-nitrophenol).

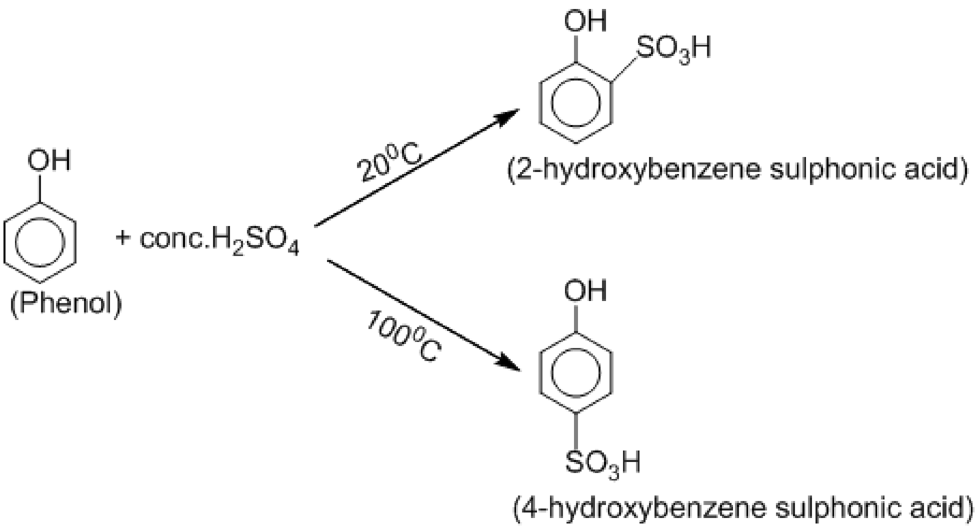


Nitration of phenol with conc. HNO_3 in presence of conc. H_2SO_4 produces 2,4,6-trinitrophenol, commonly known as picric acid but due to the oxidation of benzene by nitric acid, yield is very low.



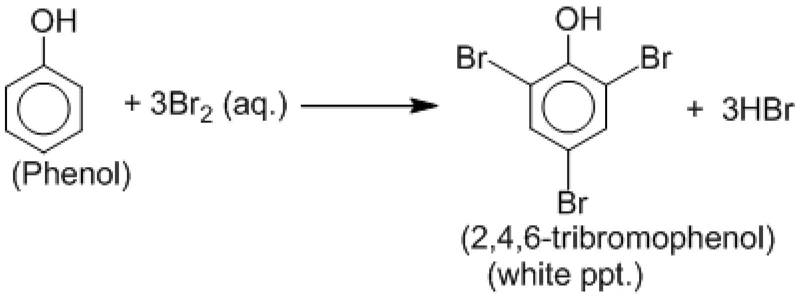
b) Sulphonation:

Sulphonation of phenol occurs in presence of conc. H_2SO_4 to produce ortho- or para-hydroxybenzene sulphonic acid. Ortho isomer is formed at lower temperature (at room temperature) and para isomer is formed at higher temperature (at about 100^oC).



c) Halogenation (Bromination):

When phenol is treated with aqueous Br_2 , then 2,4,6-tribromo phenol is obtained.

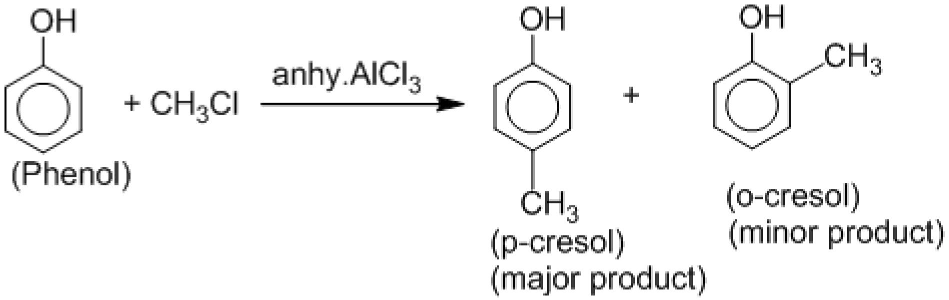


When phenol is treated with Br_2 dissolved in less polar solvent like CCl_4 or CS_2 then mono substituted product i.e. ortho- and para- bromophenol are obtained.

d) Friedel-Crafts alkylation:

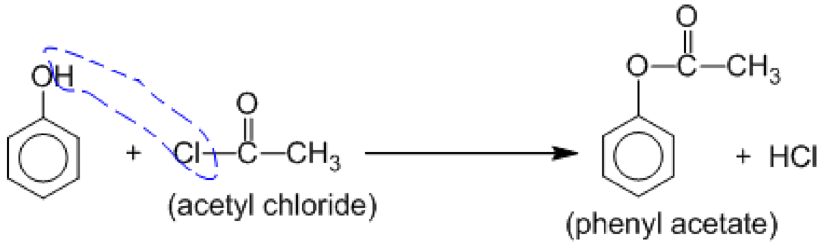
When phenol is treated with alkyl halide in presence of anhy. $AlCl_3$, ortho- and para-Methyl phenol are formed. Where p-methyl phenol is the major product.

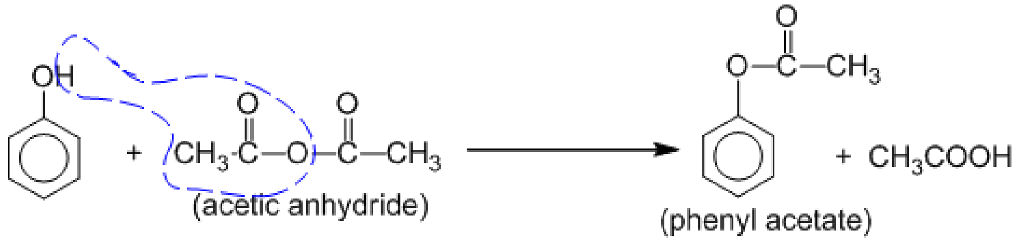
Since $AlCl_3$ is a lewis acid, so it attacks on lone pair of oxygen on phenol and is very difficult for Friedel-Crafts alkylation and acylation reaction of phenol.

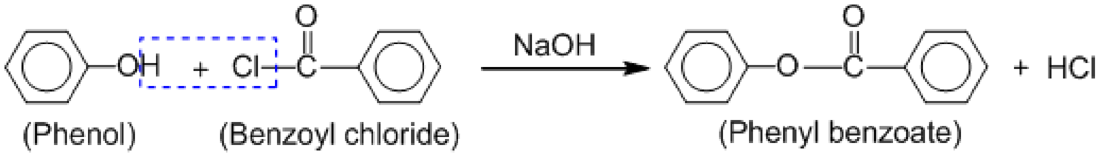


e) Friedal-Craft's acylation:

When phenol is treated with acid chloride or acid anhydride in presence of anhy. $AlCl_3$, ester will be formed.



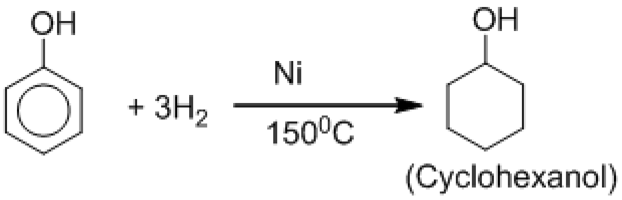




Phenol also shows following reactions-

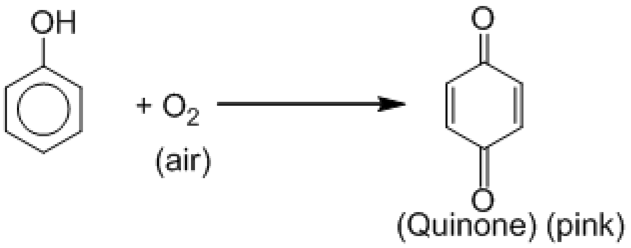
i) Catalytic hydrogenation-

When phenol is treated with hydrogen in presence of nickel at 150°C to produce cyclohexanol.



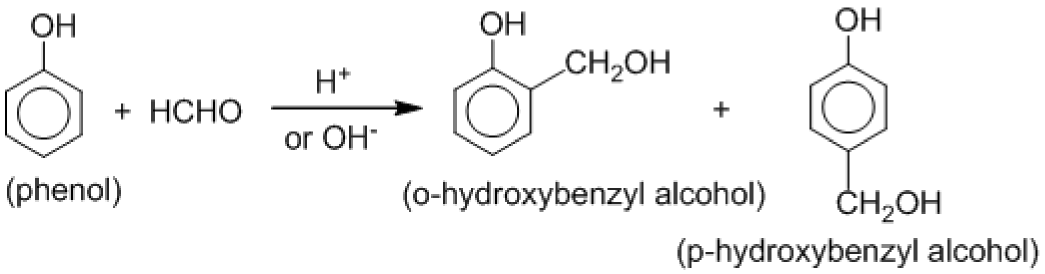
ii) Oxidation in presence of air-

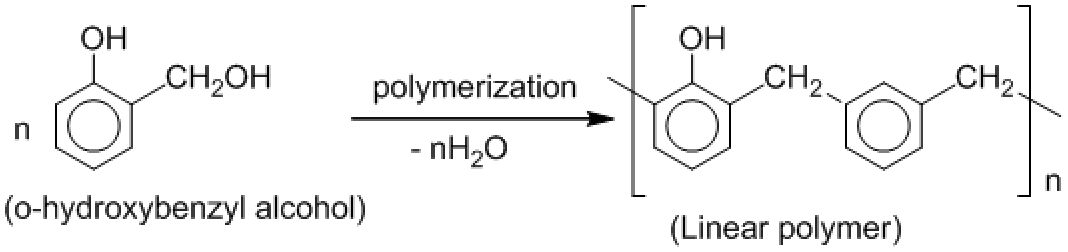
When phenol is oxidized in presence of air pink colored quinone is produced.

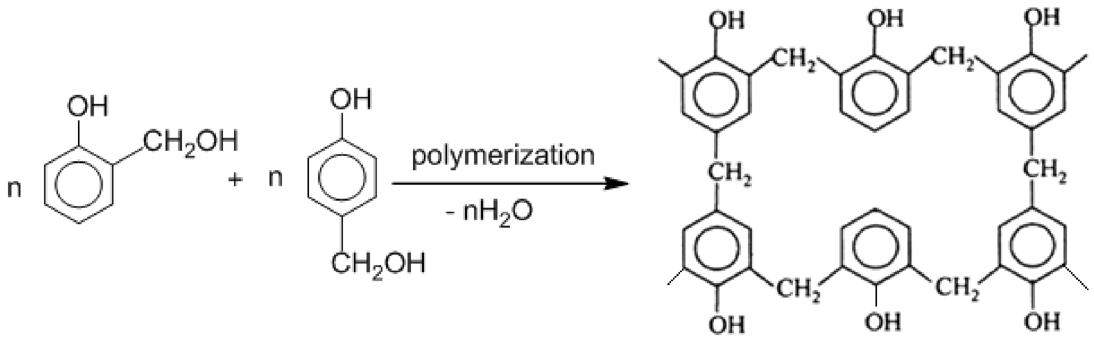


iii) Condensation with formaldehyde in acidic or alkaline medium.

In acidic or alkaline medium condensation of phenol with formaldehyde produces a polymer called bakelite.



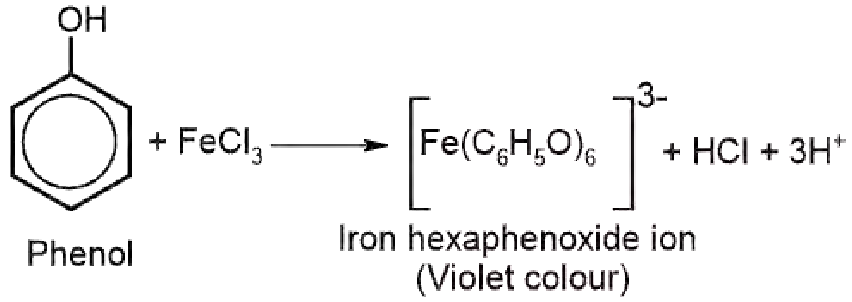




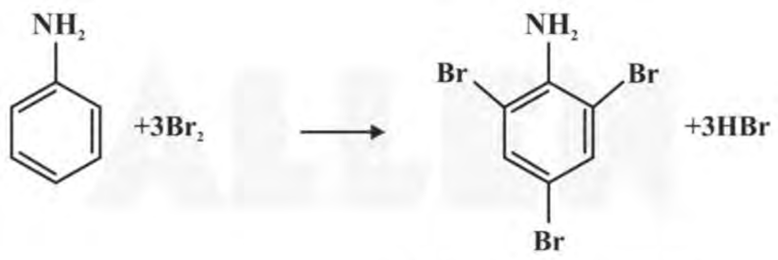
A part of Bakelite molecule
(Cross-linked polymer)

11.5 Test of phenol: (FeCl3 test, aq. Bromine test & Libermann test)

a) **FeCl3 test**: Since phenol contains -OH group attached to the carbon of benzene ring, it can form a coloured (purple or violet) complex with ferric chloride. The oxygen of phenol form coordinate Bond to donate a lone pair of electrons towards a ferric ion which forms coloured complex.



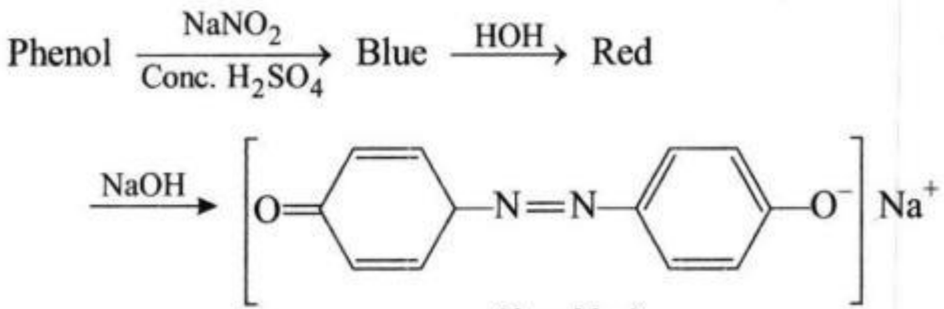
b) Bromine test:Finol undergoes electrophilic aromatic substitution reaction with bromine Which causes decolorization of bromine water and the formation of white precipitate of 2,4,6-tribromophenol



2, 4, 6 - Tribromophenylamine

Bromine water test with aniline

c) Libermann test: In this test phenol is treated with sodium nitrite (NaNO2) in presence of conc.H2SO4, deep blue colour is produced which changes to red on dilution with water. The blue colour is restored on treating with alkali like NaOH. It is the characteristic property of phenol.



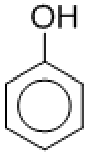
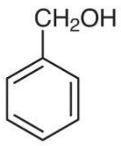
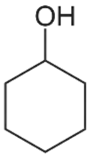
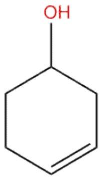
(deep blue)
(sodium salt of indophenol)

11.6 Uses of phenol

Exercise

11.1. Multiple Choice Questions:

1. Which one of the following represents phenol?

b.  b.  c.  d. 

2. The IUPAC name of phenol is-

a. *Benzenol* b. *Hydroxybenzene* c. *Carbolic acid* d. *All of the above*

3. Phenol can be prepared from chlorobenzene through:

b. *Friedel – Crafts reaction*.

b. *Dow process*.

c. *Raschig process*

d Kolbe.Schmitt reaction.

4. Which of the following condition is responsible for hydrolysis of diazonium salt to form phenol:

a. $H_2O\ (r.t.)$ b. $H_2O/H^+(warm)$ c. $NaOH(Cold)$ d. HNO_3

5. Solubility as well as boiling point of alcohol is greater than that of toluene due to:

a. *Phenol forms hydrogen bonding* .

b. *HIgher molecular weight of phenol*.

c. *Presence of benzene ring*

d. *Presence of ionic bond*

6. Which of the following is correct order of acidic strength?

a. $Water < Phenol < Ethanol$.

b. $Ethanol < Phenol < Water$.

c. $Phenol < \ Ethanol < Water$

d. $Water < Ethanol < Phenol$

7. $C_6H_5OH + Na \xrightarrow{\hspace{2em}}$, The products of this reaction are:

a. $Sodium\ phenoxide + H_2$ b. $Sodium\ benzoate + CO_2$

c. $Benzene + H_2O$ d. $No\ reaction$

8. Phenol reacts with zinc dust to give benzene, the reaction is:

a. Oxidation b. Reduction c. Nucleophilic substitution d. Elimination

9. Coupling reaction of phenol with benzene diazonium chloride produces:

a. $Azo\ dye$ b. $Nitrophenol$ c. $Benzene$ d. $Salicylic\ acid$

10. The reagent used in Kolbe's reaction to react with phenol is:

a. $CO_2 and\ NaOH$ b. CH_3COCl c. HNO_3 d. $SOCl_2$

11. Phenol reacts with Chloroform in presence of aq. KOH is called Reimer-Tiemann reaction, the poduct of this reaction is:

a. $Salicylic\ acid$ b. $Salicyalaldehyde$ c. $Picric\ acid$ d. $Aspirine$

12. When phenol reacts with acetic anhydride to produce acetophenone, the reaction is called:

a. $Reduction$ b. $Oxidation$ c. $Alkylation$ d. $Acylation$

13. Nitration of phenol is an electrophilic substitution reaction, the product of this reaction is:

a. $o - nitophenol\ and\ p - nitrrophenol$ b. $m - nitrophenol$

c. $2{,}4{,}6 - trinitrophenol$ d. $Only\ p - nitrophenol$

14. Bromination of phenol in CS_2 gives:

a. $2{,}4{,}6 - tribromophenol$ b. $o - bromophenol$

c. $p - bromophenol$ d. $Both\ B\ abd\ C$

15. Friedel-Crafts alkylation is not feasible with phenol because:

a. $Phenol\ is\ strongly\ deactivating$

b. $It\ forms\ a\ stable\ comples\ with\ AlCl_3$

c. Over − alkylation occurs

d. The −OH group is meta-directing

16. When phenol is treated with $FeCl_3$, it produces violet color due to:

a. Formation of a phenoxide ion

b. Formation of a complex with Fe^{3+}

c. Oxidation of pheno

d. Reduction of Fe^{3+}

17. Libermann's test confirms phenol by producing red color changes in deep blue color with alkali, the reagent in this reaction is

a. $FeCl_3$ b. $NaNO_2 + H_2SO_4$ c. Br_2/H_2O d. Phthalic anhydride

18. Phenol decolorizes bromine water to form

a. 2,4,6 − tribromophenol b. Bromobenzene

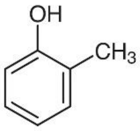
c. o − and p − bromophenol d. Only p − bromophenol

19. Which of the following is the polymer of phenol?

b. Nylon − 66 b. Bakelite c. Teflon d. Polyethene

Exercise 11.2

1. Phenol is hydroxyl derivative of benzene where –OH goup directly attached to the carbon of the benzene ring.
   i) What is the IUPAC name of the compound $C_6H_4(OH)CH_3$, with following structure?



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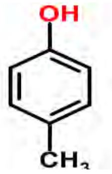


   ii) Compare the polarity of phenol and toluene.
   iii) Draw the structural formula of $C_6H_4(OH)_2$ and write IUPAC name.
2. Phenol, also known as carbolic acid, is a white crystalline aromatic compound.
   i) Compare the solubility of phenol and benzene.
   ii) Boiling point of phenol is greater than that of benzene and toluene. Explain.

iii) Arrange the following in the increasing order of boiling point.
Benzene, toluene, phenol and cresol.

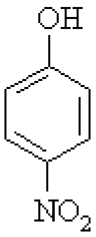
iv) Suggest the reason behind the lower boiling point and solubility of ortho nitrophenol in comparision of m- amd p- isomers.

3. Phenol is acidic in nature as it releases H^+ ion to produce phenoxide ion and turns blue litmus red.

i) Phenoxide ion is more stable than ethoxide ion? Explain

ii) Compare the acidic strength of phenol.ethanol and water.

iii) Discuss the effect of substituent on acidic strength of phenolic group and compare the acidic strength of followings-



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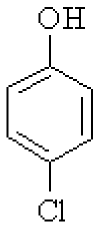

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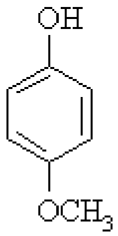
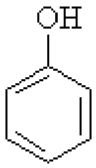


and


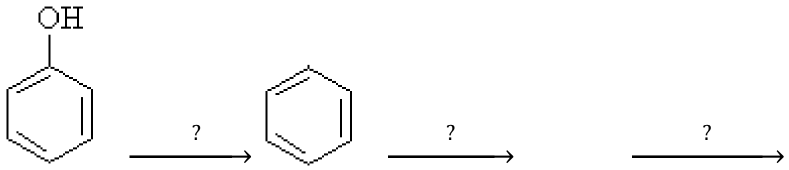
4. Hydroxyl group is the activator of benzene ring. It activates the ring towards electrophilic substitution.

i) Suggest the reason behind ortho-,para- directing nature of –OH group in phenol.

ii) Electrophilic aromatic substitution reaction in phenol is faster than benzene. Explain

iii) With aqueous Br_2, phenol produces tri-substituted product but with Br_2 in CCl_4 or CS_2, it gives mono-substituted product. Explain the reason.

5. Complete the following reactions

i)


6. In phenol –OH group is electron repelling group and activate the ring.

i) How does the presence of an electron-withdrawing group at the meta position affect the reactivity of phenol towards electrophilic substitution?

7. Phenol undergoes bromination easily, whereas benzene requires a lewis acid catalyst. Explain this difference in terms of electronic structure.

8. Predict the major product when phenol is treated with-

i) Dilute HNO_3

ii) Conc. HNO_3

iii) CH_3COCl in presence of pyridine

Bingo Game

Instructions

Instruction

1. A 5 × 5 bingo card is provided to you or draw in your notebook
2. A word bank comprising 25 terms is provided below. You should select the appropriate term that corresponds to the clue provided by the teacher.
3. The box at the center is your FREE space, which may be marked automatically.
4. Only one term should be filled per box on your Bingo card.
5. Listen carefully as your teacher reads out clues or definitions related to the terms.
6. When a clue matches a term on word bank, fill the term in that box randomly.
7. The first student to fill a full row, column, or diagonal shouts “BINGO!” and wins!

Student Bingo Card:

		FREE		

Word Bank: Phenol Bingo

Hydroxybenzene, Acidic nature, Electrophilic substitution, Nitration, Sulphonation, Bromination, Kolbe’s reaction, Reimer-Tiemann, Zn dust, Phthalic anhydride, Ferric chloride test, Aqueous bromine, Liebermann’s test, Antiseptic, Disinfectant, Phenolphthalein, Carbolic acid, Weak acid, Diazonium salt, Antioxidant, Phenoxide ion, Hydrogen bonding, Ortho effect, Cresol, FREE

Teacher Clues (Read aloud)

1. Another name for phenol
2. Reason for phenol's acidity
3. Aromatic substitution reaction type
4. Reaction with dilute HNO_3
5. Reaction with conc. H_2SO_4
6. Reaction with Br_2 water
7. CO_2/NaOH + phenol reaction

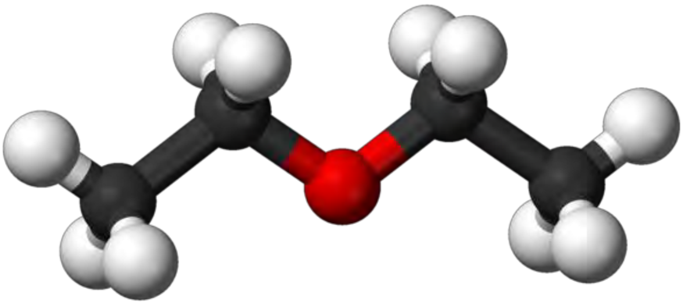
8. $CHCl_3$/NaOH reaction
9. Used to reduce phenol
10. Forms phenolphthalein
11. Turns violet with phenol
12. Is decolorized by phenol
13. Gives dye with nitrous acid
14. Kills microbes on skin
15. Kills microbes on surfaces
16. Phenol derivative pH indicator
17. Old common name of phenol
18. Acid strength of phenol
19. Intermediate in azo dye reaction
20. Prevents oxidation
21. Ion formed after losing H^+
22. Interaction with water
23. Effect from two substituents
24. Another phenol derivative

Project work:

1. To study the tests of phenol: Ferric chloride test, Aqueous bromine test and Libermann’s test.
2. To study the environmental impact and health hazards of phenol.

Unit 12
Ethers

12.1 Introduction



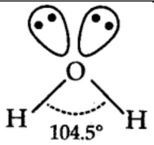
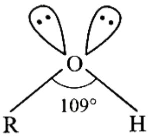
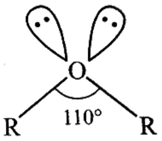
Resins 
Wax 
Gums 

- ❖ Have you ever seen such things?
- ❖ What could be the solvent that dissolves the above three things?

  ……………………………
  ……………………………

Yes, you are right the ‘ether’.

Activity:
Study the following structures of organic compounds. Count the components (atoms) present in the compounds and write to the next column.

Molecular structure	Name of the molecules	Name of the constituents of the molecules
	……………………	………………………… ………………………… …………………………
	……………………	………………………… ………………………… …………………………
	……………………… ……	…………………………… …………………………… ……………………………

What are the differences that you find the above structures?

1. ……………………………
2. ……………………………
3. ……………………………
4. ……………………………

So, the ethers are the alkyl derivative of water or alcohol.

Nomenclature, isomerism and classification of mono-halo-alkanes

Nomenclature:

Common Naming system:

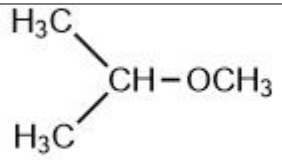
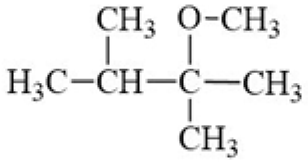
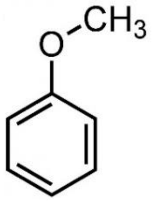
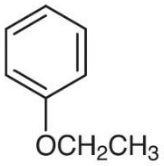
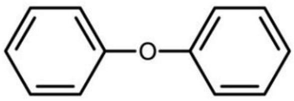
CH_3-O-CH_3	CH_3-CH_2-OCH_3	CH_3-CH_2-O-CH_2-CH_3
Dimethyl ether	ethylmethyl ether	di-ethyl ether

- Why the term-di comes in the name of first and third compound?
- Why ethyl comes earlier than methyl in the second compound?

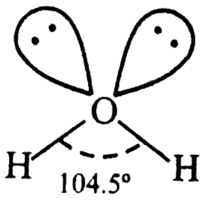
For symmetrical ethers prefix di is used. If the ethers having two different chains in either sides of oxygen, they are named in alphabetical order and the word ether is added after it.

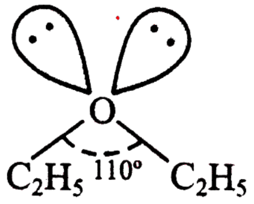
IUPAC Naming System:

Substituent + alkoxy + alkane

SN	Formula	IUPAC Name	Common Name
1.	CH_3-O-CH_3	Methoxymethane	Dimethyl ether
2.	CH_3-CH_2-OCH_3	Methoxyethane	Ethylmethyl ether
3.	CH_3-CH_2-O-CH_2-CH_3	Ethoxyethane	Diethyl ether
4.	CH_3-CH_2-O-CH_2-CH_2-CH_3	Ethoxypropane	Ethylpropyl ether
5.		2-methoxypropane	Isopropylmethyl ether
6.	 $H_3C-\overset{CH_3}{\overset{\vert}{CH}}-\underset{\underset{CH_3}{\vert}}{\overset{O-CH_3}{\overset{\vert}{C}}}-CH_3$	2-Methoxy-2,3-dimethylbutane	Tertiarybutylmethyl ether
7.		Methoxybenzene	Methyl phenyl ether Or anisole
8.		Ethoxybenzene	Ethylphenyl ether Or phenetole
9.		Phenoxybenzene	Diphenyl ether

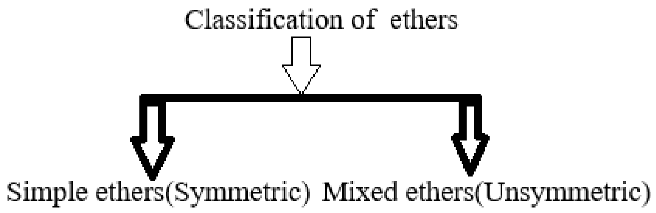
Ethers are the alkyl derivatives of water. Here, in the following structure of water and ethers support the statement.





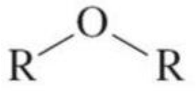
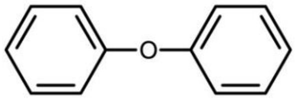
Classification of ethers:

On the basis of alkyl or aryl groups present in either side of the functional group ethers.



Activity:

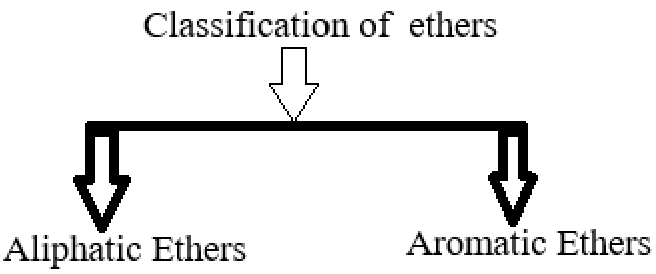
Study the following structures and write the name of the groups bonded in either side of ethereal oxygen and write their conclusion.

1.		………………………
2.		…………………………
3.	$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$	……………………
4.	$CH_3\text{-}O\text{-}CH_3$	……………………..

Conclusion:……………………..

If two similar groups are bonded in either sides, they are called symmetric ethers and vice versa.

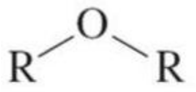
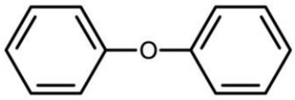
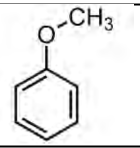
On the basis of presence of nature of groups present in the either side of functional group.



Activity:

Fill the following table according to the following information

If benzene ring is present in the ethers, the ethers are called aromatic ethers (anisole) and if only alkyl groups are present such ethers are called aliphatic ethers.

SN	Compounds	Aliphatic /Aromatic ethers
1.		………………………
2.		………………………
3.	$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$	…………………………
4.	$CH_3\text{-}O\text{-}CH_3$	………………………..
5.		………………………

Isomerism of ethers:

Study the pairs of compounds given in the following table. Write similarities and differences found in these pairs.

Table: 1

SN	Compounds	Similarity	Difference
1.	a. CH_3-CH_2-CH_2-OCH_3, b. CH_3-CH_2-CH_2-CH_2OH	....	....
2.	a. CH_3-CH_2-O-CH_2-CH_3 b. CH_3-CH_2-CH_2-OCH_3	....	....

Activity:

Study the pair of compounds given in table no. 1. Relate the following statements and fill in the following table.

Statements	Isomerism	Pair of compounds of table 1 (write S.N.)
• Same molecular formula but difference in functional group.	Functional isomerism	....
• Same molecular formula but difference in the chain present in either side of functional group.	Metamerism	....

According to the information given above ethers show only two types of isomerism, they are functional isomerism and metamerism. If the compounds have same molecular formula with different functional group are called functional isomers. And if different chain or groups are present in either sides of the functional group such isomers are called metamers.

Try Yourself:

- Write the functional isomers of C_3H_8O
- Give one more pair of isomers of types given above and submit to your teacher.

Key point: "Ethers and alcohols are functional isomers to each other".

12.2 Show the preparation of aliphatic and aromatic ethers from Williamson's Synthesis

Study the following chemical equation.

$$R\text{-}X + Na\text{-}O\text{-}R' \xrightarrow{\text{Dry ether }/\Delta} R'\text{-}O\text{-}R + NaX$$, (Where, R and R' may be same or different.

What are the requirements that are given in the above chemical equation?

SN	Requirements to complete Williamson's etherification reaction
1.	……………………………
2.	……………………………
3.	………………………………
4.	……………………………..

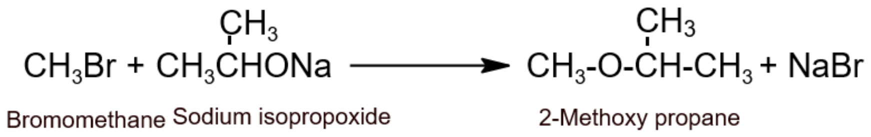
When alkyl halide reacts with sodium alkoxide in presence of dry ether it gives alkoxy alkane and sodium halide. This reaction is called Williamson's etherification reaction. Some examples are given below.

$$CH_3CH_2Cl + NaOCH_2CH_3 \xrightarrow{\text{Dry ether }/\Delta} CH_3CH_2\text{-O-}CH_2CH_3 + NaCl$$

Chloroethane sod. Ethoxide ethoxyethane

$$CH_3CH_2Cl + NaOCH_3 \xrightarrow{\text{Dry ether }/\Delta} CH_3CH_2\text{-O-}CH_3 + NaCl$$

Chloroethane sod. methoxide methoxyethane

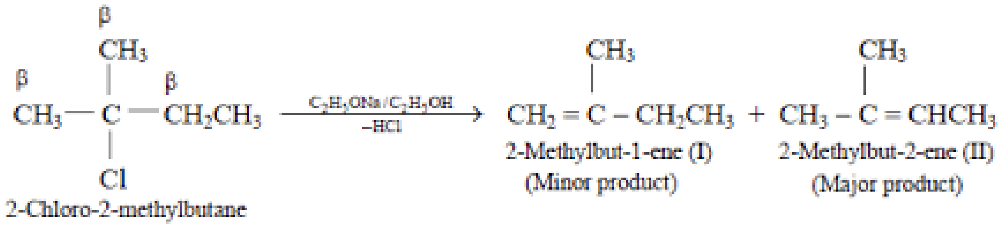


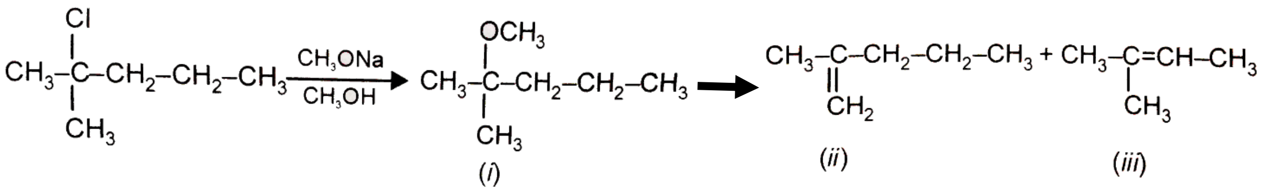
$$CH_3Br + CH_3\underset{}{\overset{CH_3}{C}}HONa \longrightarrow CH_3\text{-O-}\overset{CH_3}{C}H\text{-}CH_3 + NaBr$$

Bromomethane Sodium isopropoxide 2-Methoxy propane

Note: The alkyl halide used in Williamson's ether synthesis reaction must be primary. If secondary or tertiary alkyl halides used, the reaction gives alkene instead of ether.

Examples are given below.



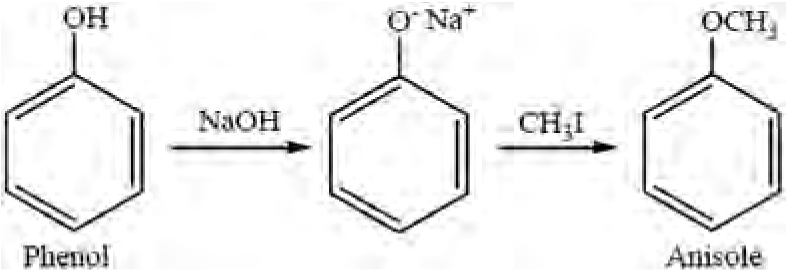


But when, 2-chloro-2-methylpropane is heated with sodium methoxide, elimination reaction is occurred instead of formation of ethers because of the following facts

a. Due to steric hindrance of tertiary alkyl halide
    - The carbon bonded to iodine is tertiary, surrounded by three methyl groups.

  - This makes SN^2 impossible — the backside attack is blocked.
- b. Due to favouring eliminatio reaction by strong base.
  - Sodium methoxide is a strong base.
  - In presence of a strong base and heat, E2 elimination is favored, especially with tertiary halides.
- c. Due to good leaving group of halogen
  - Halide (X^-) is a very good leaving group, which helps the reaction proceed.
- d. Due to heat which favours elimination reaction:
  - Heating promotes elimination over SN^1, pushing the reaction toward alkene formation.

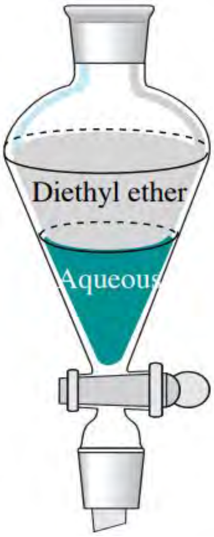
When sodium phenoxide is heated with alkyl halide it gives methoxy benzene i.e. anisole. It is an example of aromatic ether.



12.3 **Physical properties of ethers**

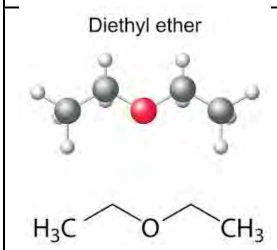
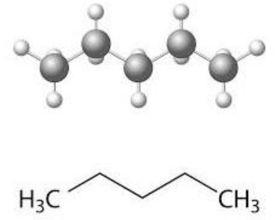
a. State: lower members are in gaseous state but higher members of ethers are in liquid state in room temperature.

b. Density: Ethers are lighter than water



c. Solubility: Ethers are sparingly soluble in water; polar solvents since ethers are slightly polar and has dipole moment (1.18D) however soluble in non-polar solvents like benzene, chloroform, carbon tetrachloride etc.

d. Boiling point of ethers are approximately similar with the comparable molecular weight of alkane.

Compounds	Boiling point	Molecular mass
	34.6°C	74 amu
	36.1°C	72 amu

12.4 Explain chemical properties of ethoxyethane with HI, Conc. HCl, conc. H2SO4, air and Chlorine

a. **Action with HI**

$R\text{-}O\text{-}R + \text{conc. } HI \longrightarrow R\text{-}X + ROH$

$CH_3CH_2\text{-}O\text{-}CH_2CH_3 + \text{conc. } HI \longrightarrow CH_3CH_2\text{-}OH + I\text{-}CH_2CH_3$

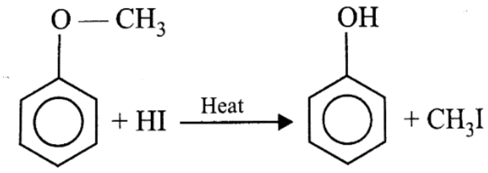
Ethoxyethane ethanol ethyl iodide

What do you find in the chemical equation given above?

When symmetrical ethers are treated with concentrated hydrogen iodide, it gives alcohol and alkyl iodide.

Are following chemical equations different from the equations given above? What are the differences?

$CH_3CH_2\text{-}O\text{-}CH_3 + \text{excess and conc } HI \longrightarrow CH_3I + CH_3CH_2OH$



Anisole phenol methyl iodide

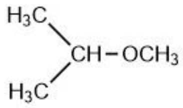
Iodobenzene and methanol cannot be formed due to the following reasons.

- Due to resonance in benzene.
- The aryl–oxygen bond is too strong to be cleaved easily.

- No driving force or mechanism exists to exchange –OCH_3 for iodine in this system.
- Methyl iodide does not have the capacity to "swap" with the methoxy group in that way

By the same way, solve the following problem.

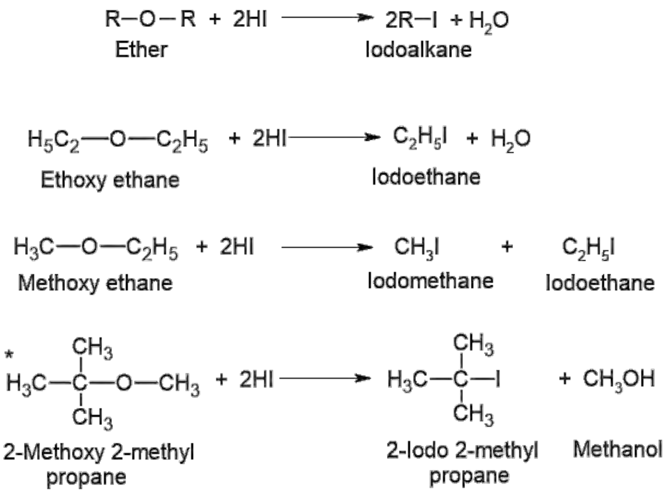
What could be the products when 2- methoxypropane is treated with conc. HI?



2-methoxypropane

In the case of unsymmetrical ethers, breaking of ether proceeds in such a way that oxygen atom remains attached to larger alkyl group to give alcohol. It is because of +I effect of larger alkyl group.

Similarly, when concentrated and excess HI is treated with ethers, then alkyl iodide is the single product.



$$R{-}O{-}R + 2HI \longrightarrow 2R{-}I + H_2O$$

Ether → Iodoalkane

$$H_5C_2{-}O{-}C_2H_5 + 2HI \longrightarrow C_2H_5I + H_2O$$

Ethoxy ethane → Iodoethane

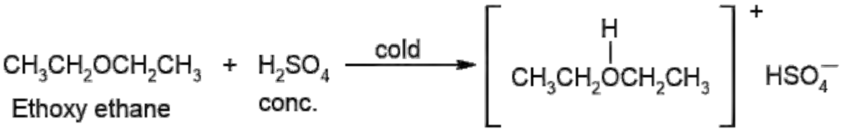
$$H_3C{-}O{-}C_2H_5 + 2HI \longrightarrow CH_3I + C_2H_5I$$

Methoxy ethane → Iodomethane, Iodoethane

$$(CH_3)_3C{-}O{-}CH_3 + 2HI \longrightarrow (CH_3)_3C{-}I + CH_3OH$$

2-Methoxy 2-methyl propane → 2-Iodo 2-methyl propane, Methanol

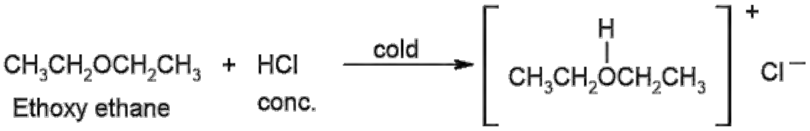
b. Action with cold and conc. H_2SO_4



$$CH_3CH_2OCH_2CH_3 + H_2SO_4 \xrightarrow{\text{cold}} [CH_3CH_2\overset{H}{O}CH_2CH_3]^+ HSO_4^-$$

Ethoxy ethane, conc.

Diethyl oxonium hydrogen sulphate
(Oxonium salt)



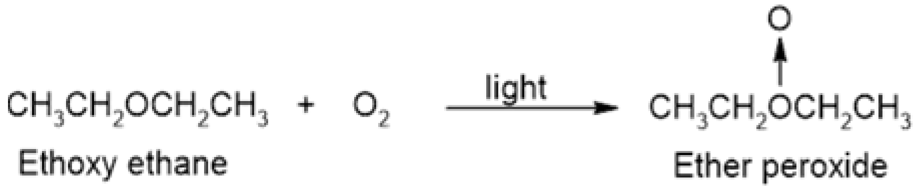
$$CH_3CH_2OCH_2CH_3 + HCl \xrightarrow{\text{cold}} [CH_3CH_2\overset{H}{O}CH_2CH_3]^+ Cl^-$$

Ethoxy ethane, conc.

Diethyl oxonium chloride
(Oxonium salt)

We can see in the examples given above that oxonium salts are obtained when ether is treated with cold and conc acids. (action with cold and conc. HCl is optional). Oxonium salts are those salts in which proton or hydrogen ion is added to the oxygen atom of the ether.

c. Action with air:



$$CH_3CH_2OCH_2CH_3 + O_2 \xrightarrow{light} CH_3CH_2\overset{\overset{O}{\uparrow}}{O}CH_2CH_3$$

When ether is exposed in air it forms peroxy ethers. Peroxy ethers are highly explosive when heated. So, there may be possibility of formation of peroxy bond in old samples of ethers.

Test of presence of peroxy bond in ethers:

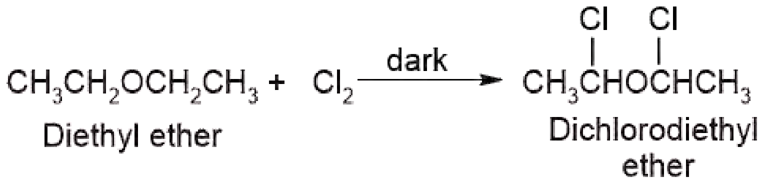
Before using old samples of ethers it is better to test the presence of peroxy bond by the following ways.

$FeSO_4 \xrightarrow{Peroxide} Fe_2(SO_4)_3 \xrightarrow{KCNS} Fe(CNS)_3$ (Blood red) + $3K^+$

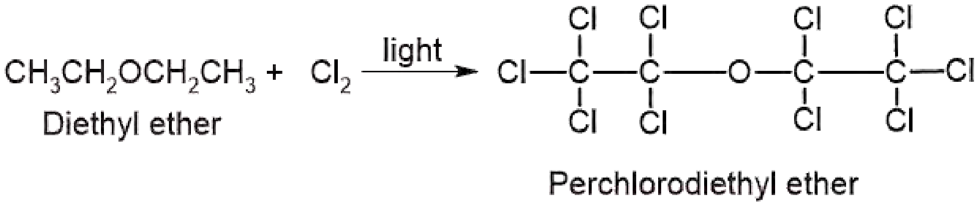
Prevention of peroxy bonds

By using iron or copper wire prevents from the formation of peroxy bond in ethers because iron or copper has more affinity towards oxygen in comparison with ethers. So, ethers can be stored in the vessel containing iron wire. Peroxy bond in ethers can be removed in trace amount by using copper or iron wire.

d. Action with chlorine



$$CH_3CH_2OCH_2CH_3 + Cl_2 \xrightarrow{dark} CH_3\overset{\overset{Cl}{|}}{C}HO\overset{\overset{Cl}{|}}{C}HCH_3$$



$$CH_3CH_2OCH_2CH_3 + Cl_2 \xrightarrow{light} Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-O-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-Cl$$

What difference did you find the above two conditions?

When ethers are treated with chlorine at dark condition α, α- dichlorodiethyl ether is obtained. But in presence of sunlight all the hydrogen atoms are replaced by chlorine atoms and perchlorodiethyl ether is formed .

12.5 State important uses of ethers.

- Used in perfumes.
- Used in anesthetics in surgery.
- Used as industrial solvents for oils, fats, resins etc.
- Used in Friedel-Craft’s reaction and Wurtz’s reaction
- Used as refrigerant

Exercise

Multiple choice questions

1. Which of the following could be the product Y?

$CH_3\text{-}O\text{-}CH_3 \xrightarrow{Excess\ HI} Y$

A. Methanol
B. Methanol and Iodomethane
C. Methanal and iodomethane
D. Iodomethane

2. Which of the following is correct about the information given in the following table?

Reactant(s)	Condtion(s)	Product(s)
…………..(w)	Dry ether/heat	$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$
Ethanol	…………………..(x)	$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$
$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$	Excess HI	……………(y)
………………(z)	Sunlight /Chlorine	$CCl_3\text{-}CCl_2\text{-}O\text{-}CCl_2\text{-}CCl_3$ +HCl

A. w-sodium methoxide and chlroethane, x- conc.H_2SO_4/heat, y- iodoethane, z-ethoxyethane
B. w-sodium ethoxide and chlromethane, x- conc. H_2SO_4/heat, y- iodoethane, z-ethoxyethane
C. w-sodium ethoxide and chlroethane, x- conc. H_2SO_4 ,y- iodoethane, z-ethoxyethane
D. w-sodium ethoxide and chlroethane, x- conc. H_2SO_4/heat ,y- iodoethane, z-ethoxyethane

3. What is Z in the following reaction sequence?
$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$ + conc. HCl (cold) $\longrightarrow$ Z
A. Ethanol + ethyl chloride
B. Oxonium chloride salt of ethoxyethane
C. Ethanol only
D. chloride salt of ethoxyethane

4. Which of the following is the most suitable requirement for the dehydration of ethanol to form an ether?
A. Sulphuric acid at 413K
B. Sulphuric acid at 443K
C. Sodium hydroxide at 413K
D. Sodium hydroxide at 443K

5. Which of the following is not favourable for the proper dehydration of alcohol to form ether?
A. Good temperature control during reaction
B. Excess of alcohol
C. Presence of protic acids
D. Presence of bulky alkyl groups in the alcohol

6. What is the major product formed when ethanol is dehydrated with concentrated H_2SO_4 at 413K?
A. Ethene
B. Methoxymethane
C. Methoxyethane
D.Ethoxyethane

7. What would be the product when sodium methoxide on heating with bromoethane?
A. methoxymethane
B. methoxyethane
C. ethoxyethane
D.diethyl ether

8. What would be the product when the reaction between tert-Butyl chloride and sodium ethoxide?
   A. tert-Butyl ethyl ether B. tert-Butyl methyl ether
   C. 2-Methylprop-1-ene D. butene

9. Which of the following is correct about boiling point of ethers and alcohols of comparable molecular mass?
   A. ether has lower than alcohol B.ether has similar to alcohol
   C. ether has little higher than alcohol D.ether has much higher than alcohol

10. Which of the following compounds is functional isomer of CH_3-CH_2-O-CH_2-CH_3
    A. CH_3-CH_2-O-CH_2-CH_3 C. CH_3-CH_2-CH_2-CH_2OH
    B. CH_3-CH_2-CH_2-CHO D. CH_3-CH_2-CO-CH_3

11. Which of the following is the least reactive functional group?
    A. Alcohols B. Ethers
    C. Aldehydes D. Ketones

12. One molecule of dialkyl ether produces how many molecules of alkyl halides with excess of halogen acid?
    A. 1 B. 2 C. 3 D. 4

13. Which of the following is the major product of Friedel-Crafts acylation of anisole with ethanoyl chloride?
    A. 2-Methoxytoluene B. 4-Methoxytoluene
    C. 2-Methoxyacetophenone D. 4-Methoxyacetophenone

14. Which of the following compound is used to detect peroxy bond in ethers?
    A. Na_2SO_4 B. $NiSO_4$ C. $FeCl_3$ D. $FeSO_4$

15. What would be the product when sodium ethoxide is heated with chloroethane in presence of dry ether?
    A. Ethyl ethanoate B. Methoxy ethane C. Ethoxyethane D. Butyl chloride

16. What would be the product when iodoethane is heated with sodium ethoxide in presence of dry ether?
    A. Ethanol b. butanol c. ethoxy ethane d. methoxy ethane

17. 4-Nitroanisole is obtained as the major product when anisole reacts with which of the following?
    A. concentrated H_2SO_4 B. concentrated HNO_3
    C. mixture of concentrated H_2SO_4 and HNO_3 D. mixture of dilute H_2SO_4 and HNO_3

Short questions

18. How are the following compounds prepared?
    i. Methoxy propane
    ii. Ethoxyethane by williamson’s method

iii. Methoxybenzene
iv. Iodoethane from diethylether

19. What happens when;
    i. Ethanol is heated with concentrated sulphuric acid in presence of about 140^0C?
    ii. Ethoxyethane is treated with excess HI?
    iii. Ethoxyethane is exposed in air
    iv. Ethoxyethane is treated with chlorine in presence of sunlight?
    v. Sodium ethoxide is heated with chloroethane in presence of dry ether?

20. Identify the P, Q, R and S in the following reaction sequence. Also write their IUPAC names with pertinent reactions.

$$P \xrightarrow{140^0\ c\ and\ conc.H2SO4} Q \xrightarrow{Excess\ HI} R \xrightarrow{Sod.ethoxide} S.$$ S is a symmetrical ether having 4 carbon atoms.

21. A second member of aliphatic alcohol 'P' reacts with sodium to form compound Q' with evolution of hydrogen gas and gives yellow compound R' when heated with sodium hydroxide and iodine. When P is heated with conc. H_2SO_4 at 140^0C it gives a compound S ($C_4H_{10}O$), which on treatment with conc. HI gives T. S is also obtained when Q is heated with T. Identify P, Q, R, S and T with pertinent chemical equations.

22. Give reasons;
    i. Ethers should be stored in bottles with iron pieces.
    ii. It is dangerous to boil old samples of ether.
    iii. Ethers are functional isomers of monohydric alcohols.
    iv. Complete the following reactions
        a. Methoxybenzene + HI $\longrightarrow$ ....
        b. Ethoxyethane + Cl_2 $\xrightarrow{Sunlight}$........................

23. Complete the following table with suitable reactants, conditions and products.

Reactant(s)	**Condtion(s)**	**Product(s)**
............(A)	Dry ether/heat	CH_3-CH_2-O-CH_3
Ethanol	......................(B)	CH_3-CH_2-O-CH_2-CH_3
CH_3-CH_2-O-CH_3	Excess HI	..............(C+ D)
.................(E)	Sunlight /Chlorine	CCl_3-CCl_2-O-CCl_2-CCl_3 +HCl

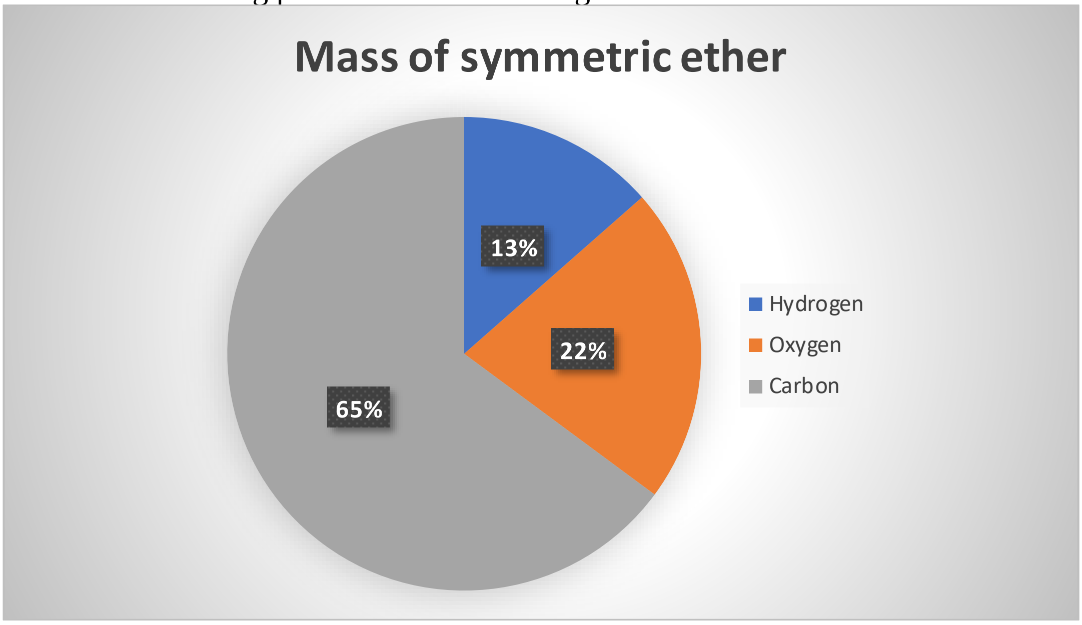
Long questions.

24. An organic compound (P) reacts with sodium to form compound (Q) with the byproduct hydrogen gas and gives a yellow precipitate (R) with iodine and sodium hydroxide while boiling. When compound P is heated with concentrated sulphuric acid at 140^0C, it gives a compound (S) having molecular formula ($C_4H_{10}O$), which on treatment with excess HI at about 100^0C gives a compound (T). (S) is also obtained when (Q) is heated with (T) . Identify P, Q, R, S and T and write the reactions with their IUPAC names.
    Complete the followings

$$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3 \xrightarrow{\text{Oxygen}} \ldots\ldots\ldots$$

$$CH_3\text{-}O\text{-}CH_3 \xrightarrow{\text{Excess HI/heat}} Y \xrightarrow{\text{Sod.phenoxide}} Z$$

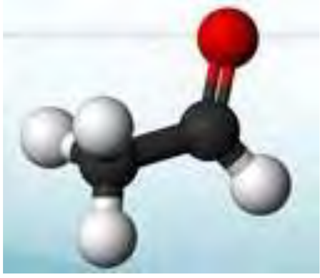
25. Solve the following problems based on the given information

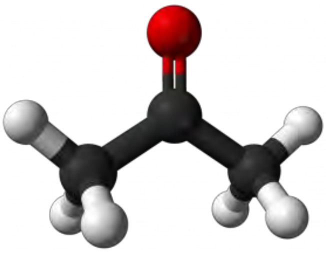


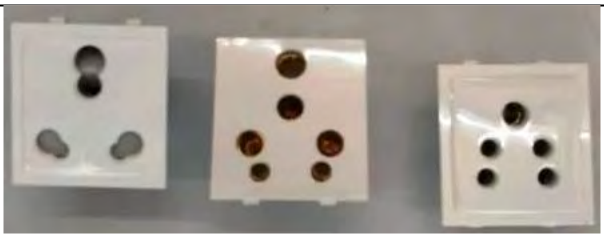
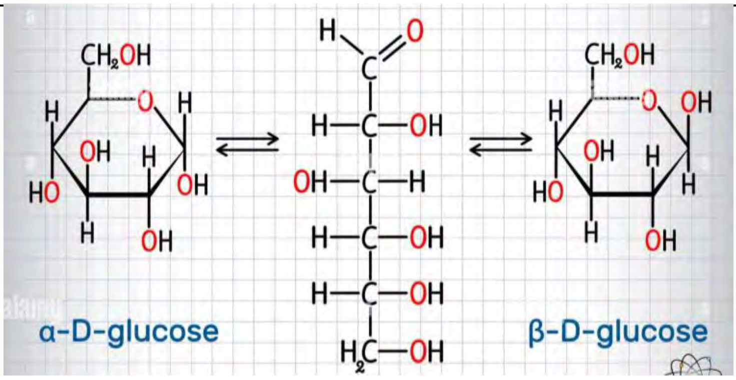
i. Write the molecular formula and IUPAC name of the ether formed from above information
ii. What would be the product when the compound is treated with concentrated hydrochloric acid in cold condition? Write the reaction involved.
iii. If you want to keep the ether for about 80 years, how to you store it? Explain.

Unit 13
Aldehydes and Ketones

13.1 Introduction



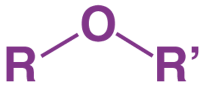
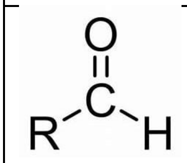
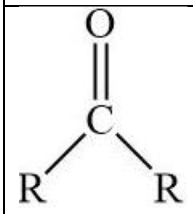


Name of the substance	Products
Formalin	
Bakelite	
Glucose	

- ❖ Have you ever seen such things?
- ❖ For what purpose do these things use?

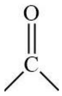
Activity:

Study the following structures of organic compounds. Find the differences and write their properties in the next column.

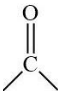
Molecular structure	Components (atoms) of the molecules
	………………………… ………………………… …………………………
	………………………… ………………………… ………………
	…………………………… …………………………… …………………………… ……………………………

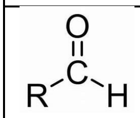
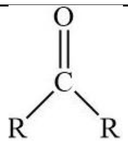
What are the differences that you find the above structures?

5. ……………………………
6. ……………………………
7. ……………………………
8. ……………………………

So, the compound which have  structure in which carbon and oxygen have made double covalent bond.

In this structure if R and H are bonded in the bonds side by side aldehyde is formed as well as R and R is bonded ketone is formed.

Due to presence of  the compounds are collectively called carbonyl compounds.

General Structure of Aldehyde	General Structure of Ketone
	

13.1.1 Nomenclature, isomerism and classification of aliphatic aldehydes and ketones

Nomenclature:

Common Naming system:

Common naming system of aldehydes and ketones are as compared with the common name of carboxylic acids. Like formaldehyde, acetaldehyde, propanaldehyde etc.

HCHO

.

IUPAC Naming System:

IUPAC name of aldehydes and ketones are written by following the given steps.

Aldehydes:

Substituent + prefix+ alkan (e) + al

An aldehyde is given below.

$Cl-CH_2-CH_2-CHO$

2-chloropropanal

Study the organic compound given above and fill in the following table.

Substituent	Prefix	Word root	Primary suffix	Secondary suffix
2-chloro	-	Prop	ane	al

Activity:

Study the following compounds and write the correct words in the given table for the following compounds as given in the above table.

a. $Cl-CH_2-CH_2-CH_2-CHO$
b. CH_3-CH_2-CHO
c. $CH_3-CH_2-CH_2-CHO$

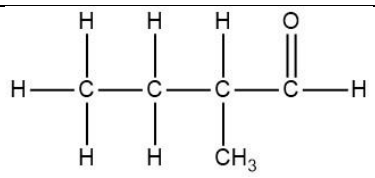
Compound	Substituent	Prefix	Word root	Primary suffix	Secondary suffix
a.					
b.					
c.					

What does the secondary suffix represent in the above examples?

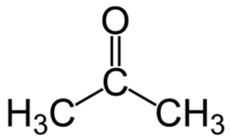
Therefore, IUPAC name of the compound is written by mentioning these things as given in the table. It can be written as;

While writing IUPAC name we need to follow following steps.

- These compounds are named as alkanals and are named by replacing 'e' of the parent alkane with 'al'.
- Select the longest chain and write respective alkane for this.
- Mention the position of substituent if present indicating by number 1, 2 3 ………..etc.

SN	Formula	IUPAC Name	Common Name
1.	HCHO	Methanal	Formaldehyde
2.	CH_3-CHO	Ethanal	Acetaldehyde
3.	CH_3-CH_2-CHO	Propanal	Propionaldehyde
4.	CH_3-CH_2-CH_2-CHO	Butanal	Butyraldehyde
5.		2-methylbutanal	2-methylbutyraldehyde
6.	CH_3-CH_2-CHCl-CHO	2-chlorobutanal	chlorobutyraldehyde

Ketones:

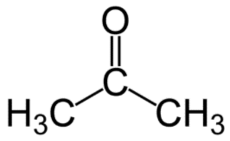


Propan-2-one

Study the organic compound given above and fill in the following table.

Substituent	Prefix	Word root	Primary suffix	Secondary suffix
-	-	Prop	ane	2-one

Write prefix, word root, primary suffix and secondary suffix of the following compounds.

CH_3-CH_2-CO-CH_3
CH_3-CH_2-CO-CH_2-CH_3


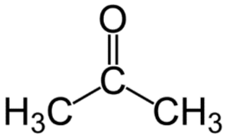
What does the primary suffix represent in these compounds?

Therefore IUPAC name of the compound is written by mentioning these things as given in the table. It can be written as;

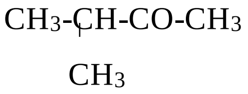
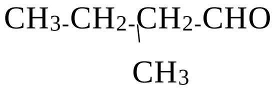
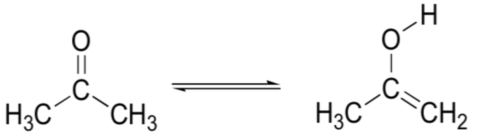
Substituent + prefix+ alkan (e) + one

While writing IUPAC name we need to follow following steps.

- These compounds are named as alkanone and are named by replacing ‘e’ of the parent alkane with ‘one’.
- Select the longest chain and write respective alkane for this.
- Mention the position of substituent if present indicating by number 1, 2 3 ………..etc.

SN	Formula	IUPAC Name	Common Name
1.		Propan-2-one	Acetone /dimethylketone
2.	CH_3-CH_2-CO-CH_3	Butan-2-one	Methyl propyl ketone
3.	CH_3-CH_2-CO-CH_2-CH_3	Pentan-3-one	di-ethylkeone

Isomerism

SN	Compounds	Similarity	Difference
1.	a. CH_3-CH_2-CH_2-$COCH_3$ b.  $CH_3-\underset{\displaystyle CH_3}{CH}-CO-CH_3$	……………… …………………	………………… …………..
	a. CH_3-CH_2-CH_2-CH_2-CHO b.  $CH_3-CH_2-\underset{\displaystyle CH_3}{CH_2}-CHO$	………………… …………………	………………… …………………
2.	a. CH_3-CH_2-CH_2-CO-CH_3 b. CH_3-CH_2-CO-CH_2-CH_3	………………… …………………	………………… ………………..
3.	a. CH_3-CH_2-CH_2-CO-CH_3 b. CH_3-CH_2-CH_2-CH_2-CHO	………………… ………………	………………… …………………
4.	 a. **keto** form of acetone **enol** form of acetone b. 	………………… ………………… ……………… ……………	………………… ……………… ………………… ……………… ………………

Study the pairs of compounds given in the following table. Write similarities and differences found in these pairs a. and b. Table: 1

Activity:

Study the pair of compounds given in table no. 1. Relate the following statements and fill in the following table no. 2

Statements	Isomerism	Pair of compounds of table 1 (write S.N.)
• Same molecular formula but difference in chain.	Chain isomerism	……………………………
• Same molecular formula but difference in position of functional group.	Position isomerism	……………………………
• Same molecular formula but difference in functional group.	Functional isomerism	……………………………
• A chemical phenomenon where a single compound can exist in multiple inter-convertible structures, called tautomer.	Tautomerism	………………………………

The phenomenon where two or more compounds have the same molecular formula but differ in their structural arrangement or spatial orientation, leading to different physical and chemical properties is called isomerism. There are two main types of isomerism: **structural isomerism** and **stereoisomerism**. We are talking about structural isomerism.

Four types of isomerism are shown by carbonyl compounds. They are-

i. Chain isomerism

ii. Position isomerism

iii. Functional isomerism

iv. Tautomerism

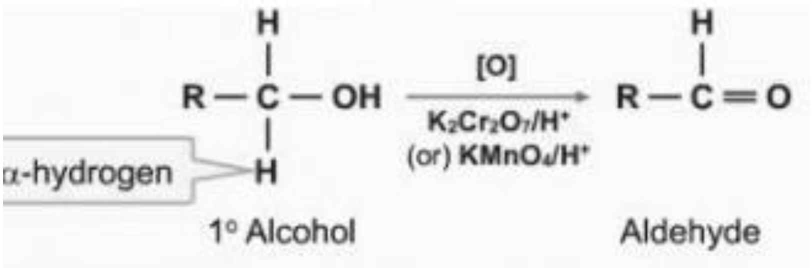
Definition is given in the table above.

- Write the functional isomers of C_3H_6O
- Give one more pair of isomers of types given above and submit to your teacher.

13.1.2 Preparation of aldehydes and ketones from;

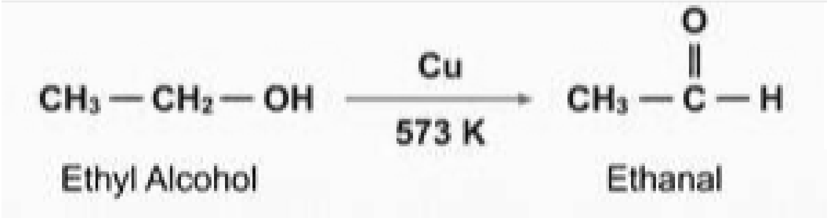
a. Dehydrogenation of alcohol

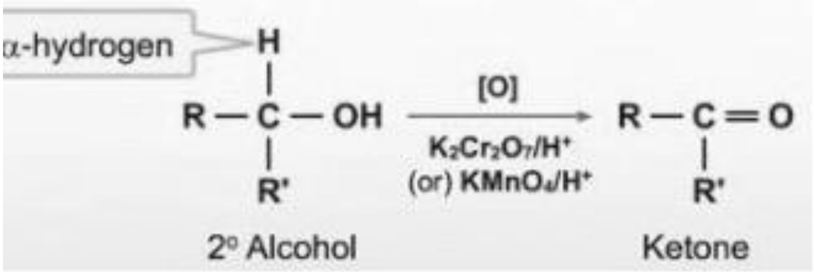
Study the following chemical equations and write the changes that occur.

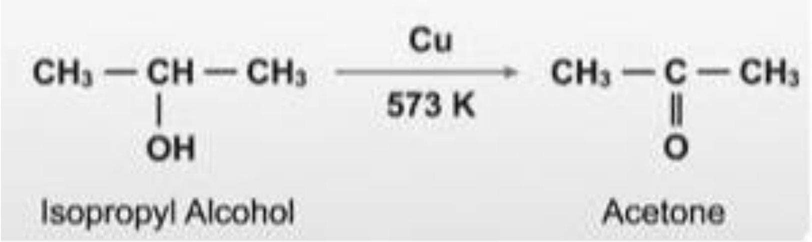


$$\underset{\text{p-alcohol}}{R-CH_2OH} \xrightarrow{Cu/573K} \underset{\text{Aldehyde}}{RCHO} + H_2$$

$$\text{e.g., } \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{Cu/573K} \underset{\text{Ethanal}}{CH_3CHO}$$







- Hydrogen molecule has been removed from the alcohol
- Removal of hydrogen molecule is called dehydrogenation.
- By dehydrogenation of primary alcohol aldehydes are formed and by the dehydrogenation of secondary alcohol ketones are formed

When primary alcohol is dehydrogenated in presence of copper or manganese oxide or copper and 300 ^{0}C aldehydes are formed**. As well as from the secondary alcohol ketones are formed.** In this reaction hydrogen from –OH group and from carbon atom hydrogen atom are removed.

b. Oxidation of alcohol

How is product formed in the following chemical equations? Fill in the following table that you find the changes.

$R\text{-}CH_2OH + [O] \xrightarrow{K2Cr2O7/H+} R\text{- }CHO + H_2O$

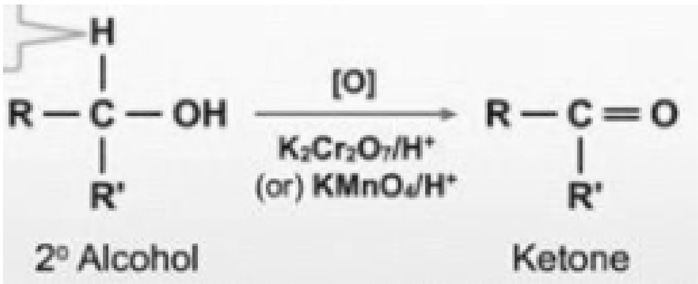
$CH_3\text{-}CH_2OH + [O] \xrightarrow{K2Cr2O7/H+} CH_3\text{- }CHO + H_2O$

SN	Reactants	Products
1.	……………………	…………………….
2.	…………………….	…………………….
3.	……………………	……………………

To obtain only aldehydes from primary alcohol, the **pyridinium chlrorochromate (PCC) i.e. Collins reagent** is used. Since it is considered as a mild oxidizing agent.

$CH_3\text{-}CH_2OH + [O] \xrightarrow{(C6H5N)2CrO3,CH2Cl2} CH_3\text{- }CHO + H_2O$

For ketones

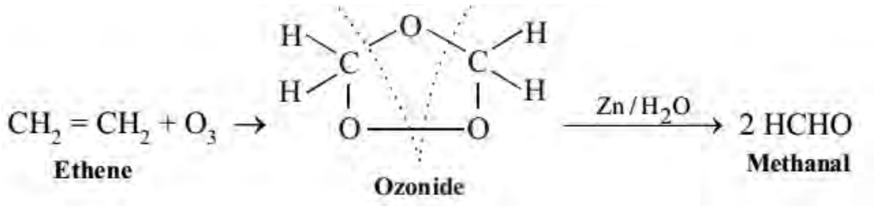


$CH_3\text{-}CH\text{-}(OH)\text{-}CH_3 + [O] \xrightarrow{K2Cr2O7/H+} CH_3\text{- }CO\text{-}CH_3 + H_2O$

C. By Ozonolysis of alkenes

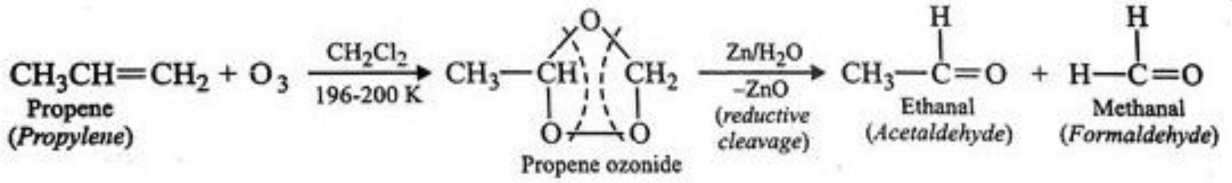
Study the following chemical equations and write the conclusion that you find as given in the example.

a. Ozonolysis of ethene



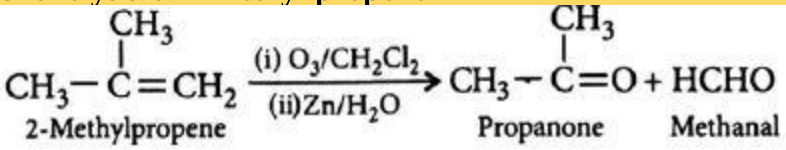
How are the products formed? Both bonds are broken and three atoms are bonded with carbon atoms and in their own which has formed a pentagonal structure. Which upon hydrolysis formed aldehydes i.e. formaldehyde. By the same process ozonolysis of other alkenes are also occurred.

b. Ozonolysis of propene



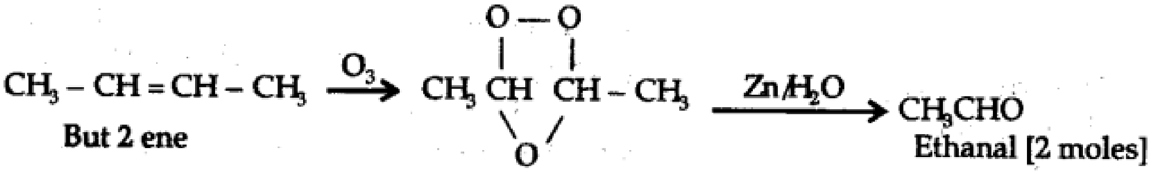
When propene is ozonolyzed ethanal and methanal are formed.

c. Ozonolysis of 2-methyl propene



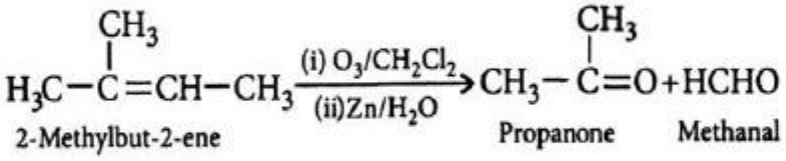
When 2-methylpropene is ozonolyzed propan-2-one and methanal are formed. Using 1,1-dichloromethane is not mandatory.

d. Ozonolysis of but-2-ene

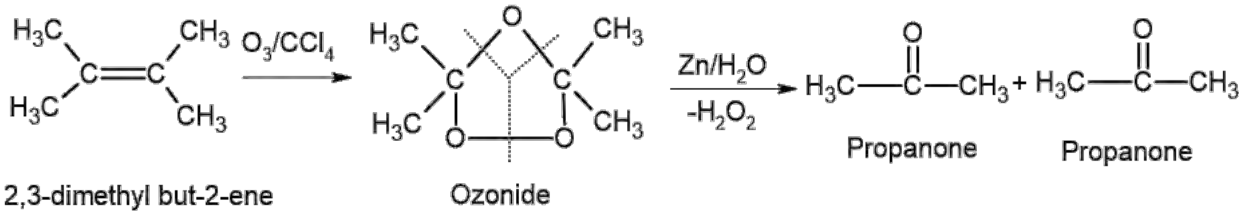


The symmetrical alkene, but-2-ene gives two similar molecules i.e. 2 molecules of ethanal during ozonolysis.

e. Ozonolysis of 2-methylbut-2-ene



f. Ozonolysis of 2,3-dimethylbut-2-ene

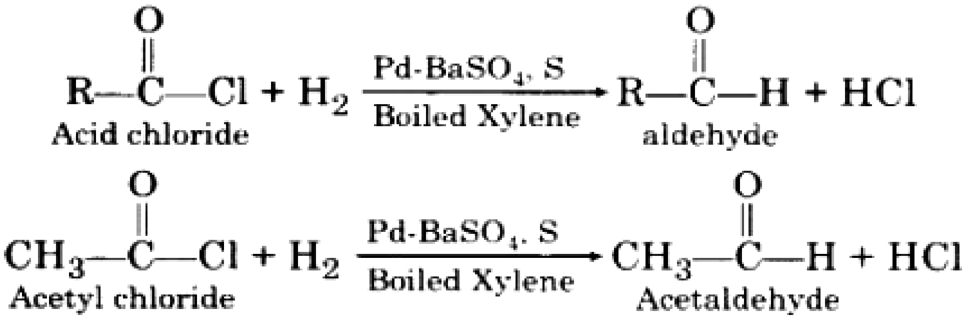


Study the chemical reactions mentioned above as ozonolysis and fill the following table as asked.

SN	Name of the reactant(alkenes)	Intermediate Product	Products
a.	Ethene	Ethene Ozonoide	2 molecules of methanal.
b.	……………	……………….	………………………..
c.	……………	……………….	………………………..
d.	………………..	……………………	…………………………..
e.	………………..	…………………….	…………………………
f.	………………..	……………………..	…………………………..

D. Preparation from acid chlorides (Rosenmund Reduction)

Is the way that the products formed in the following chemical equation similar with the ozonolysis of alkene to form carbonyl compound? If so, please mention the difference that you find between ozonolysis and Rosenmund reduction.



$$\underset{\text{Acid chloride}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + H_2 \xrightarrow[\text{Boiled Xylene}]{Pd\text{-}BaSO_4,\ S} \underset{\text{aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H} + HCl$$

$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + H_2 \xrightarrow[\text{Boiled Xylene}]{Pd\text{-}BaSO_4,\ S} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + HCl$$

Differences between ozonolysis and Rosenmund reduction

a. ………………………………………………………………………………….

b. ………………………………………………………………………………..

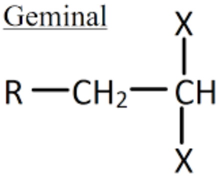
c. ………………………………………………………………………………..

By this method only aldehydes are prepared.

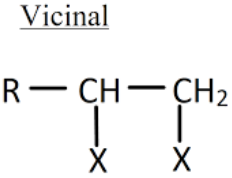
E. From gem dihalides

Are these two compounds similar? If not what are the differences between germinal and vicinal dihlaides?

Geminal



Vicinal

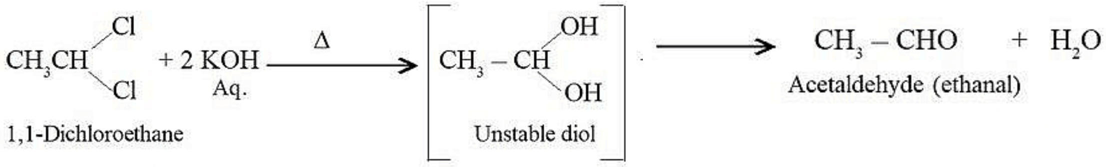


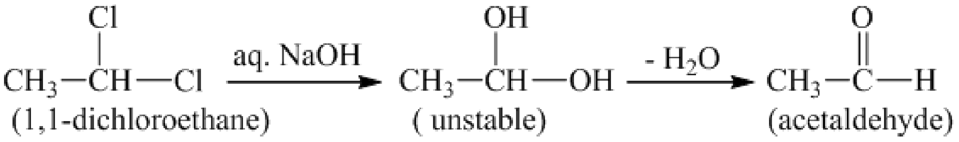
What are the differences in these two compounds?

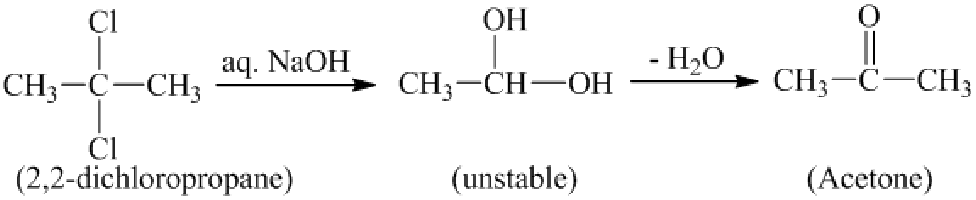
a. …………………………..

b. …………………………

c. …………………………..







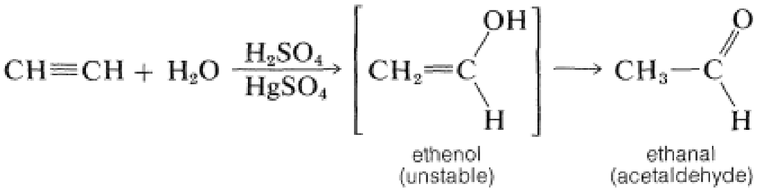
When gem dihalides are treated with alkali solution unstable dihydroxy alkane is formed. On gentle warming or slowly it turns into carbonyl compounds by the loss of water molecule by dehydration.

Test Yourself:

What would be the product when 2,2-dichloro pentane is treated with aqueous sodium hydroxide?

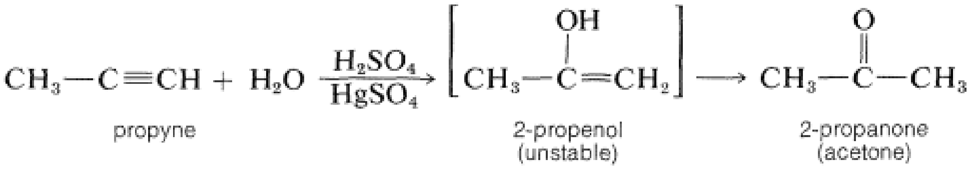
F. By catalytic hydration of alkynes

Study the chemical equations given below and find the differences in these two.



$$CH\equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \left[CH_2=C(OH)H\right] \longrightarrow CH_3-C(=O)H$$

Ethyne



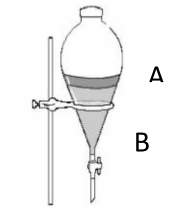
$$CH_3-C\equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \left[CH_3-C(OH)=CH_2\right] \longrightarrow CH_3-C(=O)-CH_3$$

When alkynes are hydrated in presence of dilute sulphuric acid and mercuric sulphate, en-ol is formed. Which undergoes isomerization to form aldehyde and ketones. This is supported by the following examples.

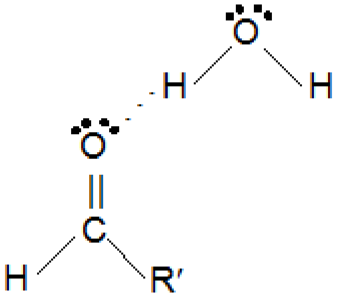
Write the name of the carbonyl compound formed by catalytic hydration of but-2-yene and submit to your teacher.

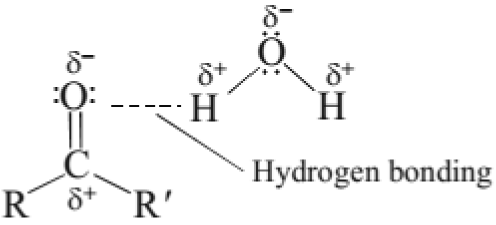
Physical properties of aldehydes and ketones

1. Physical state: formaldehyde is pungent-smelling gas at room temperature. Acetaldehyde is in liquid state including upto lower member of aldehydes and ketones as well.
2. Density: They are lighter than water.
   Which layer would be carbonyl compound in the given figure?
   ……………………………………
   ……………………………………..



3. Smell: Lower aldehydes are unpleasant odours while higher aldehydes and ketones have pleasant smell.
4. Solubility: Aldehydes and ketones upto 4 carbon atoms are soluble in water due to their ability to form hydrogen bonding with water but higher aldehydes and ketones are insoluble due to the increase in the size of alkyl groups.

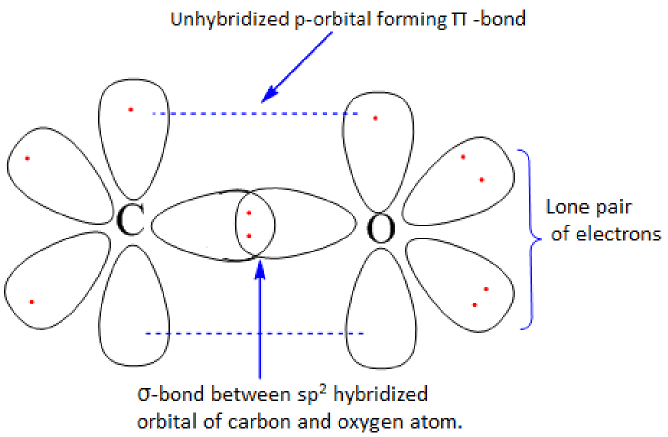


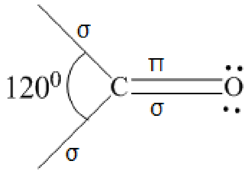


5. Aldehydes and ketones have higher boiling point than those of corresponding alkanes of comparable molecular mass but lower than the alcohols and carboxylic acids of comparable masses. Their higher boiling point than alkanes are due to intermolecular dipole interaction between opposite ends of >C=O.

Chemical Properties of aldehydes and ketones

Orbital Structure of carbonyl group can be shown as followings.





It can be written as following.

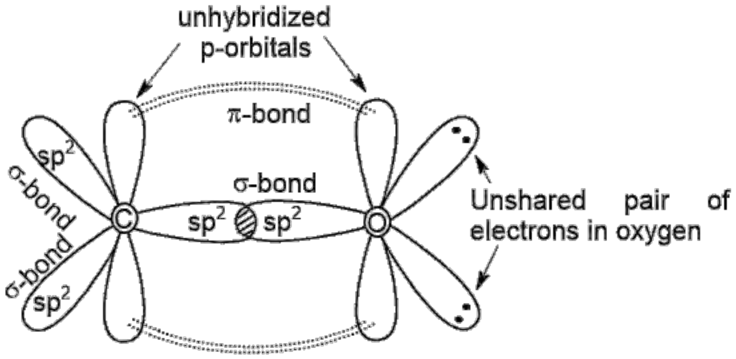
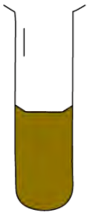


Fig: Orbital picture of carbonyl compound

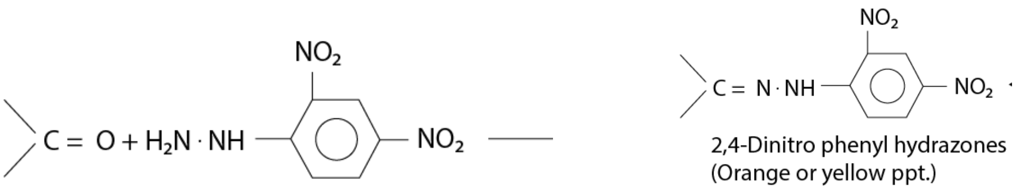
Distinction between aldehyde and ketones by using 2,4-DNP reagent, Tollen's reagent and Fe'ling's solution

a. With 2,4-DNPH (2,4-dinitrophenylhydrazine)

	
Testtube A	Testtube B

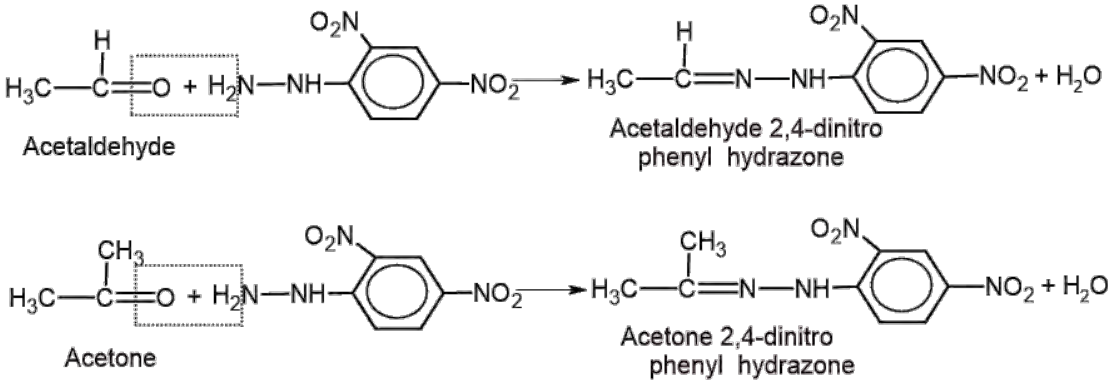
Compare the color of precipitate present in these two test tubes.

Test tubes	Differences	Remarks
A	………………..	
B	………………….	



When carbonyl compounds are treated with 2,4-DNP, it gives orange yellow precipitate of respective hydrazone of carbonyl compounds.

Study the following chemical reactions:



When carbonyl compounds are treated with 2,4-DNP solution, orange-yellow precipitate is formed. The orange yellow ppt is due to the formation of respective 2,4-dinitrophenyl hydrazine by the loss of water molecule as given in the chemical equations. This is the indication of presence of carbonyl compounds.

b. With Tollen's reagent

	
Test Tube A	Test Tube B

Compare the contents present in these two test tubes.

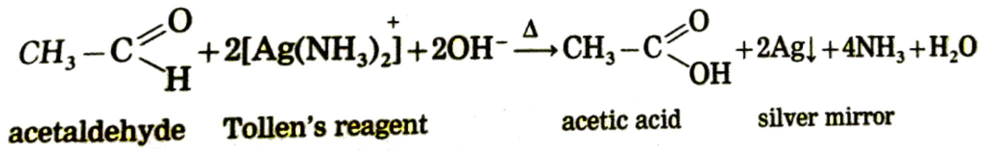
Test tubes	Differences	Remarks
A	………………..	
B	…………………	

Why was the observation?

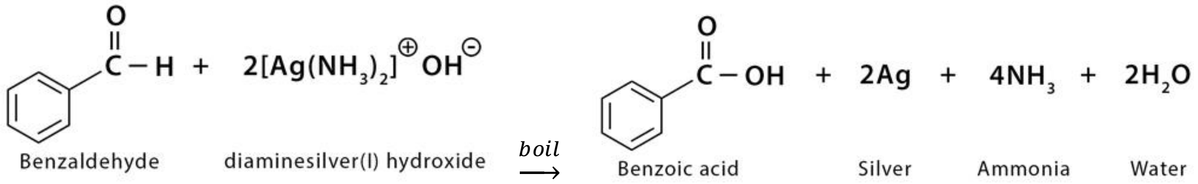
$AgNO_3 + NaOH \longrightarrow AgOH + NaNO_3$

$AgOH + 2NH_4OH \longrightarrow [Ag(NH_3)_2]OH + 2H_2O$

Diamine silver hydroxide(Tollen's reagent)



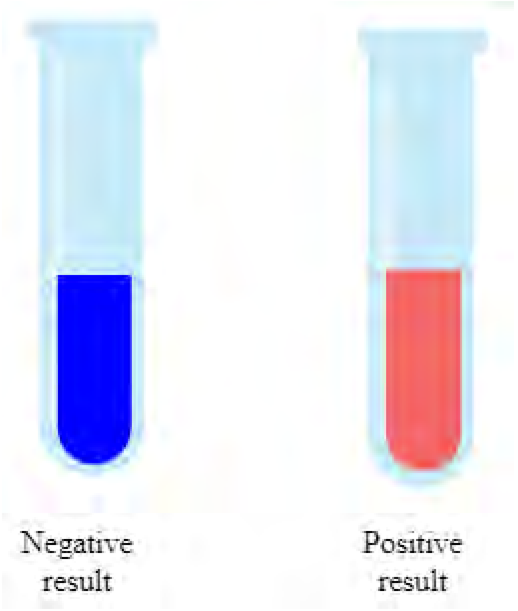
Yes due to the formation of metallic silver at the inner wall of the test tube mirror due to silver metal is appeared. So, this test is called silver mirror test.



Ketones do not react with Tollen's reagent but aliphatic and aromatic aldehydes reduces Tollen's reagent into metallic silver but aldehydes are oxidized into carboxylic acid. So, it is oxidizing agent.

c. With Fehling's solution

Study the following test tubes and fill in the table that you find.

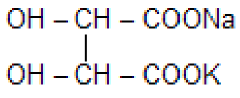


Compare the contents present in these two test tubes.

Test tubes	Differences	Remarks
First	………………..	
Second	…………………	

A : B

$CuSO_4$ solution : Alkaline solution of sodium potassium Tartarate

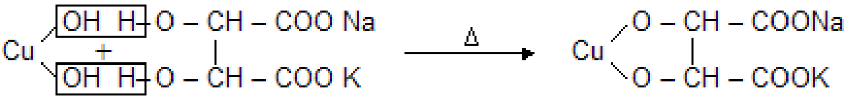


$$\begin{array}{l} OH-CH-COONa \\ \quad\;\;| \\ OH-CH-COOK \end{array}$$

Rochelle salt

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$$



$$Cu\begin{array}{l} \boxed{OH\;\;H}O-CH-COO\,Na \\ \quad + \qquad\quad\;\; | \\ \boxed{OH\;\;H}O-CH-COO\,K \end{array} \xrightarrow{\Delta} Cu\begin{array}{l} O-CH-COONa \\ \qquad\;\; | \\ O-CH-COOK \end{array}$$

Deep blue colour complex (Fehling's solution)

$$\underset{(CuO)}{\text{Deep blue colour}} \xrightarrow{RCHO} \underset{\text{Red ppt.}}{Cu_2O} + RCOOH$$

$$RCHO + Cu^{++} + 2OH^- \longrightarrow RCOOH + H_2O + Cu_2O$$

$$HCHO + Cu^{++} + 2OH^- \longrightarrow HCOOH + H_2O + Cu_2O$$

$$CH_3CHO + Cu^{++} + 2OH^- \longrightarrow CH_3COOH + H_2O + Cu_2O$$

$$C_6H_{12}O_6 + Cu^{++} + 2OH^- \longrightarrow C_6H_{12}O_7 + H_2O + Cu_2O$$

Gluconic acid

Only aliphatic aldehydes oxidize into carboxylic acid by Fehling's solution. So, it is oxidizing agent. In these chemical reactions, you may find aldehydes are oxidized into carboxylic acid. In these reactions Cu_2O is a common reduced product. The indication of reaction is formation of brown red precipitate of Cu_2O.

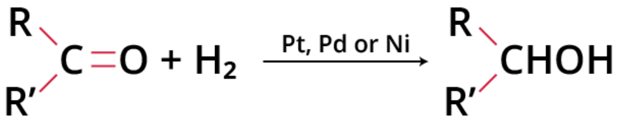
Addition reaction with H_2, HCN and $NaHSO_3$

a. With hydrogen (H_2)

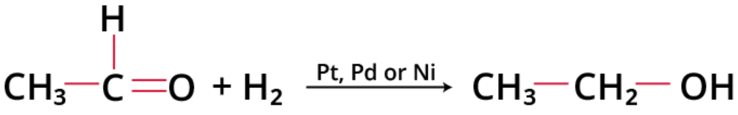
Study the following chemical equation and find the way that the product formed.

$$R-CHO + H_2 \xrightarrow{\text{Pt, Pd or Ni}} R-CH_2-OH$$

Aldehyde 1° alcohol

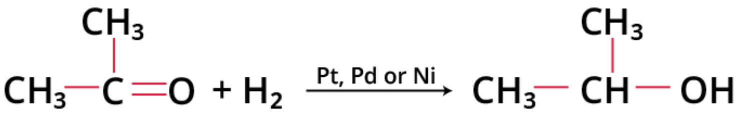


Ketone 2° alcohol



$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O + H_2 \xrightarrow{\text{Pt, Pd or Ni}} CH_3-CH_2-OH$$

acetaldehyde Ethyl alcohol



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O + H_2 \xrightarrow{\text{Pt, Pd or Ni}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-OH$$

acetone isopropyl alcohol

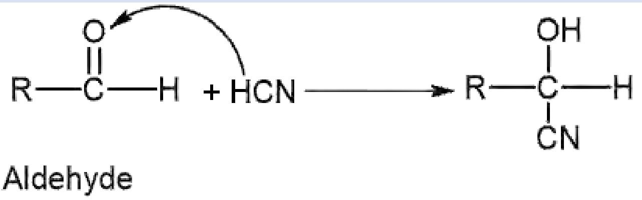
Is the process oxidation or reduction?

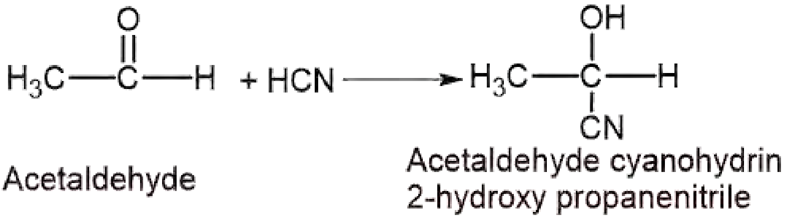
Why the process is ……………………………………..?

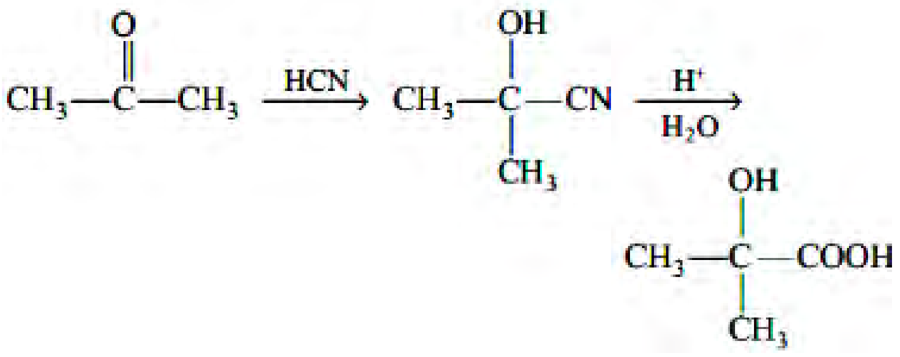
Write the answer of this question into your note copy.

In these chemical equations the products are formed by the addition of hydrogen into the aldehydes and ketones. So, by the reduction of aldehydes primary alcohols are formed as well as by the reduction of ketones, secondary alcohols are formed.

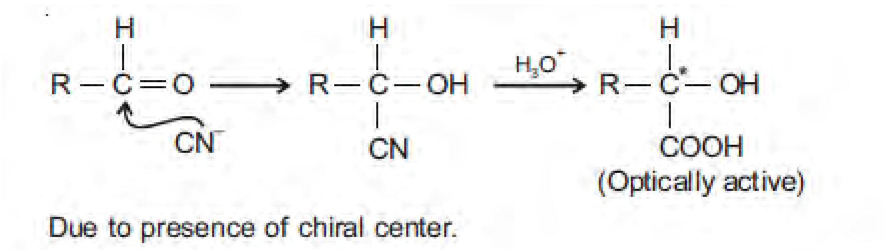
b. Action with HCN





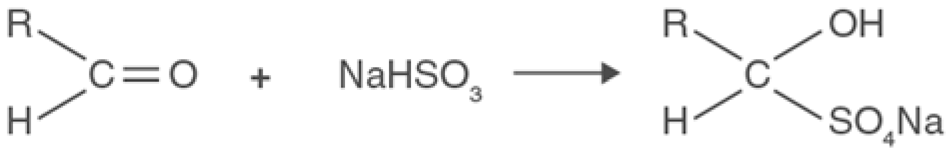


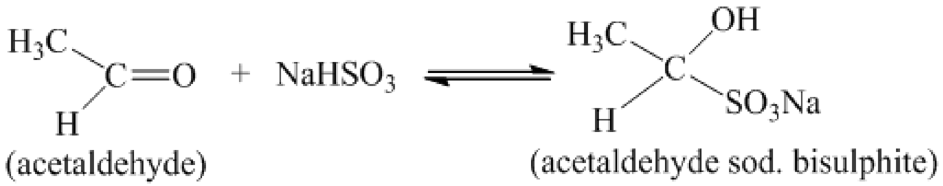
When cyanohydrin is hydrolysed in acidic medium alpha hydroxy carboxylic acid is formed which are optically active since the alpha carbon is **chiral carbon.** In this reaction nucleophile (CN^-) attacks on carbonyl carbon and cyanohydrin is formed. On hydrolysis, it gives alpha hydroxycarbonyl compound.

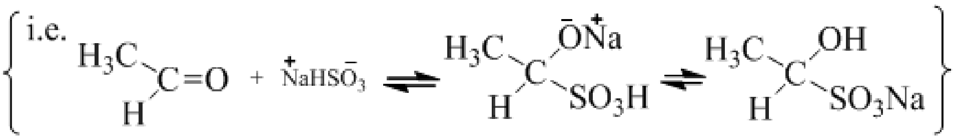


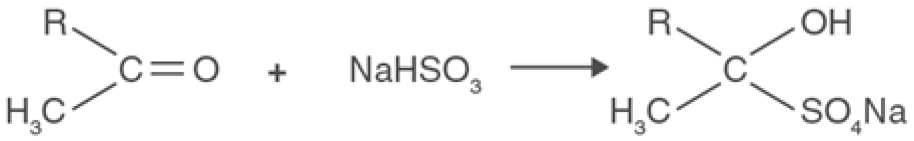
c. Addition with $NaHSO_3$

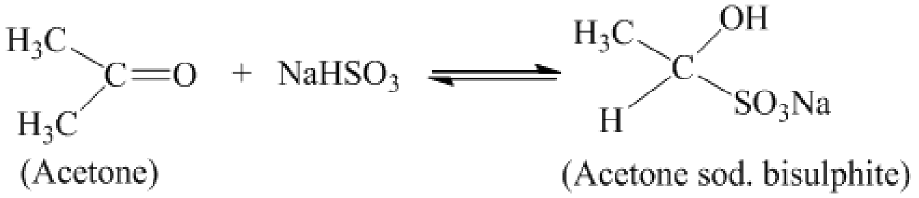
Study the following chemical equations and identify the general principles of reactions.











Is there any byproducts? Why not?

…………………………………………………………….

How are the major products form?

……………………………………..

When aldehydes or ketones are treated with sodium hydrogen sulphite, it forms a sodium salt of carbonyl bisulphite.

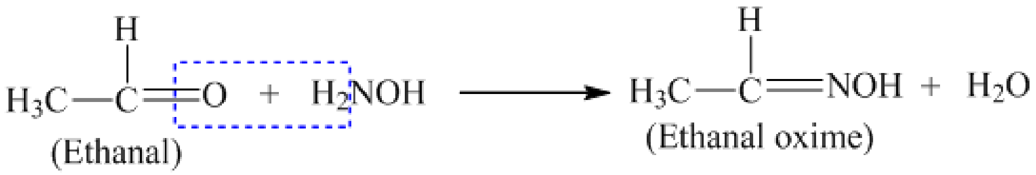
Try Yourself:

What would be the product when methanal is treated with HCN followed by hydrolysis?

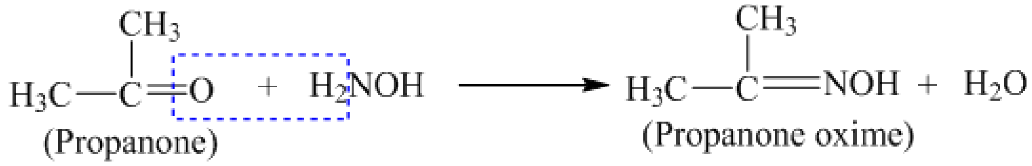
Action of aldehydes and ketones with ammonia derivatives

a. With hydroxyl amine (NH_2OH)

Study the following chemical equations and find, how is major product and byproduct is formed?



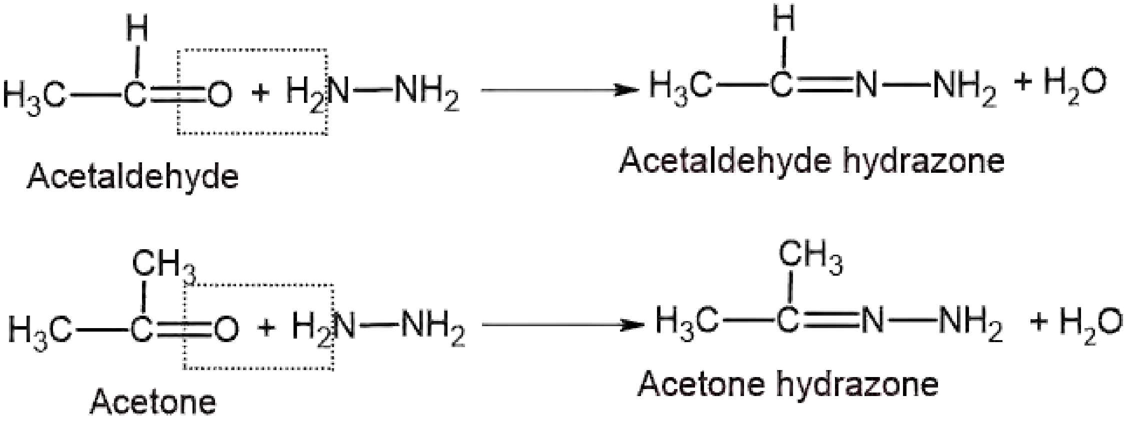
$$H_3C-\overset{\overset{\displaystyle H}{|}}{C}=O + H_2NOH \longrightarrow H_3C-\overset{\overset{\displaystyle H}{|}}{C}=NOH + H_2O$$



$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}=O + H_2NOH \longrightarrow H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}=NOH + H_2O$$

In these chemical equations, major product is formed by the loss of water molecule. Water molecule is formed by oxygen atom of carbonyl group and hydrogen atoms from hydroxyl amine.

b. With hydrazine (NH_2-NH_2)

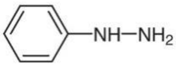


$$H_3C-\overset{\overset{H}{|}}{C}=O + H_2N-NH_2 \longrightarrow H_3C-\overset{\overset{H}{|}}{C}=N-NH_2 + H_2O$$

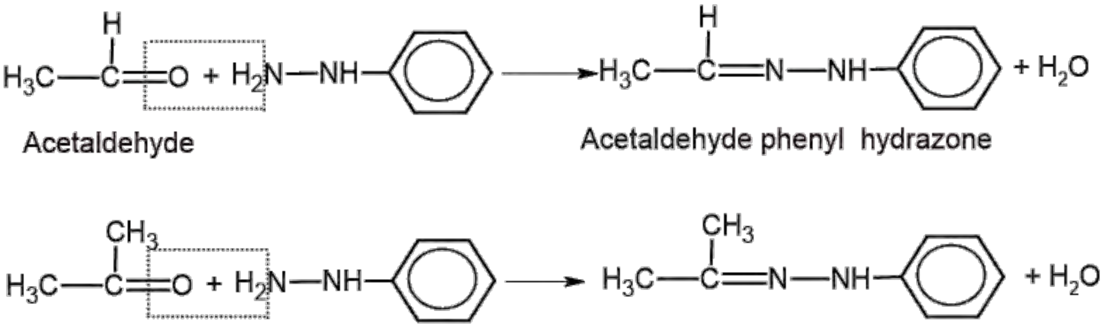
$$H_3C-\overset{\overset{CH_3}{|}}{C}=O + H_2N-NH_2 \longrightarrow H_3C-\overset{\overset{CH_3}{|}}{C}=N-NH_2 + H_2O$$

What are the similarities between the reaction of carbonyl compound and hydroxyl amine and carbonyl compound and hydrazine?

SN	carbonyl compound and hydroxyl amine	Carbonyl compound and hydrazine
1.	……………………..	…………………
2.	……………………..	………………..
3.	……………………..	………………….

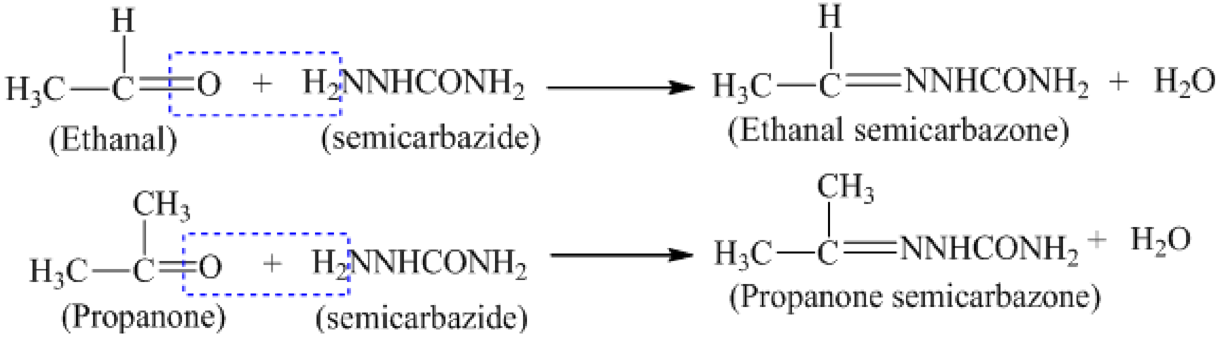
c. Action with phenyl hydrazine ()

Study the following chemical equation and find a way of producing water molecule. Remaining would be the major product



In these two chemical equations hydrogen from phenyl hydrazine and oxygen from the carbonyl compound makes water molecule and the major product is carbonyl hydrazone.

d. Action with semicarbazide

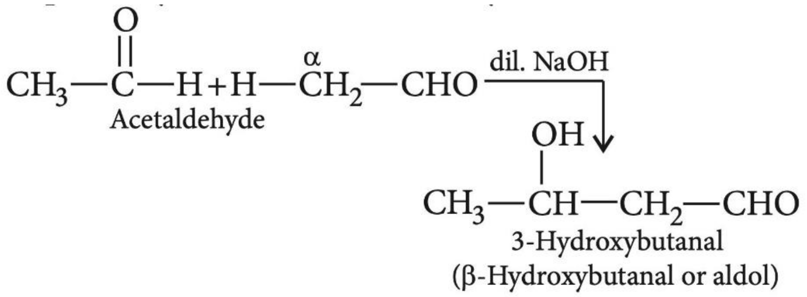


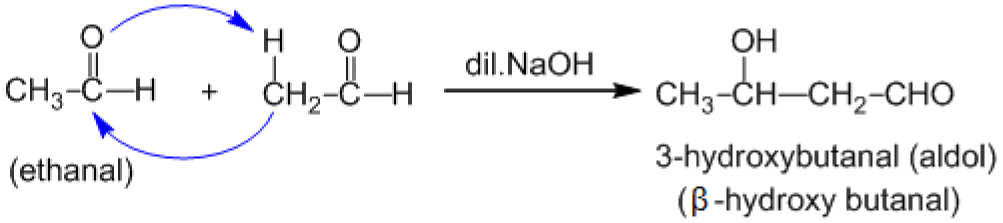
How are products formed from the reactants in these chemical equations? Fill the following table based on the chemical equation given above.

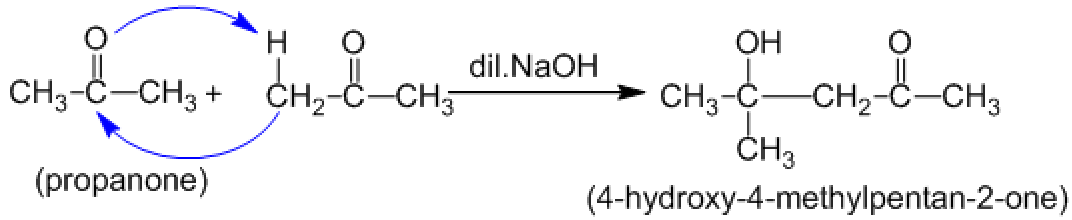
SN	carbonyl compound and semicarbazide	Products
1.	……………………..	…………………
2.	……………………..	………………..
3.	……………………..	………………….

When aldehydes and ketones are treated with semicarbazide respective semicarbazone is formed along with water molecule as byproduct.

Aldol condensation







What are the conditions that needs to be maintained in these reaction?

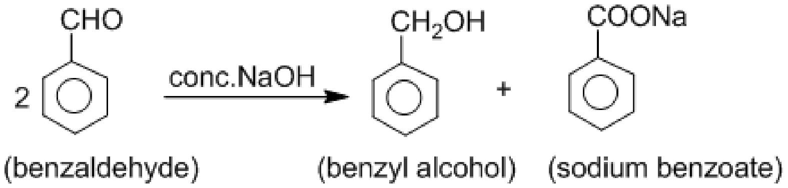
i. ………………..
ii. …………………
iii. ……………………
iv. ………………….

So, the condensed products formed when alpha hydrogen is shifted to the oxygen of another molecule to form β-hydroxy carbonyl compound. This reaction is called aldol condensation.

Cannizzaro's reaction

$$2\,HCHO \xrightarrow{conc.NaOH} CH_3OH + HCOONa$$

(methanal) (methanol) (sodium methanoate)
(formaldehyde) (methyl alcohol) (sodium formate)

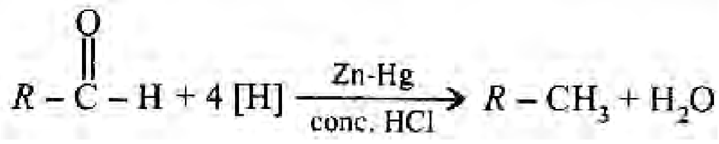


The aldehyde without α- hydrogen in presence of concentrated sodium hydroxide and heat gives a reduced product and an oxidized product. This reaction is called cannizaro's reaction.

What are the differences that you find in between aldol condensation and cannizaro's reaction? Write the differences in the following table.

SN	Aldol condensation	Cannizaro's reaction
1.		
2.		
3.		
4.		

Clemmensen's reduction

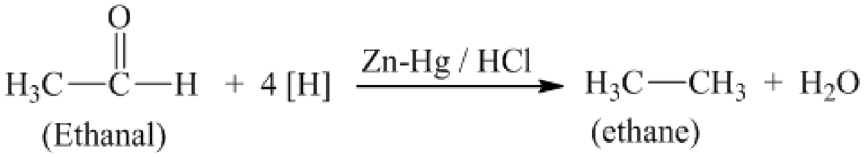


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + 4\,[H] \xrightarrow[\text{conc. HCl}]{\text{Zn-Hg}} R-CH_3 + H_2O$$

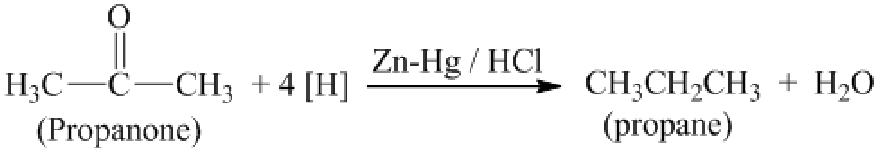
How is aldehyde changed into products in the chemical equation given above? Mention in the following three points.

a. ………………
b. ………………
c. ……………

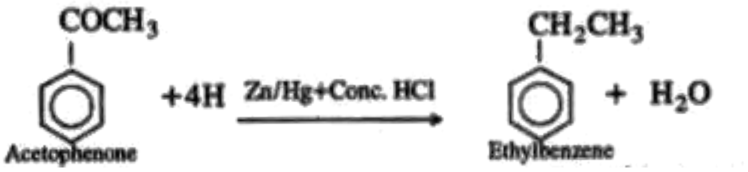
For example;



$$\underset{\text{(Ethanal)}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H} + 4\,[H] \xrightarrow{\text{Zn-Hg / HCl}} \underset{\text{(ethane)}}{H_3C-CH_3} + H_2O$$



$$\underset{\text{(Propanone)}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + 4\,[H] \xrightarrow{\text{Zn-Hg / HCl}} \underset{\text{(propane)}}{CH_3CH_2CH_3} + H_2O$$

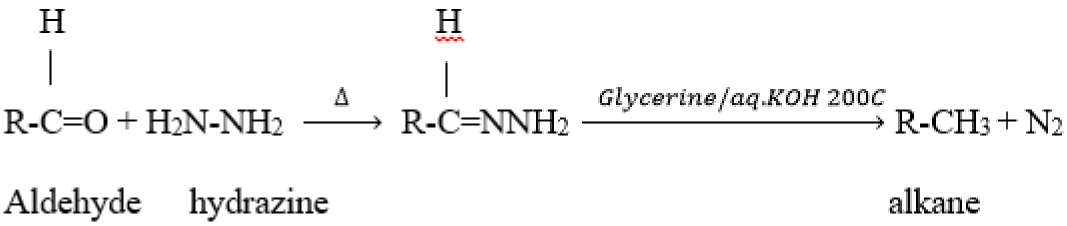


Do you know how water molecule is formed?

In all chemical equations given above have same byproduct i.e. water. Alkanes or saturated hydrocarbons are the major product formed in all chemical equation by the reduction of aldehyde and ketones in presence of zinc amalgam and conc.hydrochoric acid.

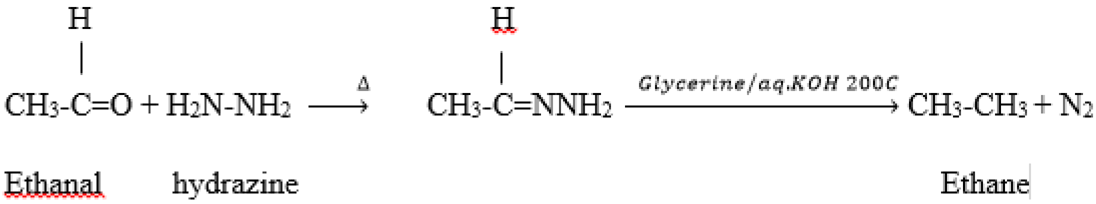
Wolff-Kishner's Reduction reaction:

When aldehydes or ketones are heated with hydrazine they form respective hydrazone. On further treatment of these hydrazones with glycerine and aq. KOH they give alkane along with nitrogen gas.

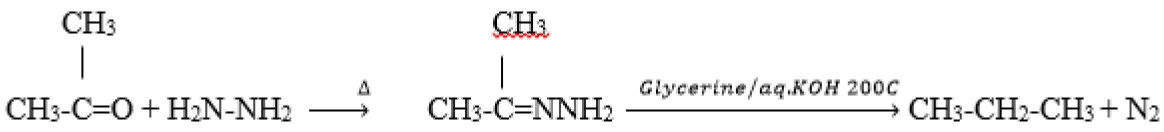


$$\underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle H}{|}}{C}=O} + \underset{\text{hydrazine}}{H_2N-NH_2} \xrightarrow{\Delta} R-\overset{\overset{\displaystyle H}{|}}{C}=NNH_2 \xrightarrow{\text{Glycerine/aq.KOH 200C}} \underset{\text{alkane}}{R-CH_3} + N_2$$

Example;



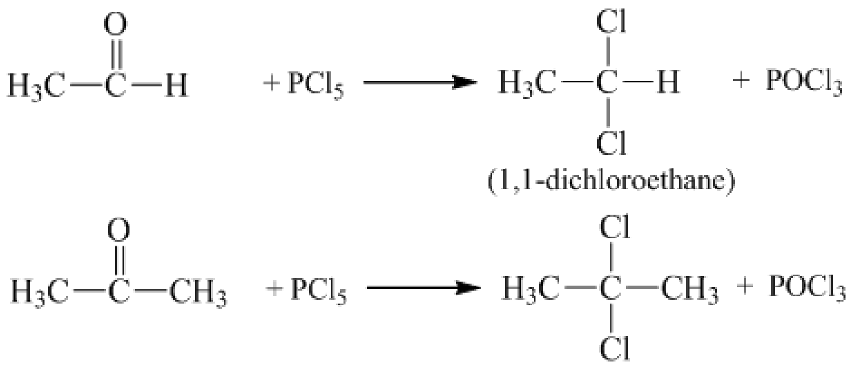
$$\underset{\text{Ethanal}}{CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O} + \underset{\text{hydrazine}}{H_2N-NH_2} \xrightarrow{\Delta} CH_3-\overset{\overset{\displaystyle H}{|}}{C}=NNH_2 \xrightarrow{\text{Glycerine/aq.KOH 200C}} \underset{\text{Ethane}}{CH_3-CH_3} + N_2$$



$$CH_3\text{-}\overset{\overset{CH_3}{|}}{C}\text{=O} + H_2N\text{-}NH_2 \xrightarrow{\Delta} CH_3\text{-}\overset{\overset{CH_3}{|}}{C}\text{=NNH}_2 \xrightarrow{Glycerine/aq.KOH\ 200C} CH_3\text{-}CH_2\text{-}CH_3 + N_2$$

Acetone hydrazine Propane

Action with PCl_5



$$H_3C-\overset{\overset{O}{\|}}{C}-H + PCl_5 \longrightarrow H_3C-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-H + POCl_3$$

(1,1-dichloroethane)

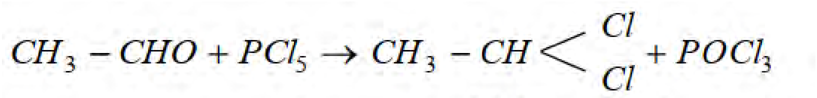
$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 + PCl_5 \longrightarrow H_3C-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3 + POCl_3$$

(2,2-dichloropropane)

As given in the chemical equations above, dihalides are obtained by the removal of oxygen from carbonyl compound alongwith phosphonyl trichloride.

What would be the product when ethanal is treated with PCl_5?

Analyze the following chemical equation.



$$CH_3-CHO + PCl_5 \rightarrow CH_3-CH\!<\!\begin{matrix}Cl\\Cl\end{matrix} + POCl_3$$

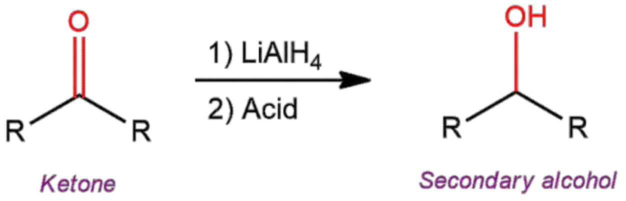
Ethylidene Chloride
or
Gem dihalide

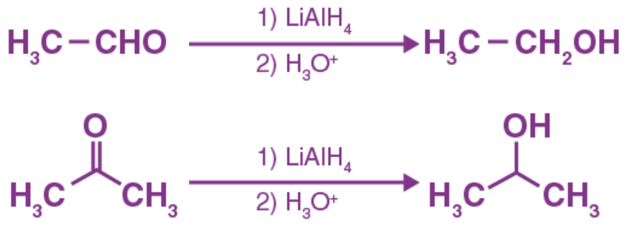
As carbon is bonded with oxygen through double bond in aldehydes and ketones, oxygen atom is lost by the addition of two atoms of chlorine.

Action with $LiAlH_4$

$$RCHO + 2[H] \xrightarrow{LiAlH_4} RCH_2OH$$

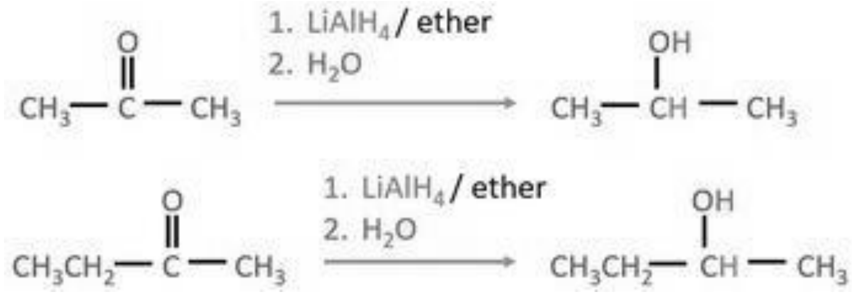
Aldehyde Primary alcohol





$$H_3C-CHO \xrightarrow[2)\ H_3O^+]{1)\ LiAlH_4} H_3C-CH_2OH$$

$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[2)\ H_3O^+]{1)\ LiAlH_4} H_3C-\overset{OH}{\overset{|}{C}H}-CH_3$$



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{1.\ LiAlH_4/\text{ether}\quad 2.\ H_2O} CH_3-\overset{OH}{\overset{|}{CH}}-CH_3$$

$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{1.\ LiAlH_4/\text{ether}\quad 2.\ H_2O} CH_3CH_2-\overset{OH}{\overset{|}{CH}}-CH_3$$

Do you know about reduction reaction?

In what respect oxidation is different from reduction?

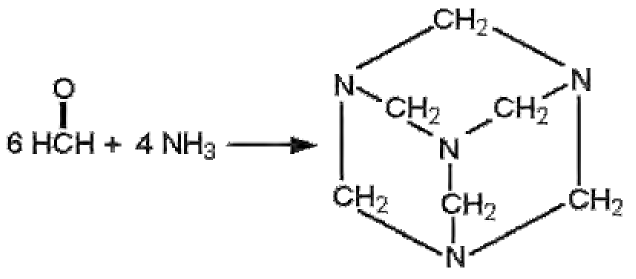
Yes, as you have thought that the reduction is a process in which addition of hydrogen occurs. You can find the same condition in the chemical equations given above. Addition of hydrogen is occurred in these chemical equations. Primary and secondary alcohols are formed by the reduction of aldehydes and ketones respectively.

Action of methanal with ammonia

$HCHO + NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$

Methanal hexamethylenetetramine

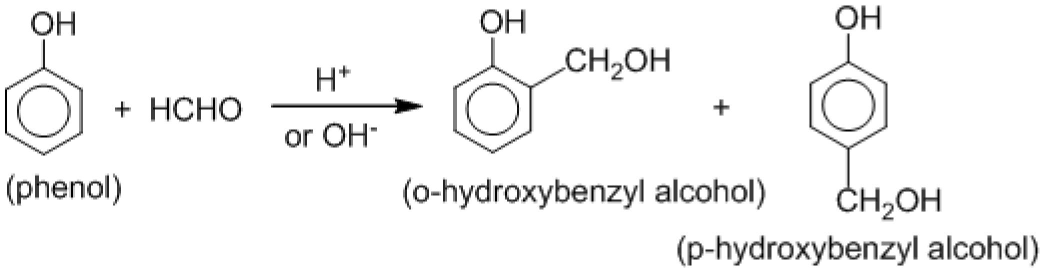
OR



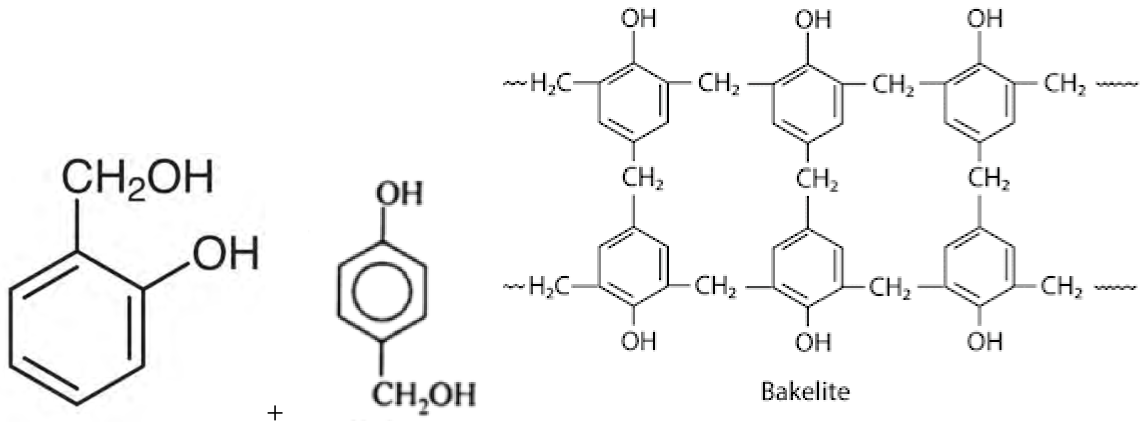
hexamethylenetetramine
urotropine

By condensation of ammonia and formaldehyde hexamethylenetetramine is formed. Which is also known as urotropine commonly. It is also used for the treatment of urinary diseases. Most commonly it is used as urinary antiseptic.

Action of methanal with phenol



Structure of Bakelite



When phenol and formaldehyde are treated in presence of acid, it gives o-hydroxy benzyl alcohol and p-hydroxybenzyl alcohol. Which undergoes further polymerization and gives a chain of Bakelite.

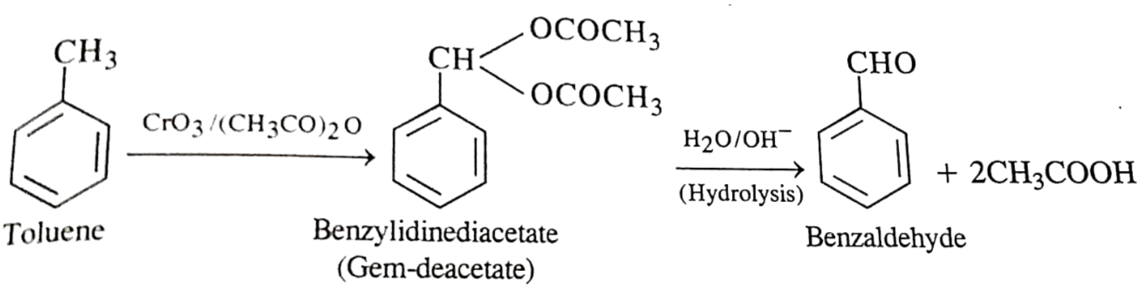
Formalin and its uses

37−40% solution of formaldehyde in water is called formalin. It is used as disinfectant and preservative for biological specimens.

a. Preservation: Formalin is used to preserve biological specimens, such as tissue samples for histological studies, and human remains in embalming fluid.
b. Disinfectant: Formalin is used as a disinfectant and preservative for household products and in industries.
c. Automotive: Formaldehyde is used in the automotive industry to make interior components, exterior primers, clear coat paints, tire cord adhesives, brake pads, and fuel system components.
d. Cosmetics: Formaldehyde is used in cosmetics, especially in hair shampoos. Cosmetic goods often contain preservatives that release formaldehyde to stop microbiological growth.
e. Fuel efficiency: Formaldehyde is blended with fossil fuels for vehicles to increase their fuel efficiency.
f. Drying skin: Formaldehyde is used to dry skin before or after surgical removal of warts.
g. Disinfection of rooms: Solid paraformaldehyde is used as a source of formaldehyde vapor for the disinfection of rooms.

Aromatic aldehydes and ketones

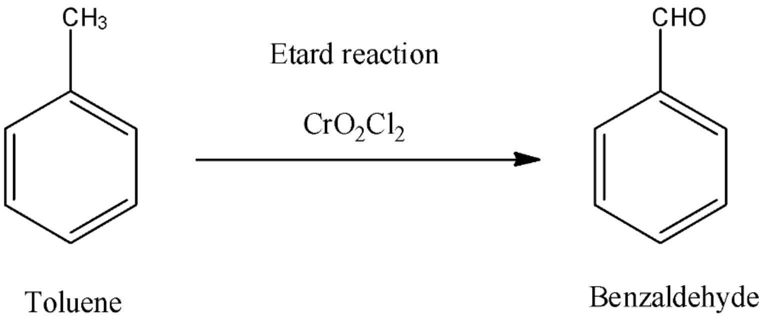
Preparation of benzaldehyde from toluene



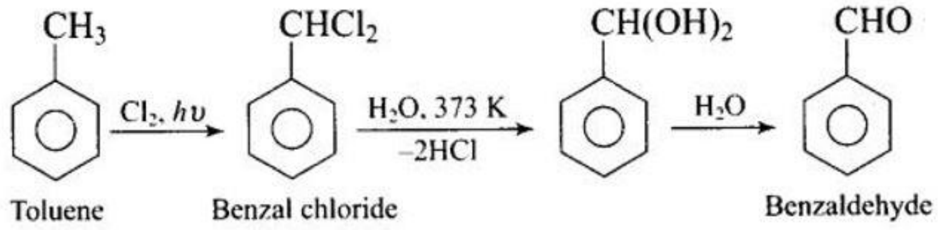
Study the chemical equation given above and analyze how is benzaldehyde formed. What changes do you see in these steps? Write.

Step I…………………………..

Step II………………………..

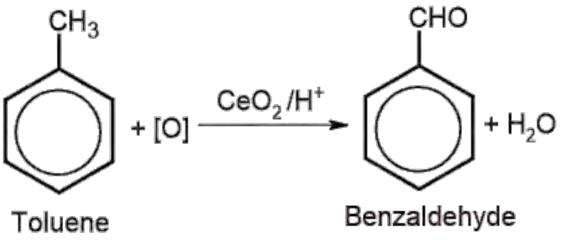


In this chemical equation benzaldehyde is formed by the direct oxidation of toluene in presence of chromyl chloride. This reaction is also known as Etard reaction.



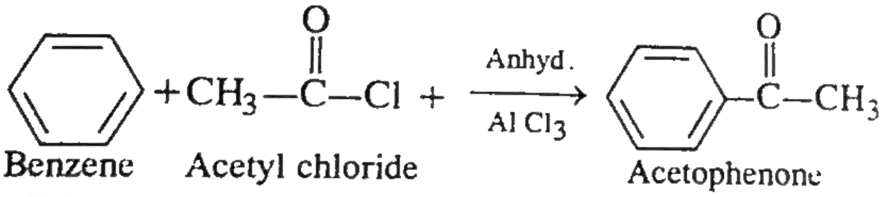
Analyze various steps of the equation given above and write the changes that you find in the following table

Step I	Step II	Step III
……………………..	……………………………..	………………………..

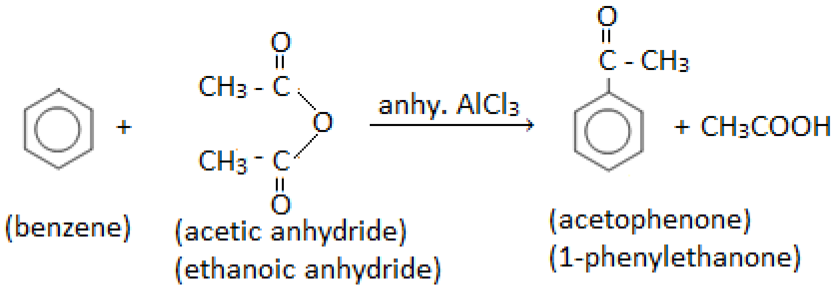


As you see in the given chemical equation that the toluene is oxidized in presence of CeO_2/H^+ which gives benzaldehyde as an oxidized product.

Acetophenone from benzene



I. When benzene is treated with acetyl chloride in presence of anhydrous aluminium chloride acetophenone is obtained.

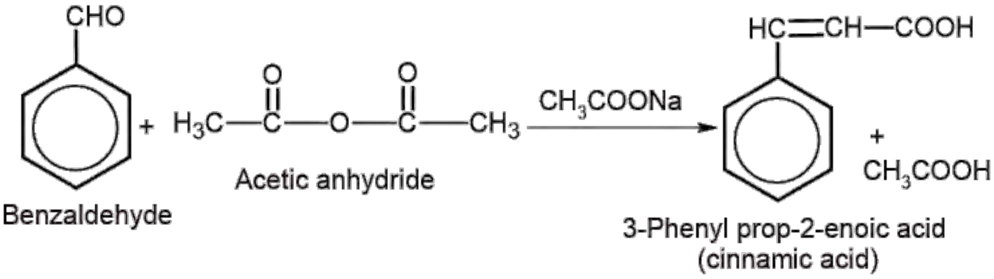


II. In this reaction, benzene is treated with acetic anhydride which gives acetophenone and acetic acid

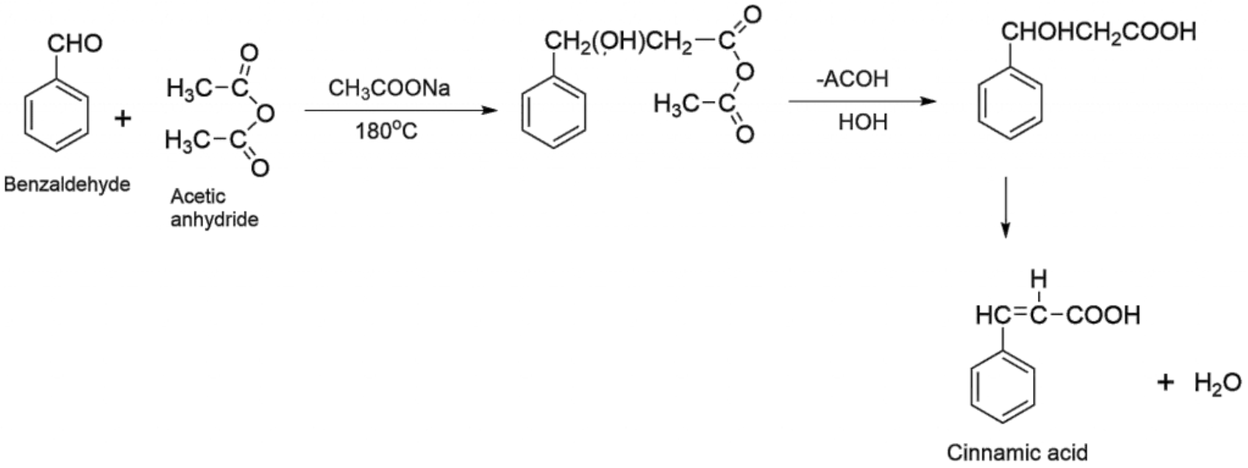
Find the differences that you find in the above chemical equations.

SN	I	II
1.		
2.		
3.		

Perkin's Condensation

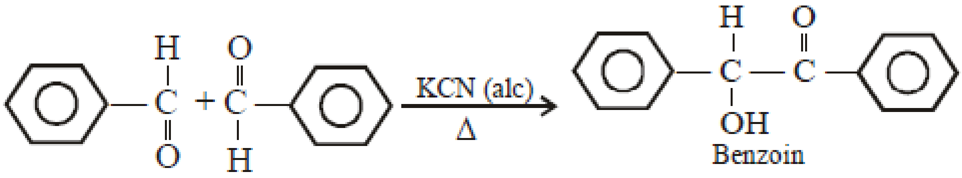


OR



As it has obtained cinnamic acid (3-phenyl-prop-2-en-oic acid) by condensing benzaldehyde and acetic anhydride in presence of sodium acetate. Byproducts are water and acetic acid (ACOH). This reaction is called Perkin's condensation.

Benzoin condensation



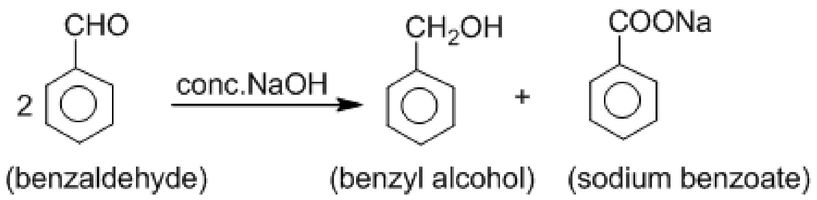
Benzoin

How is the product obtained? Can you explain?

a. ………………………..
b. ……………………….

Yes, in the above equation benzaldehyde is heated with alcoholic potassium cyanide, benzoin is obtained by condensation of two molecules of benzaldehydes.

Cannizaro's reaction



Does the benzaldehyde consists α-hydrogen? ……………

What are the required conditions for this reaction?

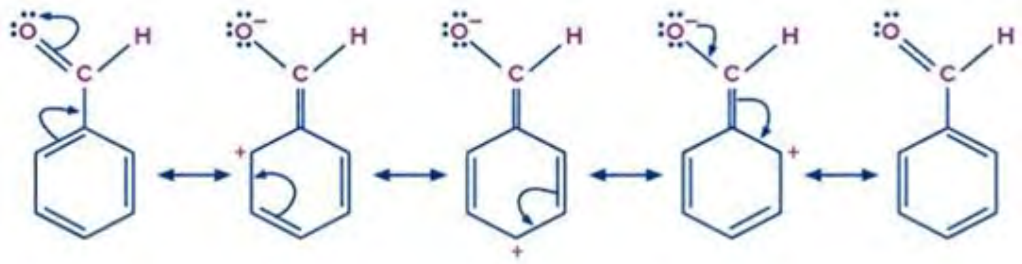
a. ………….
b. ……………..
c. …………….
d. …………….

When two molecules of benzaldehyde are heated with concentrated sodium hydroxide, one molecule gets oxidized to form sodium benzoate and another molecule is reduced and forms benzyl alcohol. This reaction is given by aliphatic aldehyde without α-hydrogen.

What are the relationship between benzaldehyde with benzyl alcohol and sodium benzoate?

	Benzyl alcohol	Sodium benzoate
Benzaldehyde	…………….	………………..

Electrophilic substitution reaction of benzaldehyde

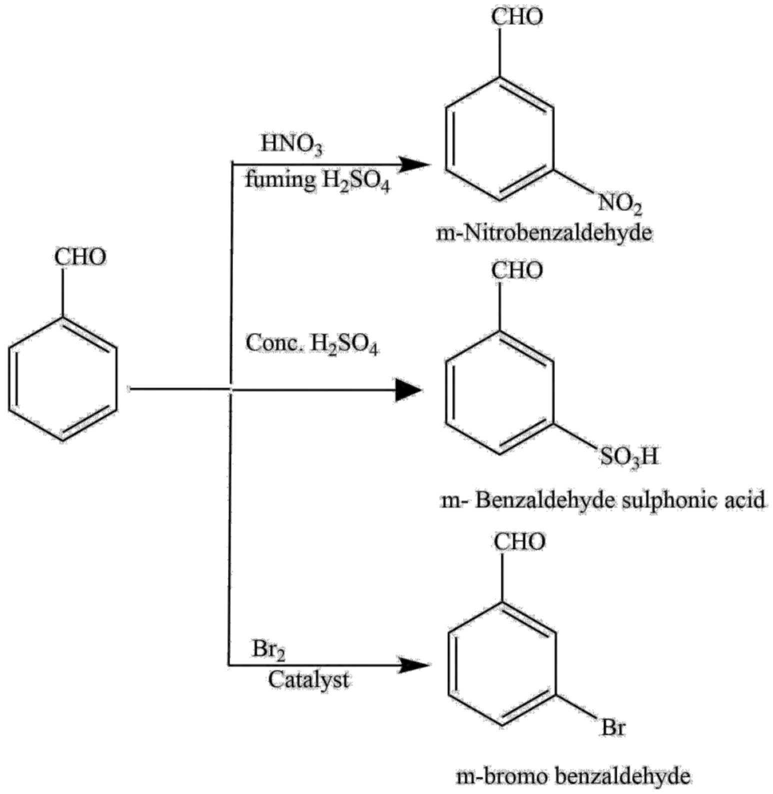


Resonance Structures in Benzaldehyde

As oxygen is electron withdrawing species, formyl group also has the same nature due to which pi-electron of the carbon with which formyl group attached is withdrawn outside. Again the electron of ortho carbon is shifted back resulting carbocation. Due to differences in electron density in adjacent carbon atoms, delocalization of electron occurs throughout the benzene ring. Hence, carbocation is formed at para and another ortho carbon. So, electrophilic substitution occurs at meta-position because meta-carbon has comparatively higher density of electron as compared to ortho and para carbon.

Some examples of electrophilic substitution reaction are as follows.

a. Nitration
b. Sulphonation
c. Halogenation



In electrophilic substitution reaction, electrophile gets substituted at meta-position. So, the products are m-nitrobenzaldehyde, m-benzaldehyde sulphonic acid and m-halobenzaldehyde respectively.

Exercise

A. Multiple Choice Questions.

1. Which one could be true about the information given in the following table?

SN	Compounds	Possible reactions/products
1.	A	Gives Tollen's test but not Fehlings's test
2.	B	Gives Cannizaro's reaction
3.	C	Gives 2-hydroxy-2-methylpropanoic acid by reacting C with HCN followed by hydrolysis

A. A is acetone, B is acetaldehyde and C is formaldehyde
B. A is benzaldehyde , B is acetone and C is acetaldehyde
C. A is acetaldehyde, B is acetone and C is benzaldehyde
D. A is benzaldehyde, B is formaldehyde and C is acetone

2. Which of the following is true about carbonyl compound?

A. They give positive iodoform test
B. They give positive claisen condensation test
C. They give negative iodoform test
D. They give positive DNP test

3. What would be the product when 2-methylbut-2-ene is ozonolyzed?

A. 2 molecules of ethanal
B. Ethanal and propanal
C. Ethanal and propan-2-one
D. Ethanal and methanel

4. Choose the best alternative from the following table

Reactants	Condition	Products
……………X	$Cu(OH)_2$ + boil	Ethanoic acid
CH_3CHO	Dil NaOH	……………Y
CH_3-CO-CH_3	………………Z	cyanohydrin

A. X is ethanal, Y is sodium ethanoate and Z is Potassium cyanide
B. X is ethanal, Y is 3-hydroxy butanol and Z is Potassium cyanide
C. X is ethanol, Y is 3-hydroxy butanal and Z is hydrogen cyanide
D. X is ethanal, Y is 3-hydroxy butanal and Z is hydrogen cyanide

5. Which of the following correct for Z ?

$CH_3CHO \xrightarrow{Zn-Hg\ /HCl} Z$

A. Z is ethene
B. Z is ethane

C. Z is ethanol
D. Z is ethanal

6. Which reaction represents the following chemical equation?

$CH_3COCl + H_2 \xrightarrow{Pd/BaSO4} CH_3CHO + HCl$

A. Clemmensen's reduction
B. C. Wolff-Kishner's reduction
C. Rosenmund's reduction
D. D. Catalytic reduction

7. How is ketones prepared?
A. By the oxidation of primary alcohols
B. By the oxidation of secondary alcohol
C. By the oxidation of tertiary alcohols
D. By the oxidation of aldehydes

8. Which of the following compounds gives cannizaro's reaction?
A. Formic acid
B. Acetaldehyde
C. Acetone
D. Formaldehyde

9. Which of the following combination is correct for the preparation of bakelite?
A. Phenol + formaldehyde
B. Phenol + formic acid
C. Phenol + acetaldehyde
D. Phenol + acetic acid

10. Which of the following compounds give both iodoform and Fehling's test?
A. Acetone
C. Acetaldehyde
B. Ethanol
D. Propan-2-ol

11. What would be the product when acetone reacts with chloroform in presence of KOH?
A. Trichloromethanol
C. Chloretone
B. Chloropicrin
D. Trichloroacetaldehyde

12. Which of the following compounds is used to distinguish pentan-2-one and pentan-3-one?
A. Zn-Hg/HCl
B. B. dil NaOH
C. C. NaOH + I_2
D. D. $K_2Cr_2O_7/H^+$

13. Which of the following is correct about the information given in the table?

A. Perkin's condensation	1. Benzoin
B. Aldol condensation	2. Beta hydroxyl butanal
C. Claisen condensation	3. Cinnamic acid
D. Benzoin condensation	4. Beta keto ester

A. A-3, B-2, C-1, D-4
B. C.A-3, B-1, C-2, D-4
C. A-3, B-2, C-4, D-1
D. D.A-3, B-1, C-4, D-2

14. The aromatic organic compound Z which does not gives Fehling's test but gives Tollen's test. What would be the compound Z?

A. Acetophenone
B. benzophenone
C. benzaldehyde
D. benzoic acid

15. What would be the product when propyne is catalytically hydrated in presence of dil. H_2SO_4 and 1% $HgSO_4$?

A. CH_3CH_2CHO
B. $CH_3CH_2CH_2OH$
C. CH_3COCH_3
D. CH_3-O-CH_2CH_3

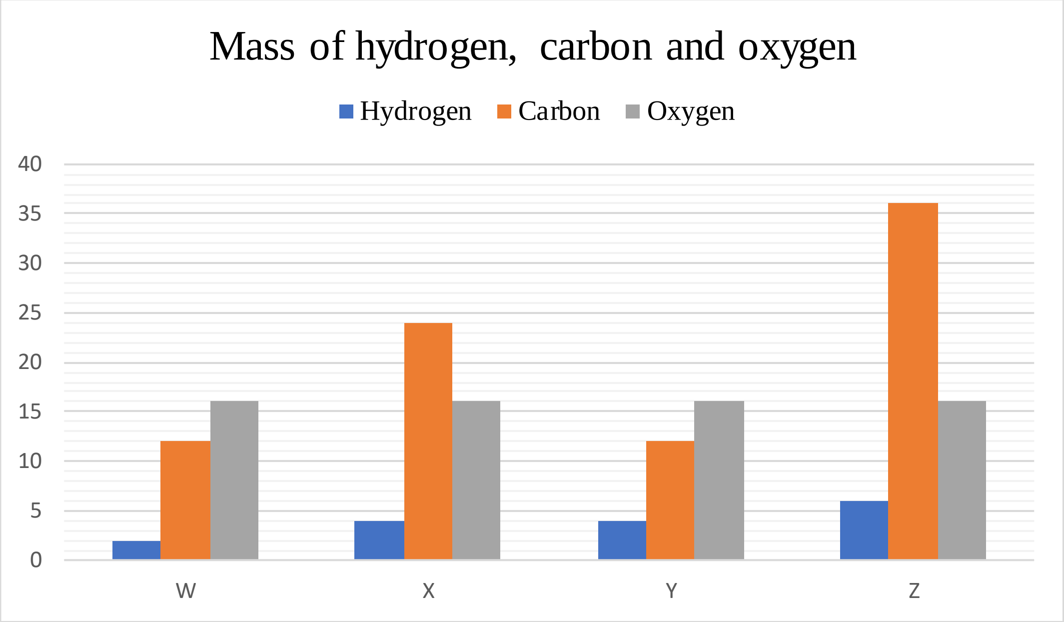
16. Which of the following condition is correct for the cannizaro's reaction?

A. Dil. NaOH, Heat, alpha hydrogen
B. conc. NaOH, Heat, alpha hydrogen
C. Dil. NaOH, Heat, without alpha hydrogen
D. conc. NaOH, Heat, without alpha hydrogen

17. Which of the following is correct about butan-2-one?

A. It does not give iodoform test but gives Tollen's test
B. It does not give Tollen's test but gives Fehling's test
C. It does not give Fehling's test but gives DNP test
D. It does not give DNP test but gives iodoform test

18. The following diagram shows the four compounds W, X, Y and Z .Each compounds have hydrogen, carbon and oxygen. The histogram shows the mass of these elements.



A. W is methanol, X is methanal, Y is ethanal and Z is propanal
B. W is methanal, X is methanol, Y is ethanal and Z is propanol
C. W is methanol, X is ethanal, Y is ethanol and Z is propanal
D. W is methanal, X is ethanal, Y is methanol and Z is propanal

19. What is formalin?

A. 30% formaldehyde
B. 50% formaldehyde
C. 40% formaldehyde
D. 60% formaldehyde

20. Which of the following is correct about the following table?

Compounds	Products
a. CH_3CHO	1. cinnamic acid
b. CH_3COCH_3	2. 4-hydroxy-4-methylpentan-2-one
c. C_6H_5CHO	3. formalin
d. HCHO	4.ethane

A. a-1, b-2, c-3, d-4
B. a-3, b-4, c-1, d-2
C. a-2, b-3, c-4, d-1
D. a-4, b-2, c-1, d-3

21. Which of the following is true about benzaldehyde?

A. It gives DNP test, iodoform test and gives benzoin condensation
B. It gives aldol condensation, iodoform test and perkin's condensation
C. It gives Tollen's test, perkin's condensation and clemmensen's reduction
D. It gives Perkin's condensation, Fehling's test and clemmensen's reduction

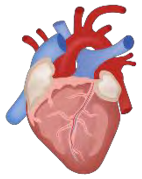
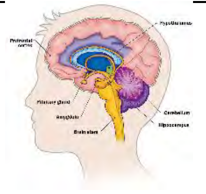
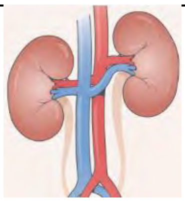
22. $CH_3CHO \xrightarrow{HCN} X \xrightarrow{H_3O+} Y$

In the above sequence of the reaction what could be Y?

a. Ethanoic acid　　c. α-hydroxy propanoic acid

b. β-hydroxy propanoic acid　　b. α-hydroxy ethanoic acid

23. Which of the following is related with $(CH_2)_6N_4$

			
A	B	C	D

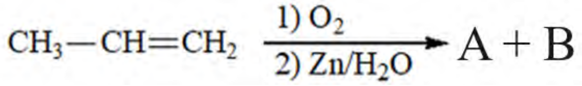
24. Choose the best alternative from the followings

Reaction condition	**Name of the reaction**
a. Dil. NaOH	1. Tollen’s test
b. Zn-Hg/HCl	2. Aldol condensation
c. Hydrazine/glycerol/KOH	3. Clemensen’s reduction
d. Ammoniacal $AgNO_3$	4. Wolff-Kishner’s reduction

A. a-1, b-2, c-3, d-4　　C. a-2, b-3, c-4, d-1

B. a-3, b-4, c-1, d-2　　D. a-4, b-2, c-1, d-3

25. What would be the products A and B in the following reaction sequence?



$$CH_3{-}CH{=}CH_2 \xrightarrow[\text{2) Zn/H}_2\text{O}]{\text{1) O}_2} A + B$$

A. A is ethanol and B is methanol　　C. A is ethanal and B is methanol

B. A is ethanol and B is methnal　　D. A is ethanal and B is methanal

26. The reaction : $A \xrightarrow{Acetone/alkali}$ chloretone, identify compound A.

A. Trichloromethane　　B. Bromoform　　C..Iodoform　　D.Haloalkane

27. What would be the major product when propan-2-one is treated with dil. NaOH?

A. 3-hydroxy butan-2-one　　C. 3-hydroxy 3-methyl butan-2-one

B. 4-hydroxypentan-2-one　　D. 4-hydroxy 4-methyl pentan-2-one

28. Which of the following compounds give iodoform test?

A. Methanal　　B. propanal　　C. butanal　　D. propan-2-one

29. What could be W, X, Y and Z in the following reaction sequence?

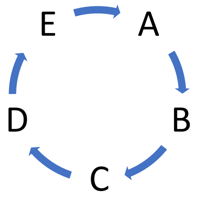
- W gives positive test with 2,4-DNP
- X gives Tollen's test
- Y gives Fehling's test
- Z is carboxylic acid

A. W- alcoholic compounds, X- ketone, Y- aliphatic aldehyde and Z can be ethanoic acid
B. W, carbonyl compounds, X- aldehyde, Y-aliphatic aldehyde and Z can be ethanoic acid
C. W-carboxylic acid, X- aldehyde, Y-aliphatic aldehyde and Z can be benzoic acid
D. W, alcohol, X- ketone, Y-aliphatic aldehyde and Z can be benzoic acid

Short questions

30. How do you confirm CH_3CHO and CH_3COCH_3 by chemical test? Write the molecular structure of butan-2-one and 3-hydroxybutanal.

31. Study the following cyclic pattern of reaction and complete the cycle with suitable compounds in place of A, B, C, D and E with their name where A is an aromatic aldehyde having molecular mass 106 amu.



32. An organic compound A, $C_5H_{10}O$ gives positive 2,4-DNP test but a negative silver nitrate test. Compound A is oxidized in the presence of alkaline $KMnO_4$ in vigorous condition to carboxylic acid B, $C_3H_6O_2$. The sodium salt of B gives a hydrocarbon C on kolbe's electrolytic reduction. Identify A, B and C with suitable reactions.

33. Identify the compounds in the following reaction sequence and complete the reactions. $W \xrightarrow{Zinc\ dust/heat} X \xrightarrow{CH3Cl/AlCl3\ /heat} Y \xrightarrow{CeO2/H+} Z$. X is aromatic hydrocarbon having molecular mass 78 amu.

34. What happens when;
a. Formaldehyde is treated with 2,4-DNP?
b. Methanal is heated with ammonia?
c. Acetone is reacted with hydroxyl amine
d. Ethanal is treated with HCN followed by acid hydrolysis?
e. Benzaldehyde is Heated with alc.KCN?

35. Give an example of each of the followings

  a. Tollen's test

  b. Fehling's test

  c. Aldol condensation

  d. Cannizaro's reaction

  e. Clemmensen's reduction reaction.

36. The given table shows the compounds and their molecular formula. How would you convert A to B. How A obtained from E, where E is primary alcohol. Write down the reactions involved in conversion A to C and D. (5x1=5)

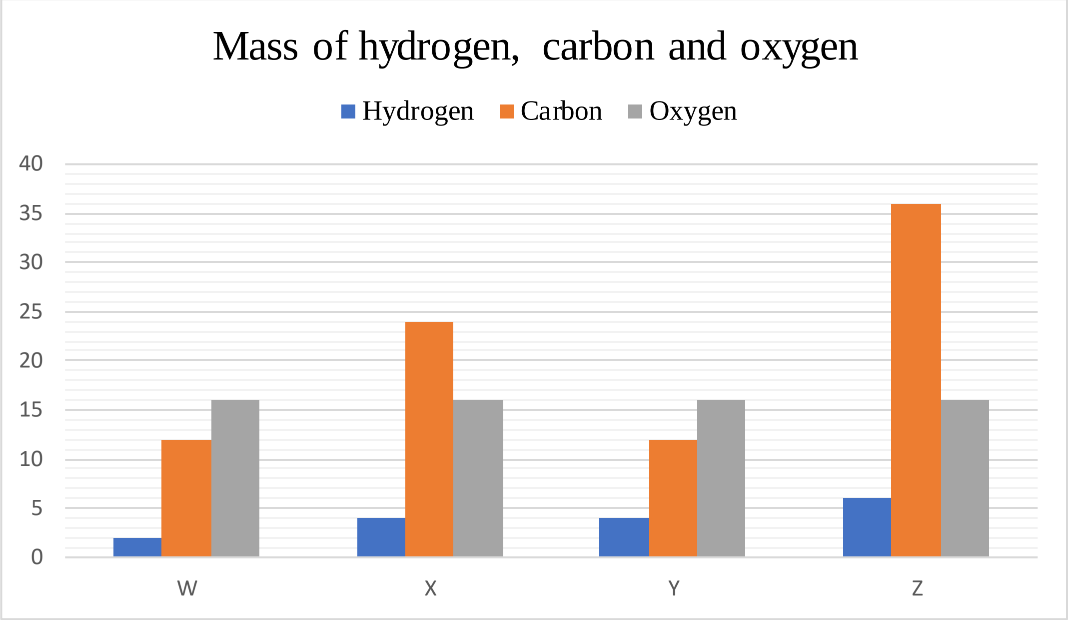
Compound	Molecular formula
A	C_2H_5Cl
B	C_4H_{10}
C	CH_2O
D	C_2H_4O
E	C_2H_6O

37. Compound A ($C_4H_{10}O$) does not react with phenyl hydrazine but when it is oxidized in presence of acidified potassium dichromate gives B having molecular formula (C_4H_8O). Compound B reacts with 2,4-DNP but does not give Tollen's test. When the compound A is dehydrated in presence of conc.sulphuric acid it gives a compound C(C_4H_8). After ozonolysis of C, two similar molecules are formed? Identify the compounds A, B, C with pertinent reactions. What would be the product when acetone is treated with HCN followed by acid hydrolysis?

38. An alkene 'A' with molecular formula C_6H_{12} on ozonolysis gives only one type of carbonyl compound 'B'. The carbonyl compound does not give red precipitate with Fehling's solution but gives yellow precipitate of compound 'C' with iodine solution in presence of sodium hydroxide. The compound C on heating with silver powder gives a gas 'D'. The gas 'D' gives a compound 'E' when treated with aq. Sulphuric acid in presence of 1% $HgSO_4$. Finally, when the compound E is oxidized, ethanoic acid is formed. Identify the compounds 'A', 'B', 'C', 'D' and 'E' with pertinent reactions.

Long Questions

39. The following diagram shows the four compounds W, X, Y and Z .Each compounds have hydrogen, carbon and oxygen. The histogram shows the mass of these elements.



a. Identify the compounds W, X, Y and Z based on above diagram
b. What happens when compound W is heated with ammonia?
c. Write the isomers of compound Z.
d. Write difference between compounds X and Y with a chemical test of each.

40. A. V $\xrightarrow{Zn/heat}$ W $\xrightarrow{CH3Cl/AlCl3}$ X $\xrightarrow{CeO2/H+}$ Y $\xrightarrow{CH3COONa/heat}$ Z. W is also obtained by passing acetylene gas into red hot iron or copper tube at about 15- 25 atmospheric pressure. [1+1+1+1+1]

B. Compound M C_6H_{12} decolorizes bromine, but gives no reaction with sodium metal or phenyl hydrazine. Ozonolysis of compound M gives two compounds N and O, both react with phenyl hydrazine. Compound N gives positive Tollen's and iodoform tests. Compound O has molecular masss 72 amu. Suggest the structures for A, B and C. Give chemical equations for the reaction.[1+1+1]

41. A.Identify P, Q, R, S and T from the following information.

- Compound P is a compound having same functional group as of ethanol.
- Compound Q gives cannizaro's reaction but is not aliphatic compound
- Compound R is obtained when compound Q is oxidized
- Compound S is a compound of ammonia
- Compound T is a compound which is obtained by nitration of fundamental aromatic compound.

B.W $\xrightarrow{K2Cr2O7/acid}$X $\xrightarrow{2,4-DNP}$ Y . W gives positive iodoform test and is primary alcohol. Identify W, X and Y.

42. Benzene$\xrightarrow{CH3Cl/AlCl3}$ A $\xrightarrow{CeO2/H+}$ B $\xrightarrow{CH3COONa\ /heat}$ C. Identify in the given reaction sequence. [1+1+1]

B. Compound P, $C_6H_{12}O$, gives the following results.

i. P does not react with Tollen's reagent
ii. P on catalytic hydrogenation gives Q, $C_6H_{14}O$
iii. Q on treatment with conc. H_2SO_4 gives R, C_6H_{12}
iv. R on ozonolysis gives two compounds, S (C_3H_6O) and T(C_3H_6O)
v. S gives positive iodoform test and negative Tollen's test
vi. T gives positive Tollen's test and negative iodoform test.

43. a. Compound 'B' reacts with dil NaOH and gives 4-hydroxy 4-methyl pentan-2-one 'A' reacts with $Cu(OH)_2$ to give a carboxylic acid and forms antiseptic reagent by the reduction of 'A'. 'C' reacts with ammoniacal silver nitrate Solution but does not react with $Cu(OH)_2$. It reacts with acetic anhydride and gives aromatic unsaturated carboxylic acid. Identify A, B, and C with all possible reactions involved. [5]

SN	Molecule	Molecular wt.
1	A	44 amu
2.	B	58 amu
3.	C	106 amu

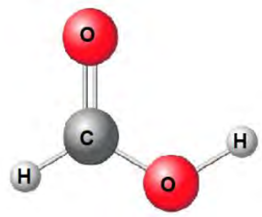
b.An aliphatic aldehyde is treated with hydrogen cyanide and gives 2-hydroxy propanoic acid after hydrolysis. Identify the compound and write the reactions followed. Also write a reaction to prepare the aldehyde. [2+1]

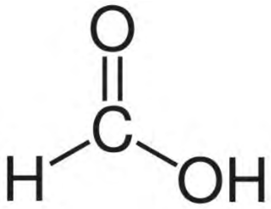
Unit 14

Carboxylic Acids and its derivatives

A) Aliphatic and Aromatic Carboxylic acids

14.1 Describe briefly the nomenclature and isomerism of aliphatic and aromatic carboxylic acids



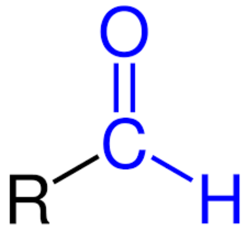
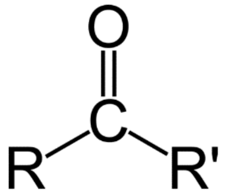
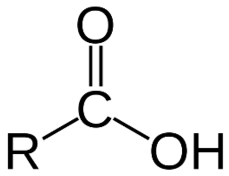


Name of the substance	Products
Formic acid	
Acetic acid	
Benzoic acid	

❖ Have you ever thought that we are having acids?

Some organic acids are safe to eat/have.

Activity:
Study the following structures of organic compounds. Count the components (atoms) present in the compounds and write to the next column.

Molecular structure	Name of the molecules	Components (atoms) of the molecules
	…………………………	………………………… ………………………… …………………………
	…………………………	………………………… ………………………… …………………………
	………………………...	…………………………… …………………………… ……………………………

What are the differences that you find in the above structures?

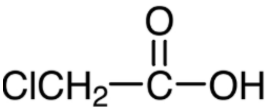
9. ………………………………………………………………………………
10. ………………………………………………………………………………
11. ………………………………………………………………………………
12. ………………………………………………………………………………

So, the carboxylic acids are hydroxyl derivative of carbonyl compounds. Carboxylic acids are the functional isomers of esters.

Nomenclature:

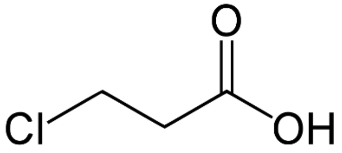
Common Naming system:

HCOOH	CH_3COOH	CH_3-CH_2-COOH
Formic acid	acetic acid	propionic acid

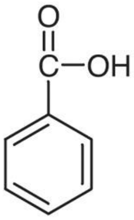


$ClCH_2-\overset{\overset{O}{\|}}{C}-OH$

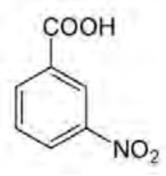
α-chloro acetic acid



β-chloropropanoic acid



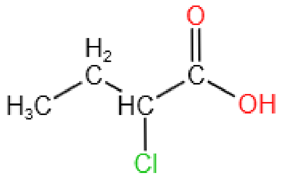
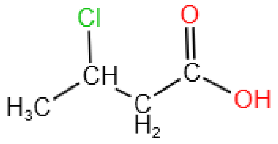
benzoic acid



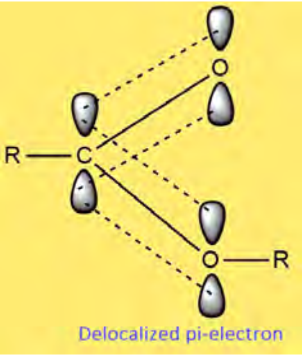
m-nitro benzoic acid

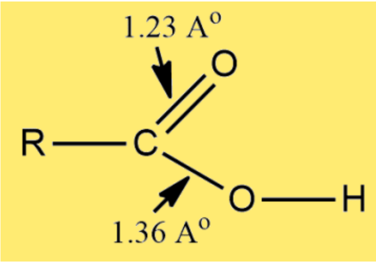
IUPAC Naming System and common names:

Substituent + prefix+ word root + primary suffix + oic acid
To write the IUPAC name of carboxylic acid oic acid secondary suffix is written and other procedures are same as nomenclature of other compounds.

SN	Formula	IUPAC Name	Common Name
1.	H-COOH	Methanoic acid	Formic acid
2.	CH_3-COOH	Ethanoic acid	Acetic acid
3.	CH_3-CH_2-COOH	Propanoic acid	Propionic acid
4.	CH_3-CH_2- CH_2-COOH	Butanoic acid	Butyric acid
5.		2-chlorobutanoic acid	α-chlorobutyric acid
6.		3-chlorobutanoic acid	β-chlorobutyric acid

Orbital Structure of carboxylic acid

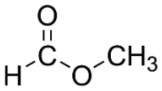
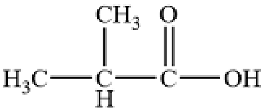




Isomerism of carboxylic acid:

Study the pairs of compounds given in the following table. Write similarities and differences found in these pairs.

Table: 1

SN	Compounds	Similarity	Difference
1.	a. CH_3-COOH b. 	....	....
2.	a. CH_3-CH_2- CH_2-COOH b. 	....	....

Activity:

Study the pair of compounds given in table no. 1. Relate the following statements and fill in the following table.

Statements	Isomerism	Pair of compounds of table 1 (write S.N.)
• Same molecular formula but difference in chain.	Chain isomerism	………………………………
• Same molecular formula but difference in functional group.	Functional isomerism	………………………………

The phenomenon where two or more compounds have the same molecular formula but differ in their structural arrangement or spatial orientation, leading to different physical and chemical properties is called isomerism. There are two main types of isomerism: **structural isomerism** and **stereoisomerism**. We are talking about structural isomerism.

Two types of isomerism are shown by carboxylic acid. They are

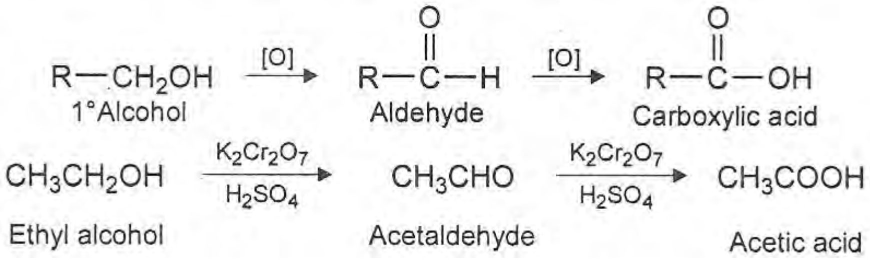
v. Chain isomerism
vi. Functional isomerism

- Write the functional isomers of $C_3H_6O_2$
- Give one more pair of isomers of types given above and submit to your teacher.

14.1.2 Preparation of monocarboxylic acids;

a. From Aldehydes

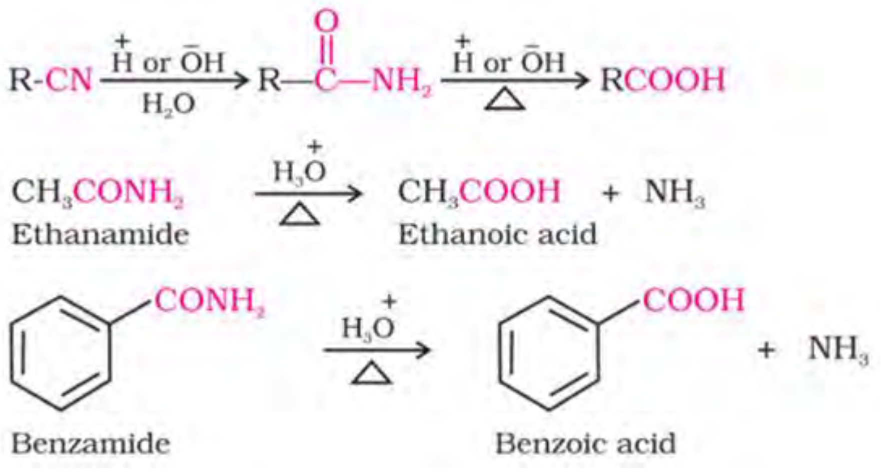
Study the following chemical equations and write how are the products formed?



Primary alcohol is oxidized in the first step and again aldehyde is oxidized which gives carboxylic acid.

b. From Nitriles

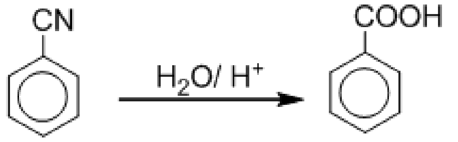
How are the carboxylic acids formed in the following chemical equations? Study the following chemical equations.



$$R\text{-}CN \xrightarrow[H_2O]{\overset{+}{H}\text{ or }\overset{-}{O}H} R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2 \xrightarrow[\Delta]{\overset{+}{H}\text{ or }\overset{-}{O}H} RCOOH$$

$$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\Delta]{H_3\overset{+}{O}} \underset{\text{Ethanoic acid}}{CH_3COOH} + NH_3$$

$$\underset{\text{(Ethane nitrile)}}{CH_3\text{-}C{\equiv}N} + 2\,H_2O \xrightarrow[\text{boil}]{HCl} \underset{\text{(Ethanoic acid)}}{CH_3COOH} + NH_4Cl$$



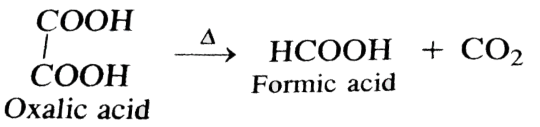
Benzonitrile
(Phenyl cyanide)

Benzoic acid

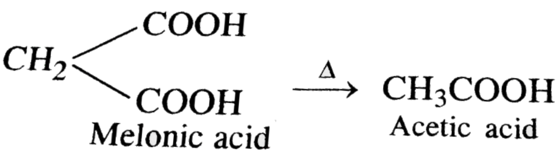
At first, nitriles react with water and give amides. Again by acidic hydrolysis of amide carboxylic acids are formed.

c. From Dicarboxylic acids

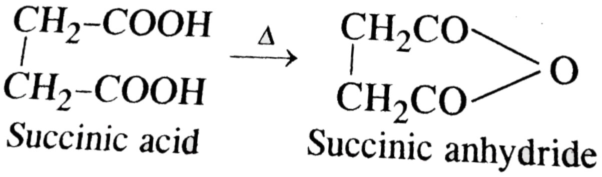
Study the following chemical equations and find the way how are products formed.



$$\underset{\text{Oxalic acid}}{\begin{array}{c}COOH\\|\\COOH\end{array}} \xrightarrow{\Delta} \underset{\text{Formic acid}}{HCOOH} + CO_2$$



$$\underset{\text{Melonic acid}}{CH_2{<}\begin{array}{l}COOH\\COOH\end{array}} \xrightarrow{\Delta} \underset{\text{Acetic acid}}{CH_3COOH}$$



$$\underset{\text{Succinic acid}}{\begin{array}{l}CH_2\text{-}COOH\\|\\CH_2\text{-}COOH\end{array}} \xrightarrow{\Delta} \underset{\text{Succinic anhydride}}{\begin{array}{l}CH_2CO\\|\\CH_2CO\end{array}{>}O}$$

In these equations products are formed by the removal of carbondioxide from the dicarboxylic acid.

d. From Sodium alkoxide

$$RONa + CO \xrightarrow{\text{Heat / Pressure}} RCOONa + HCl \rightarrow RCOOH + NaCl$$

$$CH_3ONa + CO \xrightarrow{\text{Heat / Pressure}} CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$$

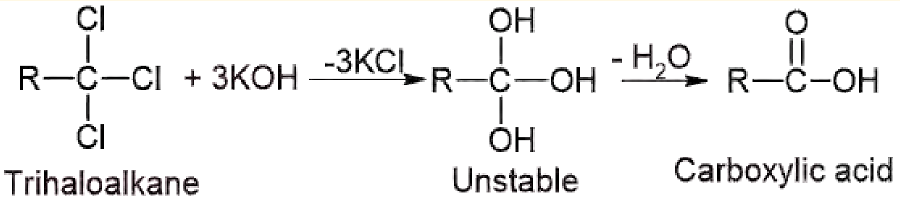
Study the chemical equations given above and write the changes in first and second step.

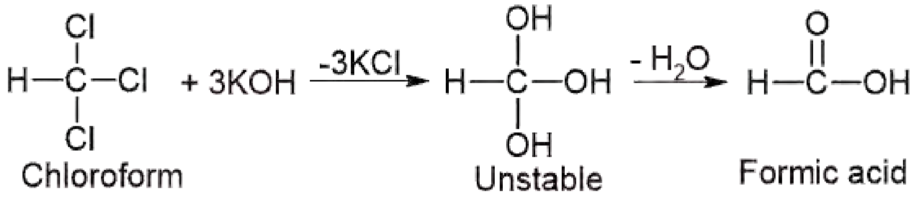
First step: …………………….
Second step: …………………….

Yes, at first step carbomonoxide is inserted at between O and Na of sodium alkoxide. which on hydrolysis in acidic medium, carboxylic acid is formed along with sodium chloride byproduct.

Complete the following chemical equations as of above.
a. $CH_3CONa + CO$ ………………………………………………………
b. $CH_3CH_2CONa + CO$ ……………………………………………….

e. From Trihaloalkanes

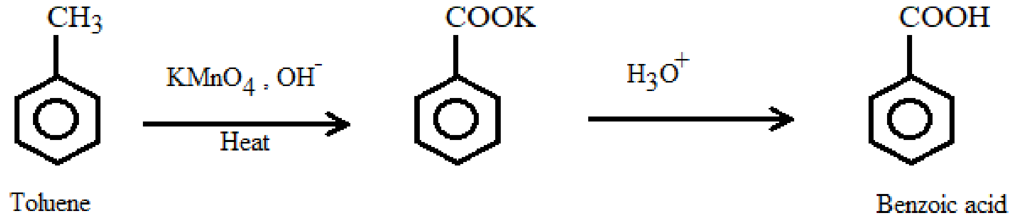


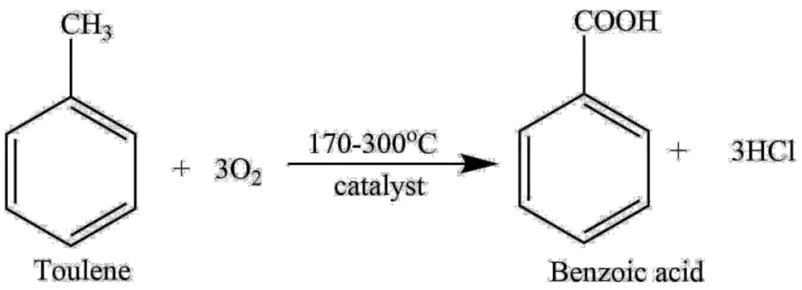


How is formic acid formed from chloroform in the example given above?

As dihalides give carbonyl compounds which has already discussed, but when trihaloalkanes are treated with alkali solution it gives unstable trihydroxy alkane which on dehydration gives carboxylic acid

14.1.3 Preparation of benzoic acid from alkyl benzene





Benzoic acid is formed by the oxidation of toluene or methyl benzene.

What is the byproducts in these chemical equations?

……………………………………………..

Activity:

Is there any other ways to obtain benzoic acid? Explain it with the help of other reference materials like other books, Google, etc.

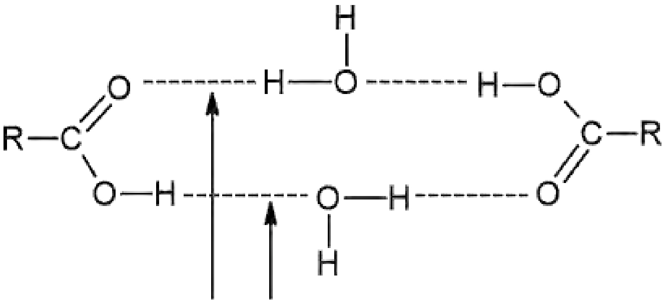
1. ……………………………………….
2. ………………………………………..

14.1.4 Physical properties of monocarboxylic acid

i. Physical State:
Lower members of carboxylic acids (C1-C3) are pungent smelling colorless liquid and the next three members (C4-C6) are oily colorless liquid with and odour of rancid butter. On the other hand, the higher members are colorless and colorless waxy solid.

ii. Boiling Points:
The boiling points of carboxylic acids are much higher than those of hydrocarbons and even higher than alcohols of comparable molecular weight. It is the evidence of strong hydrogen bonding than alcohols.

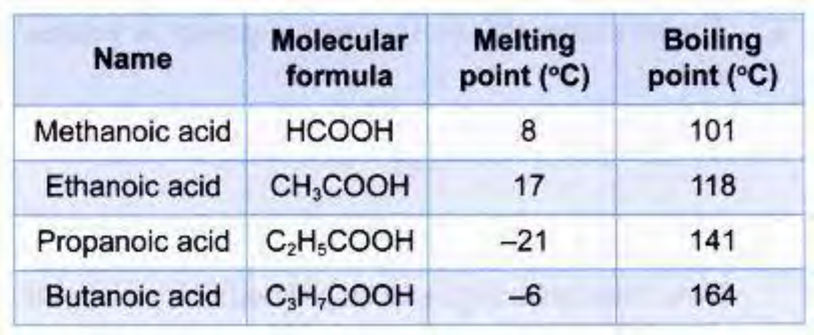
iii. Solubility
First few members of carboxylic acids are highly soluble in water since they form intermolecular hydrogen bonding between carboxylic acid and water molecule.



Intermolecular hydrogen bond between carboxylic acid water

iv. Melting point:

As compared to the respective hydrocarbons, carboxylic acids have high melting point and boiling point.



Name	Molecular formula	Melting point (°C)	Boiling point (°C)
Methanoic acid	$HCOOH$	8	101
Ethanoic acid	CH_3COOH	17	118
Propanoic acid	C_2H_5COOH	–21	141
Butanoic acid	C_3H_7COOH	–6	164

14.1.5 Chemical properties of carboxylic acid

a. Action with alkalies

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Ethanoic acid sod.hydroxide sod. acetate

$CH_3CH_2COOH + NaOH \longrightarrow CH_3CH_2COONa + H_2O$

Propanoic acid sod. propanoate

$CH_3COOH + NH_4OH \longrightarrow CH_3COO\ NH_4 + H_2O.$

Ethanoic acid ammonium acetate

What is the nature of CH_3COOH and other compounds? As well as sodium hydroxide and ammonium hydroxide has basic nature. One of the products is water and another product is the salt.

b. Action with metal oxides

Metal oxides are basic in nature and carboxylic acid is acidic. So, the reaction is acid-base reaction. Here are some examples.

$2CH_3COOH + Na_2O \longrightarrow 2CH_3COONa + H_2O$

(acetic acid) (sod. acetate)

$2CH_3COOH + CaO \longrightarrow (CH_3COO)_2Ca + H_2O$

(quick lime) (calcium acetate)

c. Action with metal carbonates

$2R\text{-}COOH + Na_2CO_3 \longrightarrow 2R\text{-}COONa + CO_2 + H_2O$

Carboxylic acid Sodium carboxylate

$2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COONa + CO_2 + H_2O$

Acetic acid Sodium acetate

Metal carbonates are basic salts or they are weak base. These compounds react with with acids to form salt and water along with carbondioxide.

d. Action with metal bicarbonates

$$\text{R-COOH} + \text{NaHCO}_3 \longrightarrow \text{R-COONa} + \text{CO}_2 + \text{H}_2\text{O}$$

Carboxylic acid — Sodium carboxylate

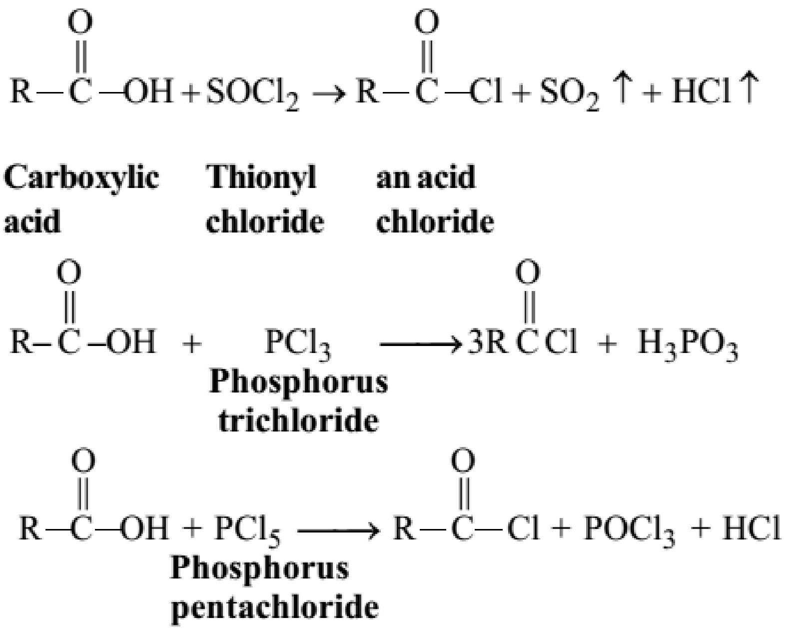
$$\text{CH}_3\text{COOH} + \text{NaHCO}_3 \longrightarrow \text{CH}_3\text{COONa} + \text{CO}_2 + \text{H}_2\text{O}$$

Ethanoic acid — Sodium ethanoate

What are the similarities in the following chemical equation?

SN	Carboxylic acid and metal carbonate	Carboxylic acid and metal bicarbonate
1.	…………………………..	……………………………….
2.	…………………………..	………………………………

e. Action with PCl_3



$$\text{R}-\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}-\text{OH} + \text{SOCl}_2 \rightarrow \text{R}-\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}-\text{Cl} + \text{SO}_2\uparrow + \text{HCl}\uparrow$$

Carboxylic acid — **Thionyl chloride** — **an acid chloride**

$$\text{R}-\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}-\text{OH} + \text{PCl}_3 \longrightarrow 3\text{R}\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}\text{Cl} + \text{H}_3\text{PO}_3$$

Phosphorus trichloride

$$\text{R}-\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}-\text{OH} + \text{PCl}_5 \longrightarrow \text{R}-\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}-\text{Cl} + \text{POCl}_3 + \text{HCl}$$

Phosphorus pentachloride

As the chemical equations have the similar major product i.e. acid chloride, only the differences are SO_2, H_3PO_3 and $POCl_3$.

Complete the following chemical equations by the help of the chemical equations given above.

$CH_3\text{-}COOH + SOCl_2 \longrightarrow$ ……………………….

$CH_3\text{-}COOH + PCl_3 \longrightarrow$ … …………………….

$CH_3\text{-}COOH + PCl_5 \longrightarrow$ ……………………….

You may write the chemical equations taking other carboxylic acids

f.Action with $LiAlH_4$

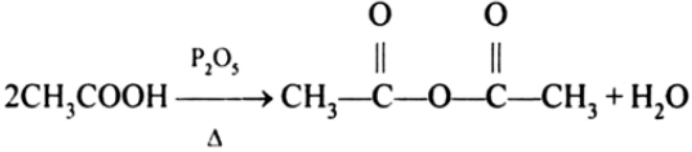
$$H_3C{-}COOH \xrightarrow[\text{2) } H_3O^+]{\text{1) 3 equiv. } LiAlH_4} H_3C{-}C{-}CH_2OH$$

$$H_3C{-}COOMe \xrightarrow[\text{2) } H_3O^+]{\text{1) 2 equiv. } LiAlH_4} H_3C{-}CH_2OH + MeOH$$

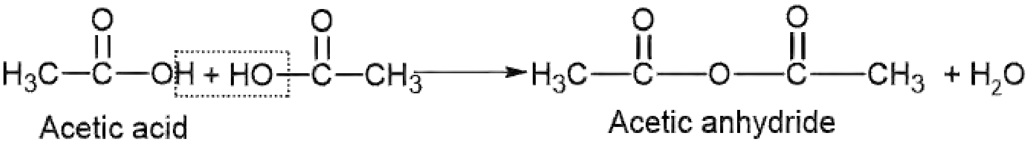
$$H_3C{-}COCl \xrightarrow[\text{2) } H_3O^+]{\text{1) 2 equiv. } LiAlH_4} H_3C{-}CH_2OH$$

As the reduced product of aldehyde is alcohol, carboxylic acid also reduces to alcohol in presence of metallic hydrides in acidic medium.

g. Dehydration of carboxylic acid



$$2CH_3COOH \xrightarrow[\Delta]{P_2O_5} CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + H_2O$$

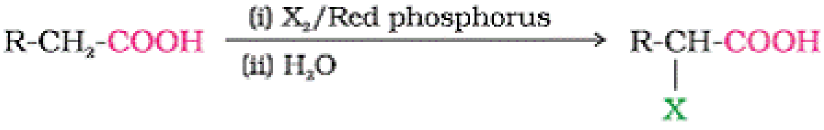


$$H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH + HO{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \longrightarrow H_3C{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + H_2O$$

What is change that you have seen in the chemical equation given above?

Water molecule is removed and two molecules of carboxylic acids are condensed to produce anhydrides.

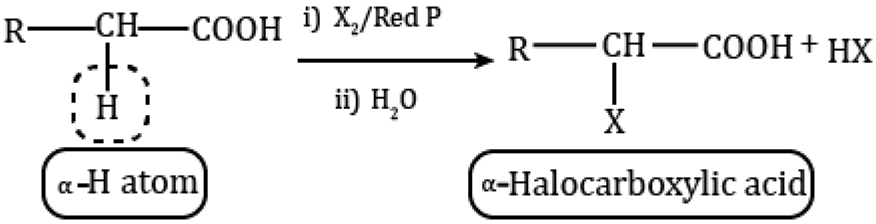
14.1.6: Hell-Volhard-Zelinsky (HVZ) Reaction



$$R{-}CH_2{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red phosphorus}} R{-}\underset{X}{\underset{|}{CH}}{-}COOH$$

X = Cl, Br

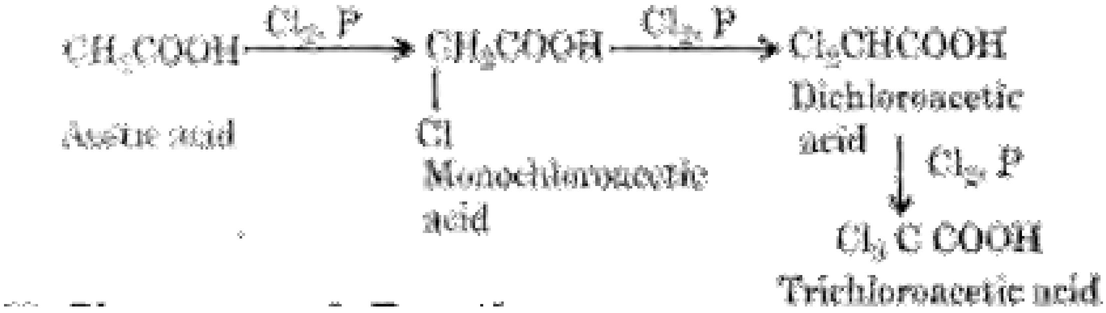
α – Halocarboxylic acid



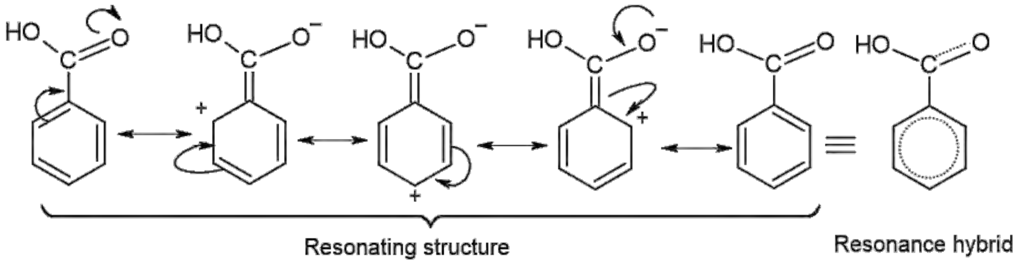
$$R{-}\underset{H}{\underset{|}{CH}}{-}COOH \xrightarrow[\text{ii) } H_2O]{\text{i) } X_2\text{/Red P}} R{-}\underset{X}{\underset{|}{CH}}{-}COOH + HX$$

The carbon which is the next to functional group is called α- carbon. The hydrogen present in the α-carbon is called α- hydrogen. Do you see α- hydrogen in the carboxylic acid given above?

Thus, the substitution of halogen at alpha carbon of carboxylic acid in presence of red phosphorous is called Hell-Volhard-Zelinsky reaction.

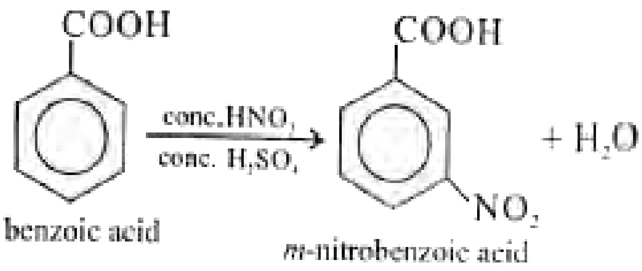


14.1.7 Electrophilic Substitution Reaction of benzoic acid



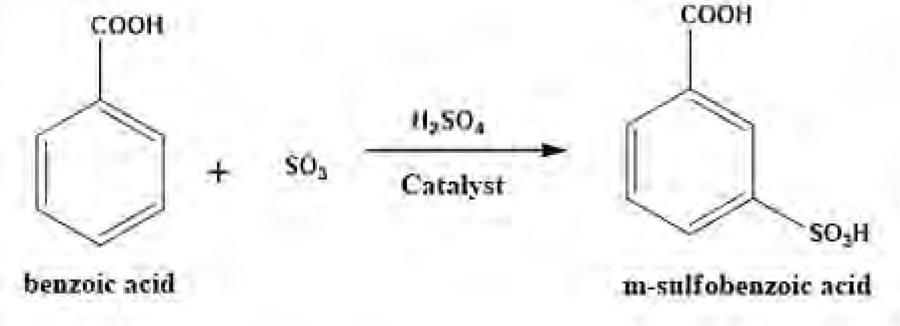
In benzoic acid, carboxylic part is electron withdrawing group. Due to which carbon of benzene ring and carbocation is formed at ortho, para and another ortho carbon atoms. So, meta-carbon is electronically rich in comparison with these carbons. So, electrophile is substituted at meta-carbon.

a. Nitration

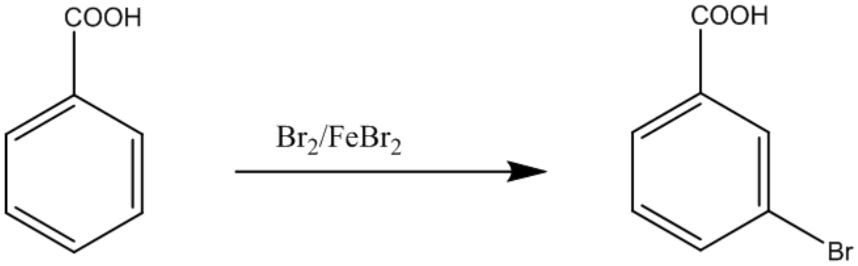


According to the resonating structures given above $^{+}NO_2$ ion is substituted at meta-position because it is an electrophile.

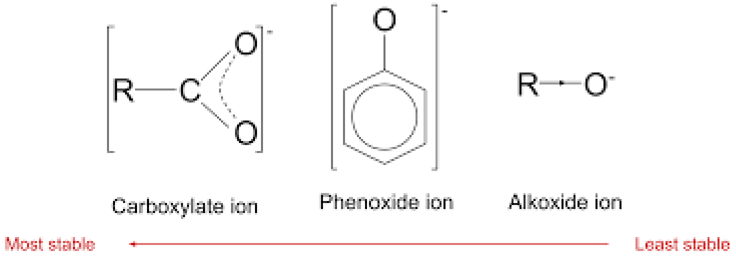
b. Sulphonation

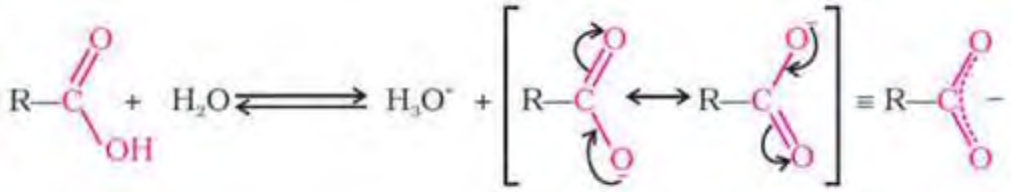


c. Bromination



14.1.8 Effects of substituent/Constituents on the acidic strength of carboxylic acid





An electron-withdrawing group (EWG) increases the acidic strength of a compound by stabilizing the negative charge on the conjugate base formed when the acid loses a proton, effectively making it easier for the proton to be released; essentially, the EWG pulls electron density away from the acidic site, making it more likely to donate a hydrogen ion.

Key points about EWGs and acidity:

Stabilization of conjugate base:

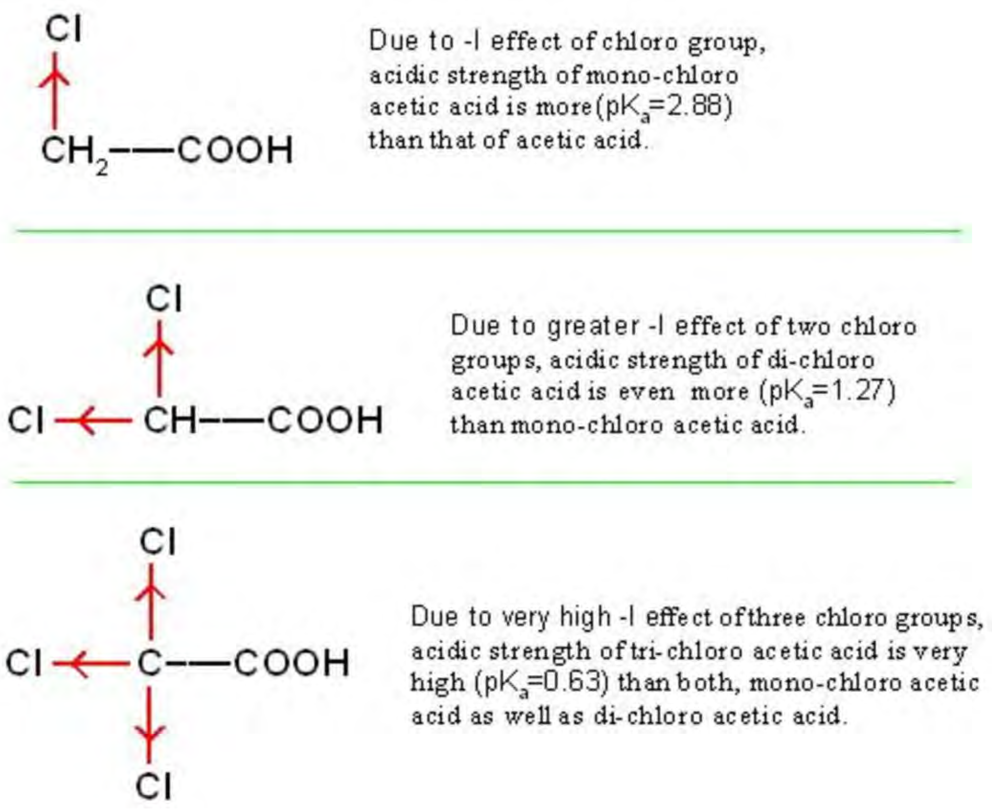
The primary mechanism behind increased acidity is the stabilization of the negative charge on the conjugate base due to the electron-withdrawing effect of the group.

EWG stabilises the (COŌ) and increases the acidity

EDG destabilises the (COŌ) and decreases the acidity

Inductive effect:

Electron-withdrawing groups can exert their effect through the inductive effect, where electron density is pulled through the sigma bonds towards the more electronegative atom in the group.



Due to -I effect of chloro group, acidic strength of mono-chloro acetic acid is more (pK_a=2.88) than that of acetic acid.

Due to greater -I effect of two chloro groups, acidic strength of di-chloro acetic acid is even more (pK_a=1.27) than mono-chloro acetic acid.

Due to very high -I effect of three chloro groups, acidic strength of tri-chloro acetic acid is very high (pK_a=0.63) than both, mono-chloro acetic acid as well as di-chloro acetic acid.

The **acidic strength of carboxylic acids** is influenced significantly by the nature and position of **substituents** attached to the molecule. The substituents can either **increase** or **decrease** the acid strength depending on their **electron-withdrawing** or **electron-donating** properties. Here's a detailed breakdown:

1. Electron-Withdrawing Groups (EWGs)

These groups **increase** the acidity of carboxylic acids by stabilizing the **carboxylate anion ($RCOO^-$)** through **inductive** or **resonance** effects.

Examples:

- $-NO_2$ (nitro)
- –Cl, –Br, –I (halogens)
- –CN (cyano)
- $-CF_3$ (trifluoromethyl)

Effect:

Increase acidity: They pull electron density **away** from the carboxylic acid group, stabilizing the negative charge on the conjugate base ($RCOO^-$).

The more **electronegative** or **closer** the substituent to the –COOH group, the stronger the acid.

Example order of acidity:

$ClCH_2COOH > CH_3COOH$ (acetic acid)

2. Electron-Donating Groups (EDGs)

These groups **decrease** the acidity of carboxylic acids by **destabilizing** the carboxylate anion.

Examples:

- $-CH_3$ (methyl)
- –OH (hydroxy)
- $-OCH_3$ (methoxy)
- $-NH_2$ (amino)

Effect:

- **Decrease acidity**: They donate electrons to the –COOH group, increasing the electron density and making it harder to lose a proton.
- The effect is stronger when the group is close to the –COOH.

Example:

CH_3CH_2COOH (propionic acid) < CH_3COOH (acetic acid)

3. Position of Substituent

The **closer** the substituent to the –COOH group, the **stronger** its effect.

Example:

$ClCH_2CH_2COOH < ClCH_2COOH$

(β-chloropropionic acid < α-chloropropionic acid)

Resonance Effects

Substituents that can **delocalize** charge through resonance can also affect acidity:

$-NO_2$, –CHO, and –COOH (when on aromatic rings) can stabilize the carboxylate ion via resonance → **increased acidity**.

$-OCH_3$ or $-NH_2$ can **donate** electrons via resonance → **decreased acidity**.

Summary:

Substituent Type	Example	Effect on Acidity
Electron-Withdrawing	$-NO_2$, –Cl	Increases acidity
Electron-Donating	$-CH_3$, –OH	Decreases acidity
Proximity to –COOH	α-position	Stronger effect

14.1.9 Abnormal Behaviour of methanoic acid

As of other carboxylic acids, methanoic acid does show additional properties i.e. other carboxylic acids do not show. In this sense it is called abnornmal properties. These properties are discussed as follows.

Action with Tollen's reagent

$$2AgNO_3 + 2NH_4OH \longrightarrow Ag_2O + 2NH_4NO_3 + H_2O$$

$$Ag_2O + 4NH_4OH \longrightarrow \underset{\substack{\text{Tollen's reagent}\\ \text{Diammine silver (I) hydroxide}}}{2[Ag(NH_3)_2]OH} + 3H_2O$$

$$HCOOH + 2[Ag(NH_3)_2]OH \longrightarrow CO_2 + \underset{\text{silver mirror}}{2Ag\downarrow} + 2NH_3 + 2H_2O$$

Other carboxylic acids do not react with Tollen's reagent but formic acid reacts and gives metallic silver which is deposited inner wall of the testtube. So, it is called silver mirror test.

Action with Fehling's solution

$$\underset{\text{Formic acid}}{HCOOH} + \underbrace{2Cu^{2+} + 4OH^-}_{\text{Fehling's solution}} \rightarrow \underset{\substack{\text{Cuprous oxide}\\ \text{(Red ppt.)}}}{Cu_2O\downarrow} + CO_2\uparrow + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underbrace{2Cu^{2+} + 4OH^-}_{\text{Fehling's solution}} \rightarrow \text{no red ppt. of } Cu_2O$$

As you have seen that when formic acid is boiled with Fehling's solution, it gives red oxide of copper oxide. But other acids do not give this reaction.

Action with potassium permanganate

$$\begin{array}{l} 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\ \quad \left. HCOOH + [O] \longrightarrow CO_2 + H_2O \right] \times 5 \\ \hline \underset{\text{(pink)}}{2KMnO_4} + 3H_2SO_4 + 5HCOOH \longrightarrow \underset{\text{(colourless)}}{K_2SO_4 + 2MnSO_4} + 5CO_2 + 8H_2O \end{array}$$

The pink color of potassium permanganate is discharged when formic acid is treated with it in presence of sulphuric acid.

What would happen in acetic acid is kept instead of formic acid?

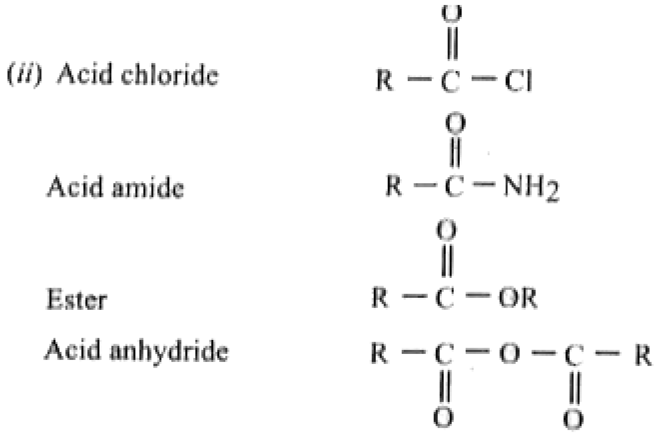
Action with mercuric chloride

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Mercuric chloride}}{2HgCl_2} \rightarrow \underset{\text{White ppt.}}{Hg_2Cl_2\downarrow} + CO_2\uparrow + 2HCl$$

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Mercurous chloride}}{Hg_2Cl_2} \rightarrow CO_2\uparrow + 2HCl + \underset{\text{Mercury (black)}}{2Hg}$$

As above other reactions, when formic acid is treated with mercuric chloride, it gives black precipitate of mercury along with carbon dioxide and hydrochloric acid.

14.8 Derivatives of Carboxylic acids



(*ii*) Acid chloride $R-\overset{O}{\overset{\|}{C}}-Cl$

Acid amide $R-\overset{O}{\overset{\|}{C}}-NH_2$

Ester $R-\overset{O}{\overset{\|}{C}}-OR$

Acid anhydride $R-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-R$

The compounds which are obtained from carboxylic acids and have their own specific properties are called derivatives of carboxylic acids. They are acid chloride, amides, esters and acid anhydrides.

General methods of preparation of acid chloride

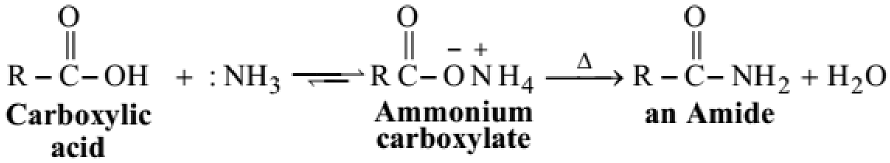
$$\underset{\text{Ethanoic acid}}{CH_3\text{-}COOH} + PCl_3 \longrightarrow \underset{\text{Ethanoyl chloride}}{CH_3\text{-}COCl} + H_3PO_3$$

$$\underset{\text{Ethanoic acid}}{CH_3\text{-}COOH} + PCl_5 \longrightarrow \underset{\text{Ethanoyl chloride}}{CH_3\text{-}COCl} + POCl_3 + HCl$$

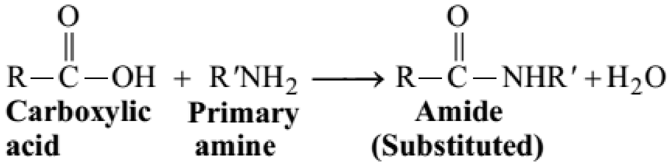
$$\underset{\text{Ethanoic acid}}{CH_3\text{-}COOH} + SOCl_2 \xrightarrow{\text{Pyridine}} \underset{\text{Ethanoyl chloride}}{CH_3\text{-}COCl} + SO_2 + HCl$$

Acid chlorides are prepared by reacting carboxylic acid with phosphorous trichloride or phosphorous pentachloride or thionyl chloride. The major product is acid chloride and by products are only the different.

General Methods of preparation of amides



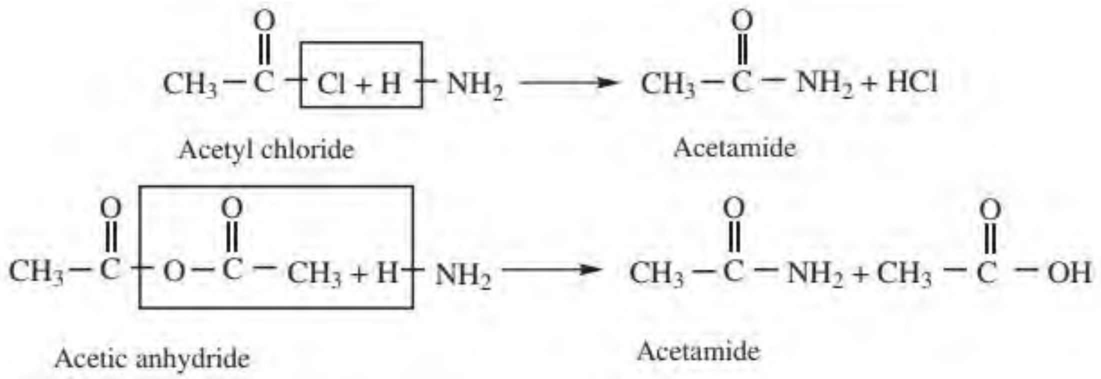
$$R-\overset{O}{\overset{\|}{C}}-OH + :NH_3 \rightleftharpoons R\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$



$$R-\overset{O}{\overset{\|}{C}}-OH + R'NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NHR' + H_2O$$

How is amide formed in the chemical equation given? What are the changes occurred in the chemical equation?

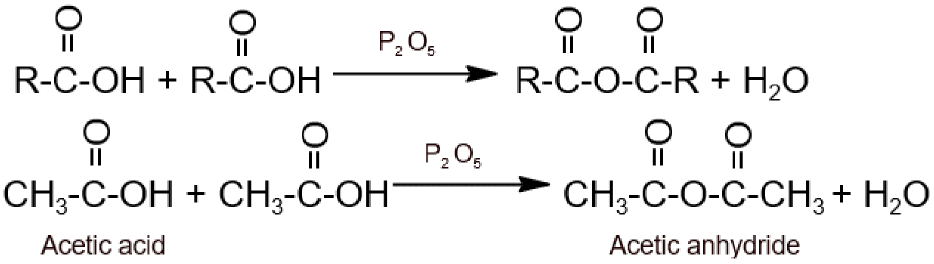
-OH group of carboxylic acid is replaced by –NH_2 group. Hence amide is formed.



$$CH_3-\overset{O}{\overset{\|}{C}}-\boxed{Cl + H}-NH_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + HCl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-\boxed{O-\overset{O}{\overset{\|}{C}}-CH_3 + H}-NH_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

General Methods of Preparation of Acid anhydride



$$R-\overset{O}{\overset{\|}{C}}-OH + R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{P_2O_5} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + H_2O$$

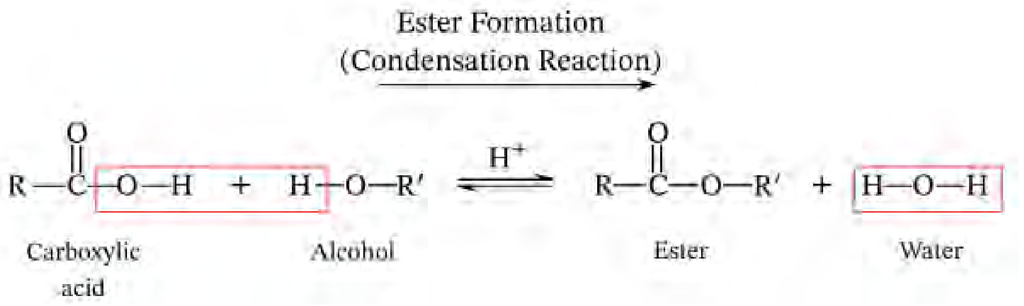
$$CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{P_2O_5} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

How is acetic anhydride formed? Write in two points:

1. ………………
2. ……………..

As given examples, acid anhydride is formed by dehydration of carboxylic acids. The byproduct is water.

General Methods of preparation of Esters



$$R-\overset{O}{\overset{\|}{C}}-O-H + H-O-R' \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-O-R' + H-O-H$$

$$CH_3COOH + C_2H_5OH \xrightarrow{conc.\ H_2SO_4} CH_3COOC_2H_5 + H_2O$$

Ethanoic acid **Ethanol** **Ethyl ethanoate** **water**

In the chemical equations given above, esters are formed by heating carboxylic acid with alcohol in presence of concentrated sulphuric acid. Water molecule would be the byproduct.

Comparative Properties of Derivatives of carboxylic acid

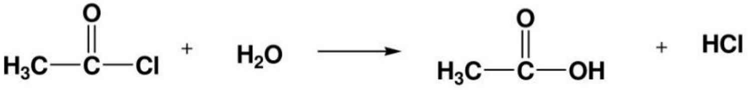
Properties	**Acid Chloride**	**Amides**	**Acid anhydrides**	**Esters**
Physical State	Lower colorless liquid higher colorless solid	Except formamide other amides are crystalline solid	Lower colorless liquid, higher are colorless solid	Lower esters are colorless liquid, higher esters are colorless and odourless solids.
Solubility	Insoluble in water due to absence of hydrogen bonding but undergoes hydrolysis	Lower amides (C1-C5) are soluble in water since they form hydrogen bonding but solubility decreases with the increase in molecular mass	They are not soluble in water	Lower members are slightly soluble in water but solubility decreases with the increase in molecular masss
Boiling point	They have lower boiling point as compared with their parent carboxylic acid since they do not form intermolecular hydrogen bonding	They have higher boiling point as compared with their parent carboxylic acid since they form intermolecular hydrogen bonding.	They have higher boiling point as compared with their parent carboxylic acid due to higher molecular mass and size.	They have lower boiling point as compared with their parent carboxylic acid since they do not form intermolecular hydrogen bonding

Chemical Properties of acid chlorides

a. Hydrolysis of acid chlorides

Study the following chemical equations.

Acid chloride water Carboxylic acid + Hydrochloric acid



Ethanoyl chloride ethanoic acid

(acetyl chloride) (acetic acid)

As you have seen carboxylic acids are formed by hydrolysis of acid chlorides.

You may write other chemical equations of the followings.
a. Hydrolysis of propanoyl chloride
b. Hydrolysis of benzoyl chloride

b. Alcoholysis of acid chlorides

Acid Chloride Alcohol Ester

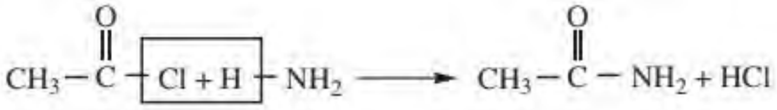
$$CH_3\overset{O}{\overset{\|}{C}}\text{-}Cl + CH_2CH_3OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_3$$

ethyl chloride ethanol ethyl ethanoate

In these chemical equations, esters are formed by condensation of acid chloride and alcohol. Byproduct of this reaction is hydrogen chloride

c. Ammonolysis of acid chlorides

Acyl Chloride Ammonia Amide

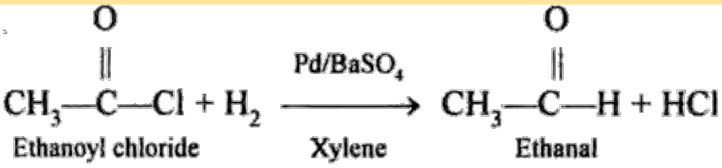


$$CH_3-\overset{O}{\overset{\|}{C}}-\boxed{Cl + H}-NH_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + HCl$$

Acetyl chloride Acetamide

When acid chloride is treated with ammonia, amides are obtained as a major product and byproduct is hydrochloric acid.

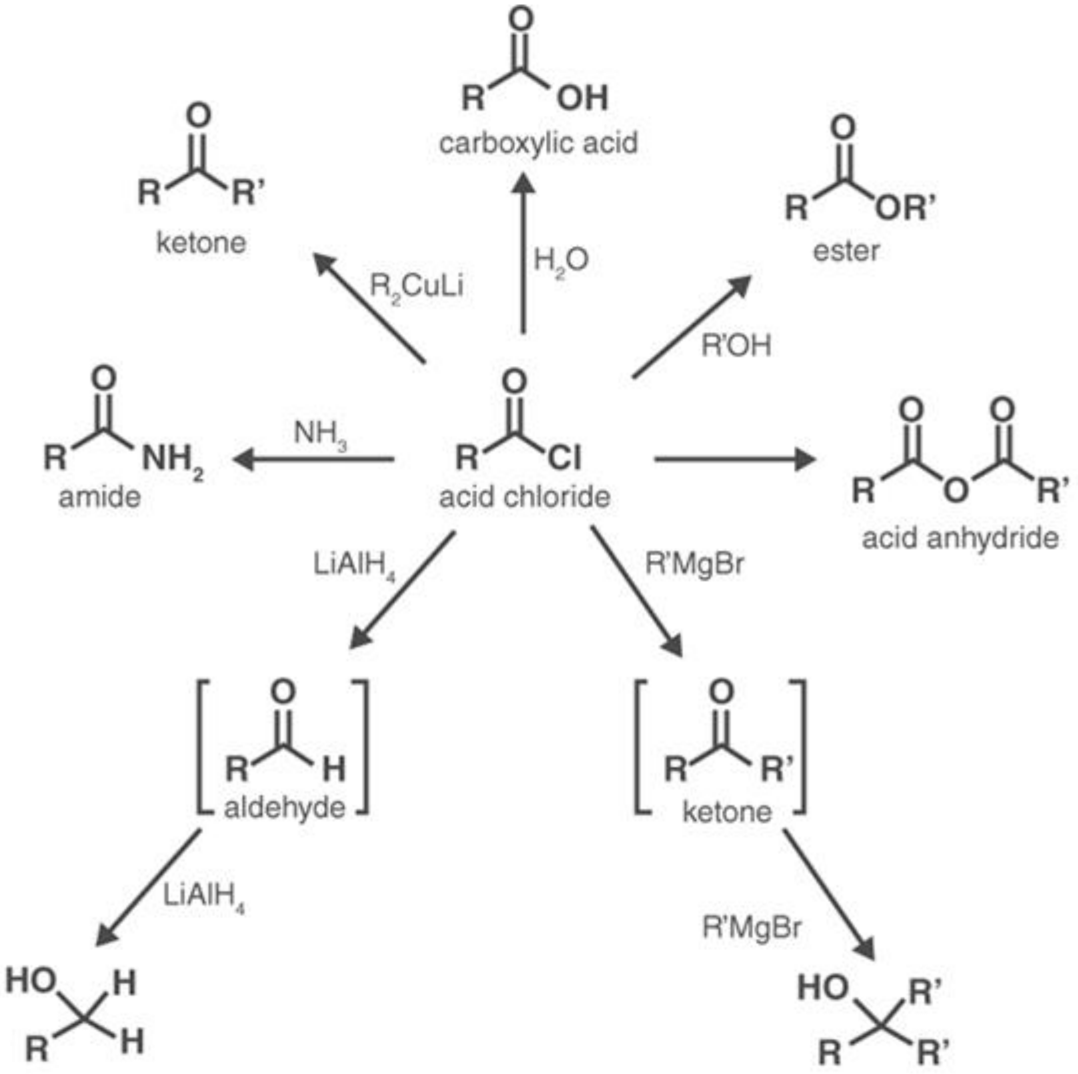
d. Reduction of acid chlorides



$$\underset{\text{Ethanoyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + H_2 \xrightarrow[\text{Xylene}]{Pd/BaSO_4} \underset{\text{Ethanal}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + HCl$$

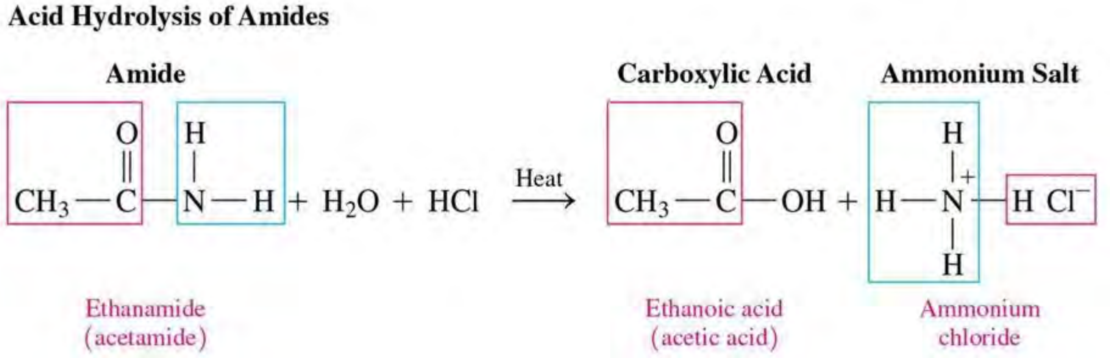
As you are looking here that aldehydes are formed when acid chlorides are reduced in presence of palladium and barium sulphate.

Summary of the reactions



Chemical Properties of Amides

a. Hydrolysis of amides



When amides are hydrolyzed in acidic medium, carboxylic acid and ammonia are formed. But the byproduct could be ammonium salt.

b. Alcoholysis of amide

R-CONH$_2$	+ ROH	→	RCOOR	+	NH$_3$
Alkanamide	alcohol		Alkyl alkanoate		ammonia

$CH_3CONH_2 + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + NH_3$

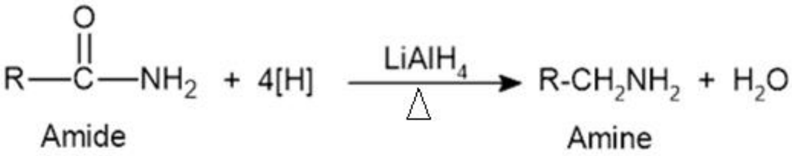
Ethanamide Ethanol Ethyl ethanoate

When amide is treated with alcohol, esters are formed along with ammonia

Compare the reactions process between alcoholysis and hydrolysis of amide

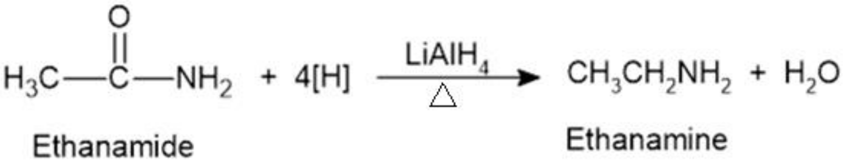
Compounds	Hydrolysis	Alcoholysis
Reactants		
Products		

c. Reduction of amides



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + 4[H] \xrightarrow[\Delta]{LiAlH_4} R\text{-}CH_2NH_2 + H_2O$$

Amide Amine



$$H_3C-\overset{\overset{O}{\|}}{C}-NH_2 + 4[H] \xrightarrow[\Delta]{LiAlH_4} CH_3CH_2NH_2 + H_2O$$

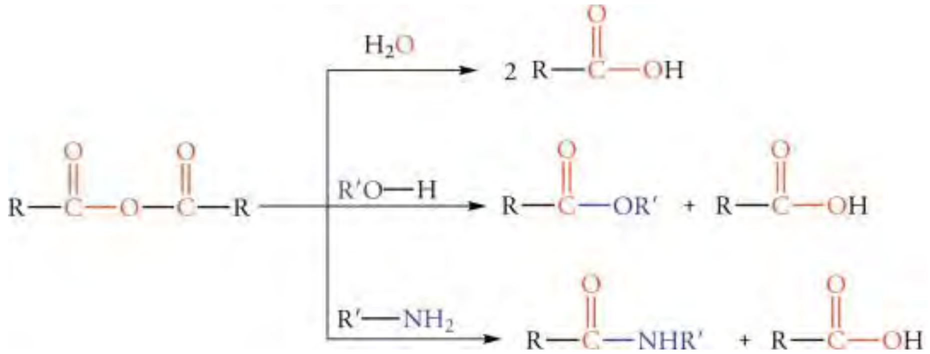
Ethanamide Ethanamine

What are the requirements that are given in the above chemical equation?

1. ………………………
2. ……………………..
3. ……………………

Primary amines are formed when amides are heated with metallic hydrides by the reduction process.

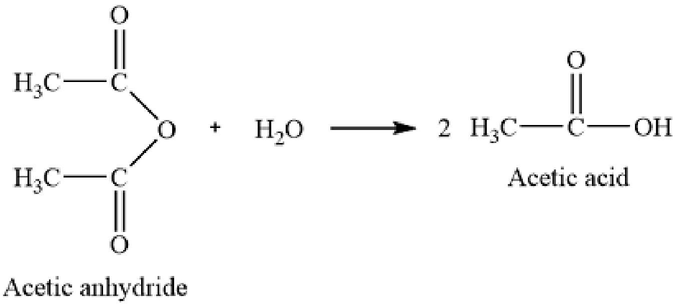
Chemical properties of acid anhydride



Study the given chemical equations. Write the differences among these chemical equations that you find.

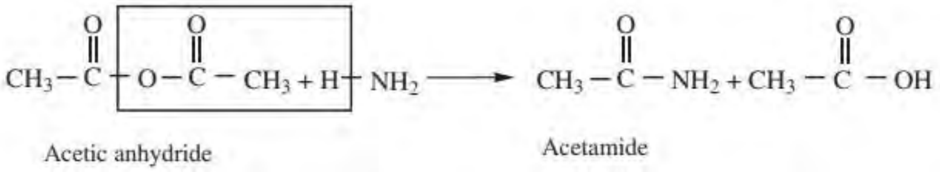
1. ………………………………………..
2. ………………………………………..
3. ………………………………………..

a. Hydrolysis



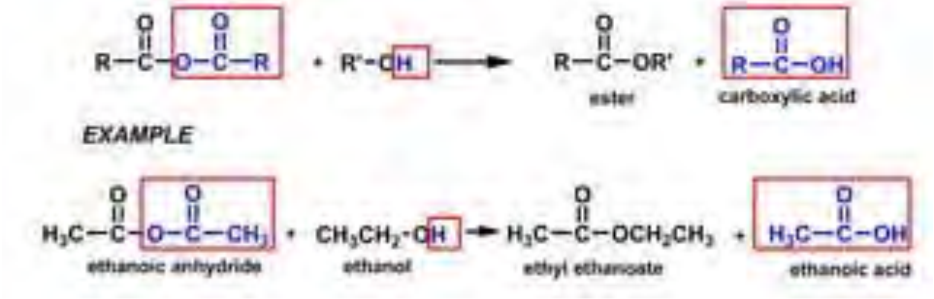
Carboxylic acid is formed when anhydrides are hydrolyzed.

b. Ammonolysis



When acid anhydrides are treated with ammonia, alkanamide is formed along with carboxylic acid byproduct.

c. Alcoholysis



When acid anhydride is treated with alcohol, ester and carboxylic acid are formed.

d. Reduction

$$RCOOOCR + [H] \xrightarrow{LiAlH4\ /\Delta} RCH_2OH + H_2O$$

$$CH_3COOOCCH_3 + [H] \xrightarrow{LiAlH4\ /\Delta} CH_3CH_2OH + H_2O$$

As in the chemical equation given above, alcohols are formed when acid anhydrides are heated with reducing agents like $LiAlH_4$.

Chemical properties of esters

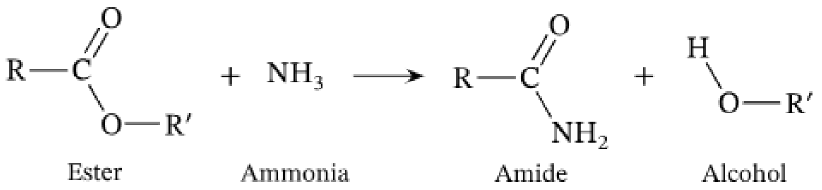
a. Hydrolysis

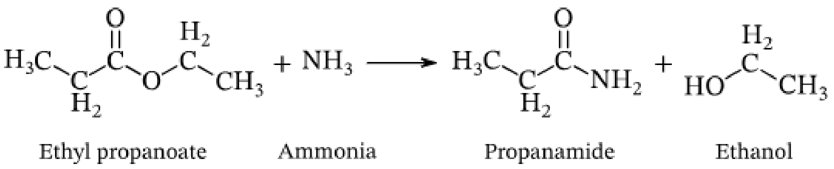
$$\underset{\text{Ester}}{RCOOR'} + \underset{\text{Water}}{H_2O} \overset{\text{acid}}{\rightleftharpoons} \underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$$

$$\underset{\text{Ethyl ethanoate}}{CH_3COOCH_2CH_3} + H_2O \overset{H^+(aq)}{\rightleftharpoons} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{CH_3CH_2OH}$$

As given in the chemical equation, carboxylic acid and alcohol are formed when esters are hydrolyzed. This is reversible reaction.

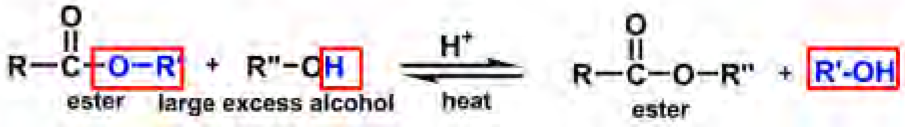
b. Ammonolysis





When ester is ammonolyzed, amides and alcohol are formed. This reaction is reversible reaction as the products give reactant if high temperature is used to occur the reaction.

c. Alcoholysis



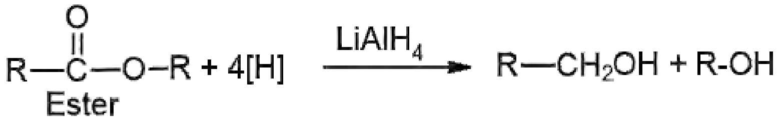
$$R-\overset{O}{\overset{\|}{C}}-O-R' + R''-OH \underset{heat}{\overset{H^+}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-O-R'' + R'\text{-}OH$$

When ester is heated with alcohol in acidic medium, same type of products are obtained i.e. ester and alcohol are obtained. So, this reaction is called trans-esterification reaction.

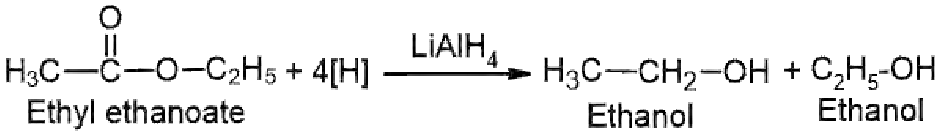
Activity:
Write the complete reaction based on the above general chemical equation when ethyl ethanoate is heated with ethanol in acidic medium.

1. Reactants:
2. Products:
3. Complete reaction:

d. Reduction



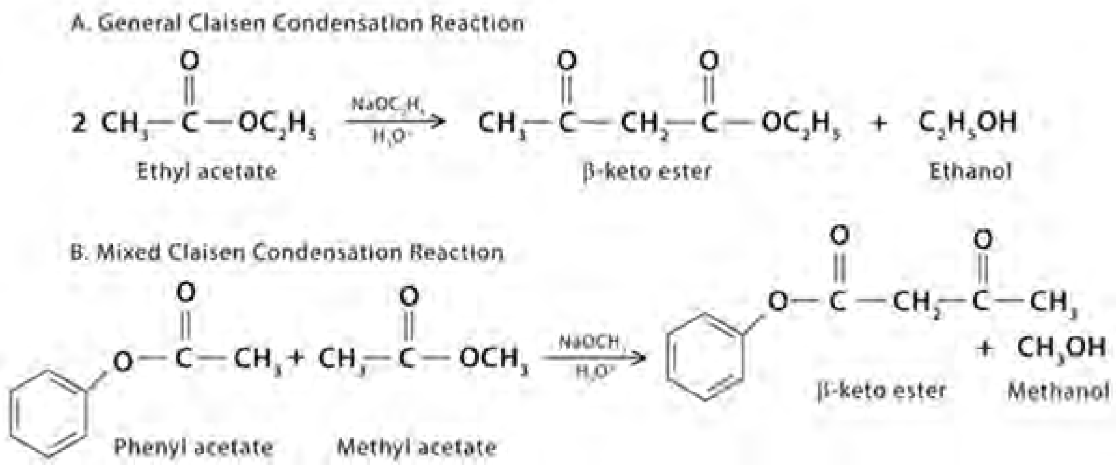
$$\underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-O-R} + 4[H] \xrightarrow{LiAlH_4} R-CH_2OH + R\text{-}OH$$



$$\underset{\text{Ethyl ethanoate}}{H_3C-\overset{O}{\overset{\|}{C}}-O-C_2H_5} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{H_3C-CH_2-OH} + \underset{\text{Ethanol}}{C_2H_5\text{-}OH}$$

As given in the above chemical equation, when esters are reduced in presence of metallic hydride, two molecules of alcohol are formed.

Claisen condensation:



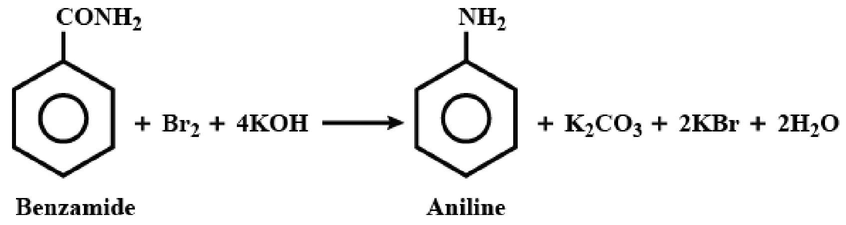
Write the difference between aldol condensation and Claisen condensation.

Properties	**Aldol Condensation**	**Claisen Condensation**
Required conditions		
Reactants		
Products		

When ester is treated with sodium ethoxide, two molecules of esters having α-hydrogen are condensed to form β-keto ester as a condensed product.

Hoffmann's Bromamide reaction

$$\underset{\text{Acid Amide}}{R-CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Primary amine}}{R-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$



$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \xrightarrow{\Delta} \underset{\text{Methanamine}}{CH_3NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

$$\underset{\text{propanamide}}{CH_3CH_2CONH_2} + Br_2 + 4NaOH \xrightarrow{\Delta} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

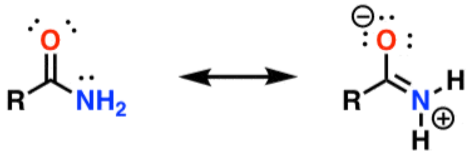
Hofmann's Bromamide Degradation Reaction (commonly called Hofmann rearrangement) is an organic reaction in which a primary amide is converted to a primary amine with one carbon atom less. This reaction is widely used to prepare amines from amides.

Where:

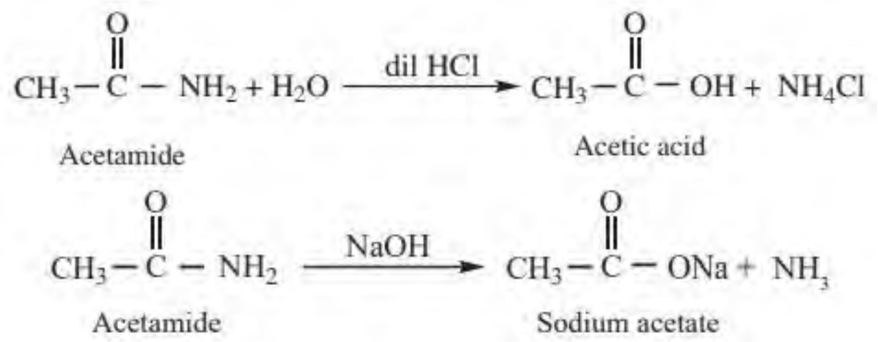
- $R–CONH_2$ = primary amide
- Br_2 = bromine
- NaOH = sodium hydroxide (aqueous base)
- $R–NH_2$ = primary amine

Amphoteric nature of amides

1) Amide nitrogens are less basic than the corresponding amines.
This is due to delocalization of the lone pair of the nitrogen.



resonance delocalization of nitrogen lone pair



$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O \xrightarrow{\text{dil HCl}} CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_4Cl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{\text{NaOH}} CH_3-\overset{O}{\overset{\|}{C}}-ONa + NH_3$$

Amides ($R–CO–NH_2$) are **not strongly amphoteric**, but under certain conditions, they can exhibit **both acidic and basic character**, making them **weakly amphoteric**.

Basic Character (Due to $–NH_2$ group)

- The lone pair of electrons on the nitrogen atom in the amide group can **accept a proton (H^+)**, showing **basic behavior**.
- However, **resonance** with the carbonyl group delocalizes the nitrogen's lone pair, reducing its availability for protonation — so **amides are much less basic** than amines.

Resonance structure:

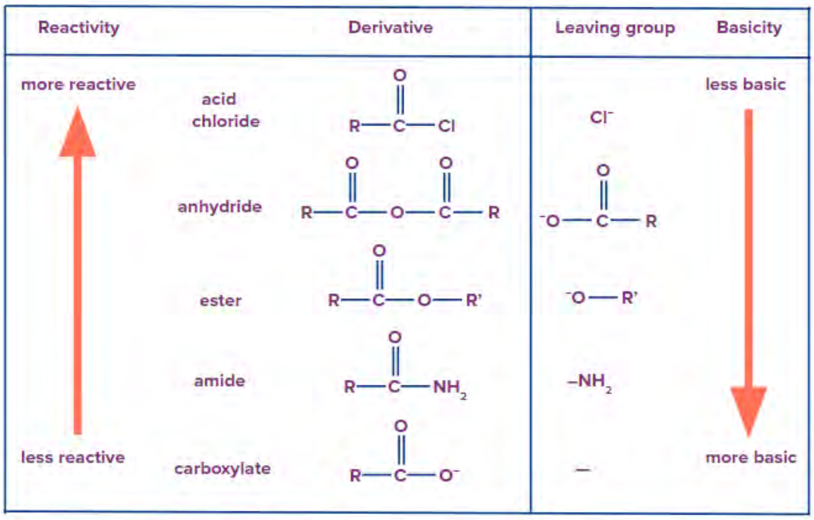
$R–CO–NH_2 \rightleftharpoons R–C(O^-)=NH_2^+$

This delocalization **decreases** the basicity of the $–NH_2$ group.

Acidic Character (Due to Slightly Acidic N–H)

- The hydrogen attached to the nitrogen ($–NH_2$) can be donated under strong basic conditions, making amides very weak acids.
- Deprotonation forms an amide anion ($R–CO–NH^-$), which is stabilized by resonance with the carbonyl group.

Relative reactivity of derivatives of carboxylic acid



Reactivity		Derivative	Leaving group	Basicity
more reactive	acid chloride	$R-\overset{O}{\overset{\|}{C}}-Cl$	Cl^-	less basic
	anhydride	$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$	$^-O-\overset{O}{\overset{\|}{C}}-R$	
	ester	$R-\overset{O}{\overset{\|}{C}}-O-R'$	$^-O-R'$	
	amide	$R-\overset{O}{\overset{\|}{C}}-NH_2$	$-NH_2$	
less reactive	carboxylate	$R-\overset{O}{\overset{\|}{C}}-O^-$	–	more basic

Acid derivatives are compounds derived from carboxylic acids and include acid chlorides, anhydrides, esters, amides, and nitriles. Their reactivity toward nucleophilic acyl substitution follows a predictable order.

Relative Reactivity Order (from most to least reactive):

Acid chloride > Acid anhydride > Ester ≈ Carboxylic acid > Amide > Nitrile

Why This Order?

The reactivity is governed mainly by two factors:

1. Leaving group ability
2. Resonance stabilization and inductive effects

Acid Derivative	Structure	Leaving Group	Resonance & Stability	Reactivity
Acid chloride	R–COCl	Cl^- (good LG)	Weak resonance	**Very high**
Acid anhydride	R–CO–O–CO–R	$RCOO^-$ (good LG)	Moderate resonance	High
Ester	R–COOR'	RO^- (moderate LG)	Better resonance	Moderate
Carboxylic acid	R–COOH	OH^- (poor LG)	Strong H-bonding	Moderate
Amide	$R–CONH_2$	NH_2^- (very poor LG)	Strong resonance	Low
Nitrile	R–C≡N	–	No typical LG, different mechanism	Very low

Main points for the order explanation:

- **Acid chlorides** react readily with water, alcohols, and amines, even at room temperature.
- **Anhydrides** are also reactive but less so than chlorides due to better resonance.
- **Esters** and **carboxylic acids** are more stable due to resonance and less reactive.
- **Amides** are the least reactive common derivative due to strong resonance between the nitrogen and carbonyl carbon.
- **Nitriles** do not undergo nucleophilic acyl substitution easily — they follow a different mechanism (addition-elimination via imidoyl intermediates).

Exercise

Multiple choice questions

1. Which reagent is suitable to test carboxylic acid?
   A. 2-4-DNP　B. $FeCl_3$　C. $(NH_4)_2[Ce(NO_3)_6]$　D. $NaHCO_3$

2. Which is the fuctional isomer of CH_3COOH?
   A. CH_3CH_2OH　B. $HCOOCH_3$　C. CH_3CHO　D. $CH_3CH_2\text{-}O\text{-}CH_2CH_3$

3. What would be the compound Z ?
   $C_6H_5COONa \xrightarrow{NaOH + Cao/heat} Z$
   A. Methane　B. hexane　C. cyclohexane　D. Benzene

4. Which one of the following is strongest acid?
   A. Methanoic acid　B. ethanoic acid　C. propanoic acid　D. Butanoic acid

5. Which chemicals are used for the esterification reaction?
   A. Acid chloride, alcohol and dil.sulphuric acid
   B. Carboxylic acid, alcohol and dil. Sulphuric acid
   C. Carboxylic acid, ether and conc. sulphuric acid
   D. Carboxylic acid, alcohol and conc. sulphuric acid

6. What happens when ethanoic acid is heated with phosphorous pentoxide?
   A. Ethane and water　C. Ethanol and water
   B. Acetic anhydride and water　D. Acetic anhydride

7. What would be the product when ethanal is oxidized?
   A. Ethanol　B. Ethanoic acid　C. ethoxyethane　D. acetone

8. Choose the correct alternative from the following

Reactants	Major Product
1. $CH_3COOH + CH_3CH_2OH +$ Conc H_2SO_4	a. Chloroacetic acid
2. $CH_3COOH + Cl_2 +$ Red P	b. 3-nitrobenzoic acid
3. $C_6H_5COOH +$ Conc. $HNO_3 +$Conc H_2SO_4	c. Ethylethanoate

   A. 1-a, 2-b, 3-c　C. 1-b, 2-c, 3- a
   B. 1-c, 2-a, 3-b　D. 1-b, 2-a, 3-c

9. What would be the product P in the following reaction sequence?
   $CH_3CH_2CONH_2 +$ aq. $Br_2 +$ aq. $KOH \xrightarrow{\sim 70\ ^\circ C} P$
   A. Propanoic acid　C. Propanamine
   B. Ethanoic acid　D. Ethanamine

10. What would be the product when acid chloride is alcoholyzed?
A. Amide B. Acid anhydride C. Acid chloride D. Ester

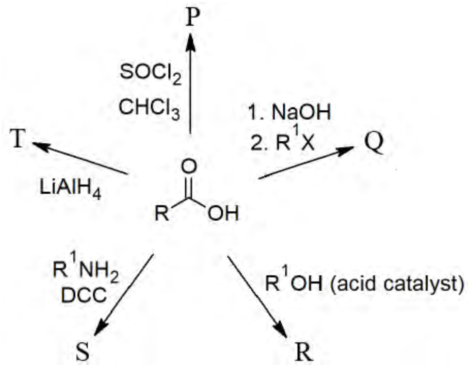
11. When phenol is treated with sodium hydroxide and is heated with carbon dioxide at pressure followed by acidic hydrolysis, compound P is obtained. What is P?
A. Benzoic acid B. o-hydroxy phenol
C. p-hydroxy benzoic acid D. o-hydroxy benzoic acid

12. Generally pleasant odour of fruits is due to which of the following compounds?
A. Sugars B. acids C. Esters D. aromatic compounds

13. Which of the followings is the compound that gives Claisen condensation reaction?
A. Ethanoyl chloride B. Ethanoic acid C. Ethanamide D. Ethylethanoate

14. Choose the best alternative from the following on the basis of information given in the the reaction sequence.
$P \xrightarrow{[O]} Q \xrightarrow{SOCl2} R \xrightarrow{NH3} S \xrightarrow{Br2/aq.KOH}$ methanamine
A. P-ethanol, Q- ethanal, R- ethanoyl chloride, S- ethanamide
B. P-ethanal, Q- ethanal, R- ethanoic acid, S- methanamide
C. P-ethanol, Q- ethanoic acid, R- ethanoyl chloride, S- ethanamide
D. P-propanol, Q- propanoic acid, R- propanoyl chloride, S- propanamide

15. Which of the following would be the suitable products?



A. P- alkyl halide, Q- ester, R- Carboxylic acid S- amide
B. P- acid chloride, Q- ester, S- amide, T- alcohol
C. P- alkyl halide, Q- ester, R- ester , T- amide
D. T- alcohol, Q- ester, R- Carboxylic acid, S- amide

16. Which of the following compounds give tranesterification reaction?
A. Alcohol B. Carboxylic acid C. Ester D. acid chloride

17. What is the process of conversion of ester into β-ketoester called?
A. Rosenmund reduction C. Hell-Volhard-Zeleinsky Reaction
B. Benzoin condensation D. Claisen condensation

18. How is nitriles give carboxylic acid?
A. By acidic hydrolysis C. By ozonolysis
B. By alcoholysis D. By ammonolysis

19. What product would you expect when ethyl ethanoate is heated with sodium ethoxide in presence of ethanol?

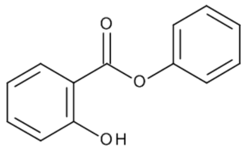
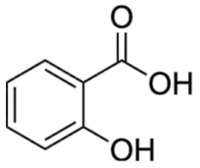
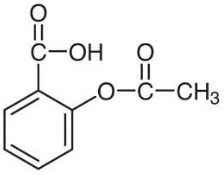
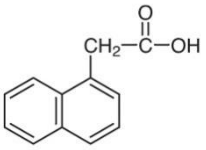
A. Alpha keto-ester	C. 2 molecules of carboxylic acid
B. Beta ethyl-beta keto ester	D. Beta keto ester

20. What could be the products formed when acetic acid is treated with chlorine in presence of red phosphorous?
    - A. α-chloroethanoic acid and water
    - B. α- chloroethanoic acid and hydrogen chloride
    - C. α- chloroethanoic acid and hydrogen gas
    - D. α- chloroethanoic acid and chlorine gas

21. Which of the following is different from others?

A. $CH_3CH_2CH_2COOH$	C. CH_3CH_2COOH
B. CH_3COOH	D. $HCOOH$

22. Which of the following is the molecular structure of aspirin?

			
A	B	C	D

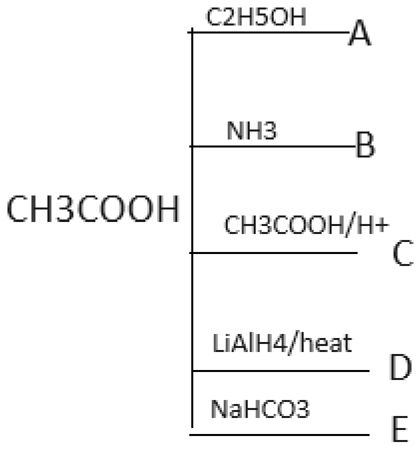
23. Why is solubility decreases with the increase in the carbon no. of carboxylic acid?
    - A. Due to increase in hydrophilic group
    - B. Due to increase in hydrophobic group
    - C. Due to decrease in hydrophobic group
    - D. Due to decrease in nucleophilic group

Short questions

24. What are the functional isomers of $C_3H_6O_2$? Give an example of esterification reaction. An organic compound P; $C_8H_{16}O_2$ was hydrolysed with dilute acid to give a carboxylic acid Q and an alcohol R. oxidation of R with chromic acid produced Q. C on dehydration produces but-1-ene. Write the chemical equations for the reactions involved.

25. What happens when,
    - a. Ethyl ethanoate is heated with sodium ethoxide?
    - b. Acetic anhydride is treated with ethanol?
    - c. Ethanoyl chloride is treated with hydrogen in presence of $Pd/BaSO_4$?
    - d. Methnoic acid is treated with ammoniacal silver nitrate solution?
    - e. Ethanoic acid is heated with phosphorous pentoxide?

26. What are the anamolous properties of methanoic acid? Explain with any two examples. Explain about the electrophilic substitution reaction of benzoic acid. Identify the compounds A, B, C, D and E in the following conditions. [2+1+5]



27. Write one example of each of the following.
    a. Claisen condensation
    b. Hell-vollhard-Zelinsky reaction
    c. Ethanolysis of ethanoyl chloride
    d. Electrophilic substitution reaction of benzoic acid

28. What happens when,
    a. Ethyl ethanoate is heated with sodium ethoxide?
    b. Acetic anhydride is treated with ethanol?
    c. Ethanoyl chloride is treated with hydrogen in presence of Pd/$BaSO_4$?
    d. Methnoic acid is treated with ammoniacal silver nitrate solution?
    e. Ethanoic acid is heated with phosphorous pentoxide?

Long questions.

29. A. An aliphatic compound V reacts with $SOCl_2$ to give W. The compound W is heated with ammonia to produce X. The compound X is further heated with Br_2/KOH to yield Y. The compound Y gives Z when treated with $NaNO_2$/HCl at low temperature. The compound Z is primary alcohol which gives positive iodoform test. Identify V, W, X, Y and Z.

    B. A secondary alcohol 'P' having 3 carbon atoms are oxidized which gives 'Q'. 'Q' is again treated with dilute NaOH at cold condition which gives 'R'. Identify the compound sand write the reactions involved.

30. Identify the compounds P, Q, R, S and T in the following reaction sequence.[5]

$$P \xrightarrow{NaOH/CaO/} Q \xrightarrow{CH3Cl/Alcl3} R \xrightarrow{CeO2/H+} S \xrightarrow{alc.KCN} T$$

The compound Q can also be obtained by the reduction of chlorobenzene. Write any three methods of preparation of ethanoic acid. [3]

31. A. An organic compound A which gives effervescence with $NaHCO_3$ is heated with phosphorous pentoxide to obtain B. Ammonolysis of B yields compound C along with ethanoic acid. The compound C on decarbonylation yields D. If methanol can be obtained from D on treatment with $NaNO_2$ and dil. HCl. Identify A, B, C and D with suitable reaction. [4]

B. Identify P, Q, R and S in the following reaction sequence. [4]

$$CH_3COOH \xrightarrow{SOCl2} P \xrightarrow{H2/Pd/BaSO4} Q \xrightarrow{HCN} R \xrightarrow{H2O/H+} S$$

32. A. An aliphatic compound V reacts with $SOCl_2$ to give W. The compound W is heated with ammonia to produce X. The compound X is further heated with Br_2/KOH to yield Y. The compound Y gives Z when treated with $NaNO_2$/HCl at low temperature. The compound Z is primary alcohol which gives positive iodoform test. Identify V, W, X, Y and Z.

B. A primary alcohol 'P' having 2 carbon atoms are oxidized which gives 'Q'. 'Q' is again treated with dilute NaOH at cold condition which gives 'R'. Identify the compound sand write the reactions involved.

33. A. Identify A, B, C, D and E in the following reaction sequence. [1+1+1+1+1]

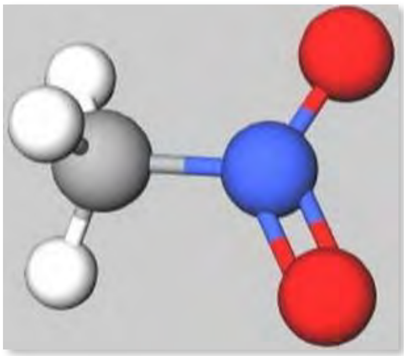
$A \xrightarrow{NH3} B \xrightarrow{Br2/aq.KOH} C \xrightarrow{HNO2} D \xrightarrow{NaOH/I2/heat} E$, the compound C is an aliphatic primary amine having molecular mass 45 amu.

B. Write one example of each of the following. (3x1=3)

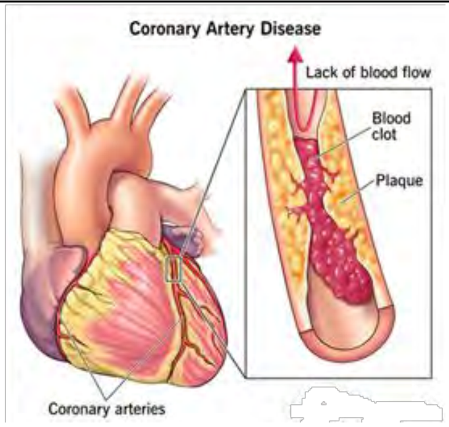
i. Claisen condensation
ii. Hell-vollhard-Zelinsky reaction
iii. Ethanolysis of ethanoyl chloride

Unit 15

Nitro-compounds



15.1 Introduction

Name of the substance	**Use in**
Nitrocompounds	

- ❖ Have you ever seen such things/ activities?

Do the following activity:

Activity:
Study the following structures of organic compounds. Count the components (atoms) present in the compounds and write to the next column.

Molecular structure	Name of the molecules	Components (atoms) of the molecules
R- H	…………………………	………………………… …………………………
R-NO_2	…………………………	………………………… …………………………

What are the differences that you find the above structures?

13. ....
14. ....
15. ....
16. ....

So, the nitroalkanes are the nitro derivative of alkane.

15.1Nomenclature, isomerism and classification of nitroalkane

Nomenclature:

Common Naming system:

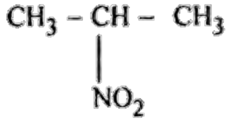
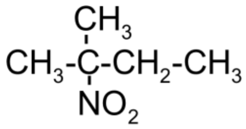
$CH_3\text{-}O\text{-}CH_3$	$CH_3\text{-}CH_2\text{-}OCH_3$	$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$
Dimethyl ether	ethylmethyl ether	di-ethyl ether

- Why the term-di comes in the name of first and third compound?
- Why ethyl comes earlier than methyl in the second compound?

For symmetrical ethers prefix di is used. If the ethers having two different chains in either sides of oxygen, they are named in alphabetical order and the word ether is added after it.

IUPAC Naming System:

Substituent +nitro+ word root + ane

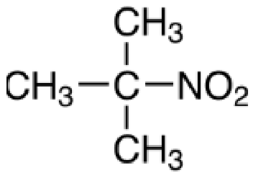
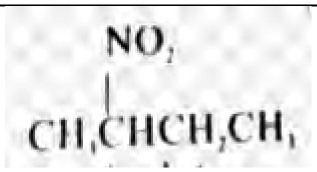
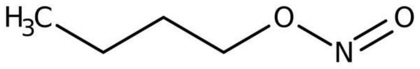
SN	Formula	IUPAC Name
1.	$CH_3\text{-}NO_2$	Nitromethane
2.	$CH_3\text{-}CH_2\text{-}NO_2$	Nitroethane
3.	$CH_3\text{-}CH_2\text{-}CH_2\text{-}NO_2$	1-nitropropane
4.	 $CH_3-\underset{NO_2}{CH}-CH_3$	2-nitropropane
5.	 $CH_3\text{-}\underset{NO_2}{\overset{CH_3}{C}}\text{-}CH_2\text{-}CH_3$	2-nitro-2-methylpropane

Isomerism of nitroalkanes:

Study the pairs of compounds given in the following table. Write similarities and differences found in these pairs.

Table: 1

SN	Compounds	Similarity	Difference
1.	a. $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NO_2$	....	....

	b.  $CH_3-\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}-NO_2$		
2.	a.  $CH_3\overset{\overset{NO_2}{\mid}}{C}HCH_2CH_3$ b. $CH_3-CH_2-CH_2-CH_2-NO_2$	……………………………… ……………………………	…………………………… ……………………………
3.	a. $CH_3-CH_2-CH_2-CH_2-NO_2$ b. 	……………………………… ……………………………	…………………………… ……………………………

Activity:

Study the pair of compounds given in table no. 1. Relate the following statements and fill in the following table.

Statements	Isomerism	Pair of compounds of table 1 (write S.N.)
• Same molecular formula but difference in chain.	Chain isomerism	………………………………
• Same molecular formula but difference in position of functional group.	Position isomerism	………………………………
• Same molecular formula but difference in functional group.	Functional isomerism	………………………………

The phenomenon where two or more compounds have the same molecular formula but differ in their structural arrangement or spatial orientation, leading to different physical and chemical properties is called isomerism. There are two main types of isomerism: **structural isomerism** and **stereoisomerism**. We are talking about structural isomerism.

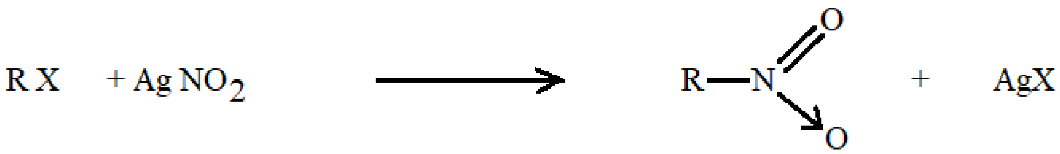
Three types of isomerism are shown by nitroalkanes. They are

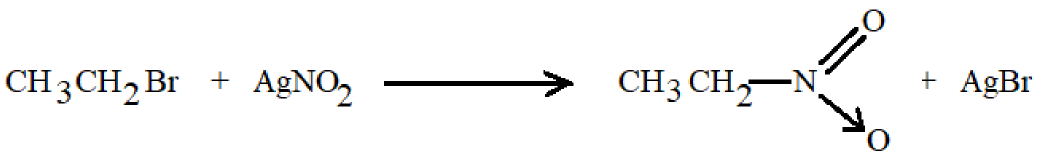
vii. Chain isomerism
viii. Position isomerism
ix. Functional isomerism

- Write the functional isomers of $C_3H_5NO_2$

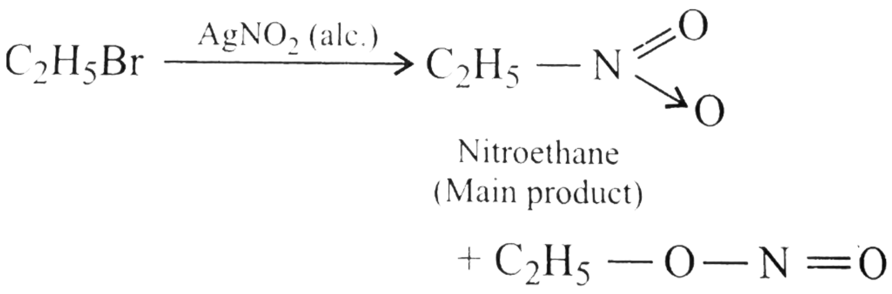
12.2 Show the preparation of nitroalkanes

a. from alkyl halide


Nitroalkane


Bromoethane

Nitro ethane


Nitroethane
(Main product)

Ethyl nitrite

When alkyl halide is heated with silver nitrite, nitroalkane is obtained. Alkyle nitrites are also formed at the same time. In this condition major product is nitroalkane.

b. By nitration of alkanes

$$R\text{-}H + HNO_3 \longrightarrow R\text{-}NO_2 + H_2O$$

Alkane Nitroalkane

$$C_2H_6 + HNO_3 \longrightarrow C_2H_5NO_2 + H_2O$$

Ethane Nitroethane

$$CH_3\text{-}CH_2\text{-}CH_3 + \text{Conc. } HNO_3 \xrightarrow{\text{fuming}} CH_3\text{-}CH_2\text{-}CH_2\text{-}NO_2 + H_2O$$

$$CH_3\text{-}CH_2\text{-}CH_3 + \text{Conc. } HNO_3 \xrightarrow{\text{Conc.}H_2SO_4} CH_3\text{-}CH_2\text{-}CH_2\text{-}NO_2 + H_2O$$

When alkane is fuming with concentrated nitric acid or alkane is under nitration, nitroalkane is obtained as a major product along with water as byproduct.

What are the difference between fuming of nitric acid and nitration?

1. ……………………..
2. ……………………..

Physical Properties of nitroalkanes

a. Generally found in liquid and solid states.
b. Slightly acidic in nature due to electron withdrawing nature of nitrogroup.
c. Polar in nature due to nitro group
d. They have higher boiling points as compared to comparable hydrocarbons.
e. They have pleasant or sweet smell.

Reduction of nitroalkanes

a. Catalytic reduction

$$\underset{\text{Nitroalkane}}{R\text{-}NO_2} + 3H_2 \xrightarrow{Ni} \underset{\text{Amine}}{R\text{-}NH_2} + 2H_2O$$

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + 3H_2 \xrightarrow{Ni} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + 2H_2O$$

How is ethanamine formed in the chemical equation given above, can you explain? In the chemical equation nitro compounds are reduced and amines are formed. By catalytic reduction both aliphatic and aromatic nitrocompounds give amines.

b. Reduction in acidic medium

$$\underset{\text{Nitroalkane}}{R\text{-}NO_2} + 6[H] \xrightarrow{Sn/HCl} \underset{\text{Amine}}{R\text{-}NH_2} + 2H_2O$$

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + 6[H] \xrightarrow{Sn/HCl} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + 2H_2O$$

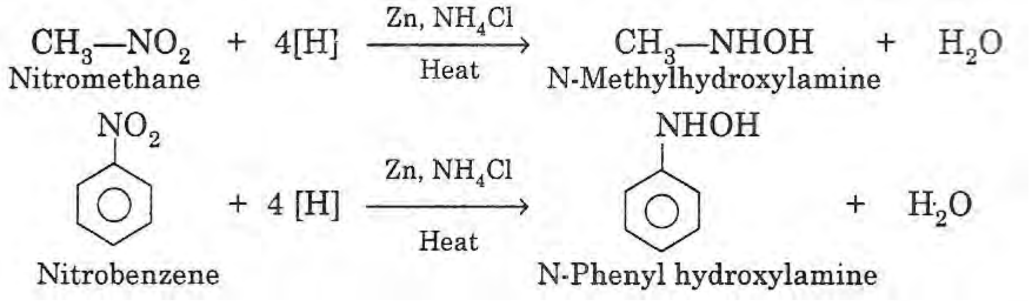
What is the nature of HCl?

Yes, reduction is taken place in acidic medium in presence of tin. But the product is same i.e. amine.

Complete the following equations:

1. Nitromethane is heated with tin and hydrochloric acid.
2. Nitropropane is heated with conc. hydrochloric acid and tin?

c. Reduction in neutral medium



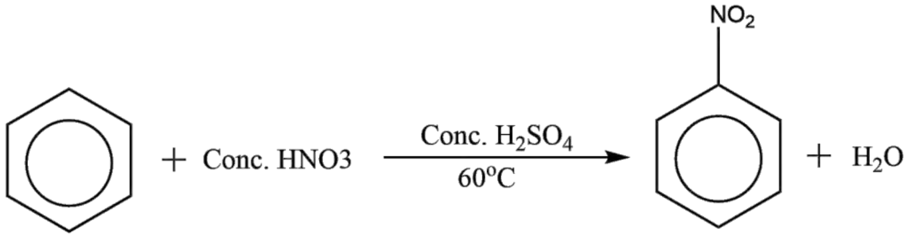
Zn is basic in nature and ammonium chloride is weak acidic salt. Due to presence of this combination, reaction condition becomes neutral and acts as reducing agent and nitrocompounds are reduced to form hydroxyl amine.

Test Yourself:
What would be the product when nitroethane is reduced in neutral medium?

Aromatic nitrocompounds:

Preparation of nitrobenzene

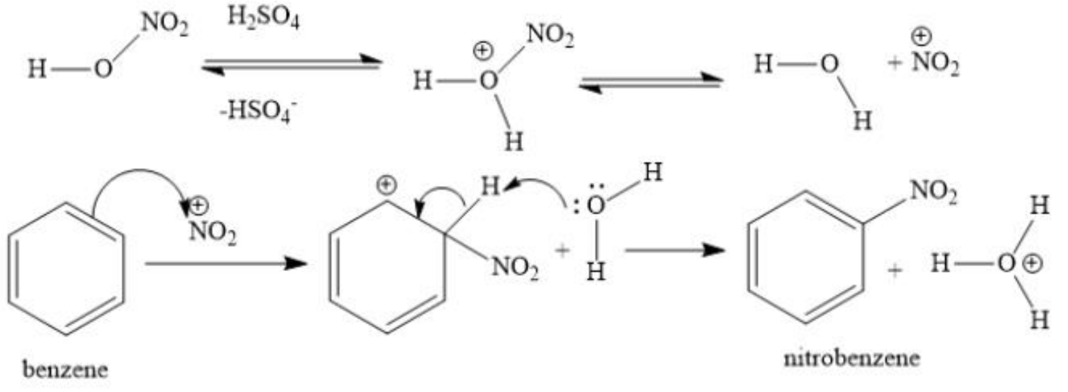
a. From benzene



Nitrobenzene

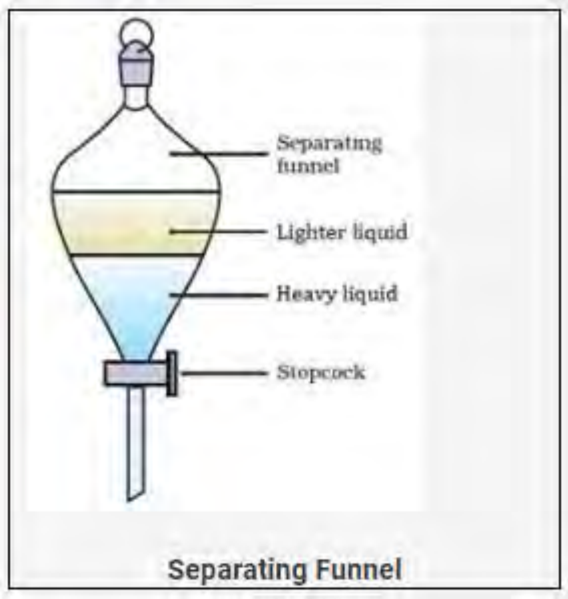
When benzene is heated with concentrated nitric acid in presence of concentrated sulphuric acid, nitration of benzene occurs resulting, nitrobenzene. This reaction is occurred by electrophilic substitution process.

Mechanism:



Physical properties of nitrobenzene

a. Pale yellow oily liquid, also known as 'oil of mirabane'
b. Insoluble in water but soluble in organic solvents
c. Heavier than water

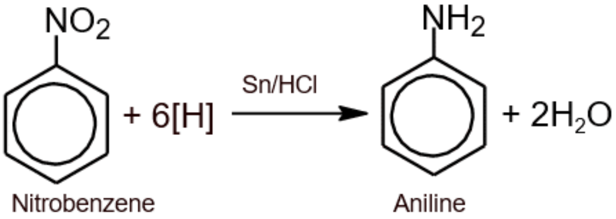


Separating Funnel

d. It is like bitter almond smell.

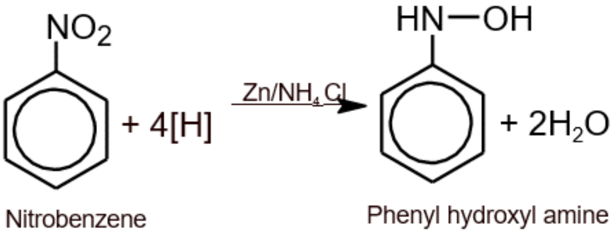
Chemical properties of nitrobenzene

a. Reduction in acidic medium



As in aliphatic nitrocompounds, in nitrobenzene also, reduction occurs by the same process i.e. the nitro group is reduced to amino group when treated in acidic medium.

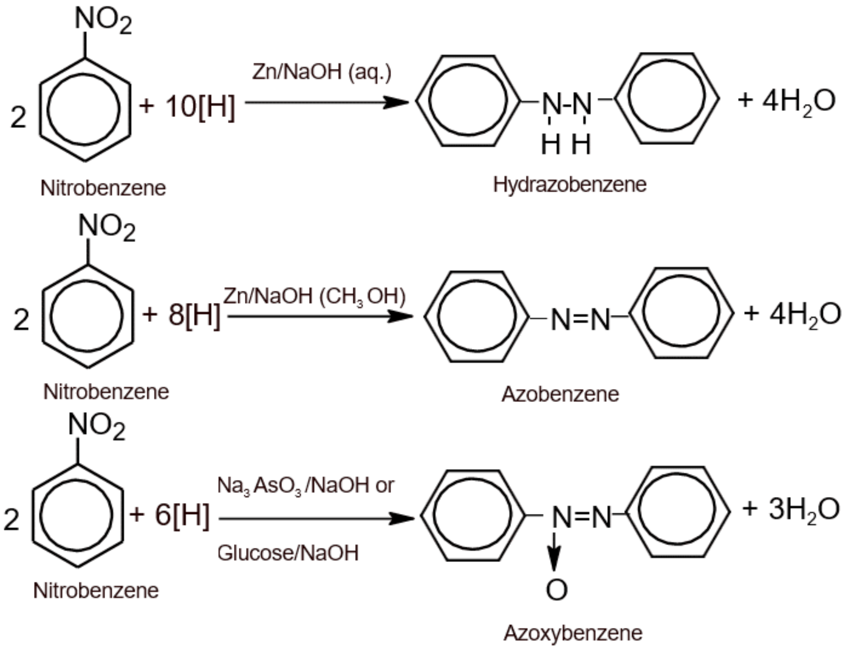
b. Reduction in neutral medium



In neutral medium, nitrobenzene gives N-phenyl hydroxyl amine as a reduced product which is the similar product as we had discussed in aliphatic amine

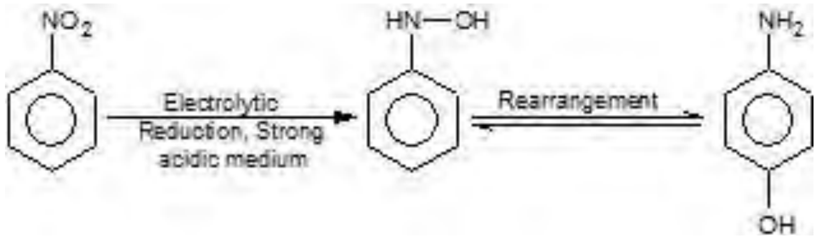
c. Reduction in alkaline medium

Nitrobenzene gives different types of the product at different reduction conditions. Which are given in the following chemical equations.



d. Electrolytic reduction

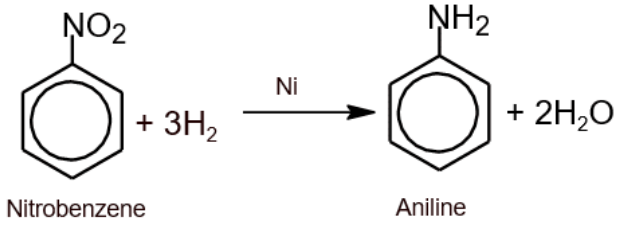
Study the following chemical equation. How is product formed from nitrobenzene?



Nitrobenzene N-phenyl hydroxyl amine p-hydroxy aniline

When nitrobenzene is reduced at electrolytic condition in presence of strong electrolyte, it gives N-phenyl hydroxyl amine (unstable) which undergoes rearrangement and formd p-hydroxy aniline a stable product.

e. Catalytic reduction



When nitrobenzene is reduced in presence of molecular hydrogen along with metals like nickel (Ni) or platinum (Pt) or palladium, aniline is obtained.

Test Yourself:

What are the difference between catalytic reduction and electrolytic reduction of nitrobenzene?

Catalytic reduction	Electrolytic reduction

Electrophilic substitution reaction

What is an electrophile? How do we recognize it?

Can it be substituted at benzene ring?

Think a while and make some preliminary ideas/imaginations and study the followig.

If an electrophile is substituted at benzene ring, the reaction is called elctrophilic substitution reaction.

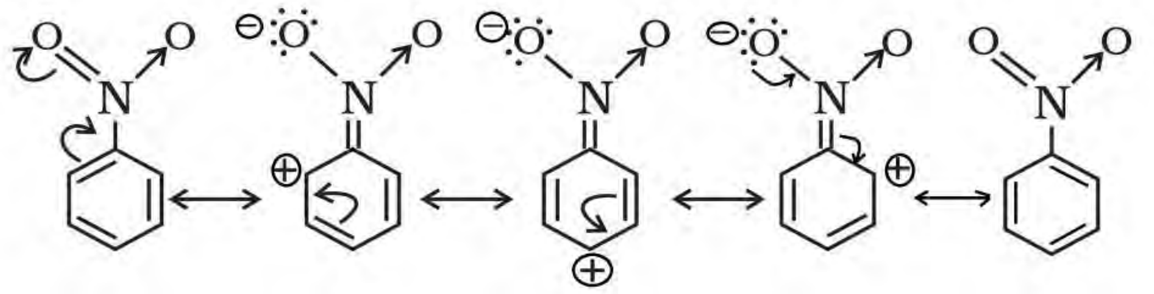
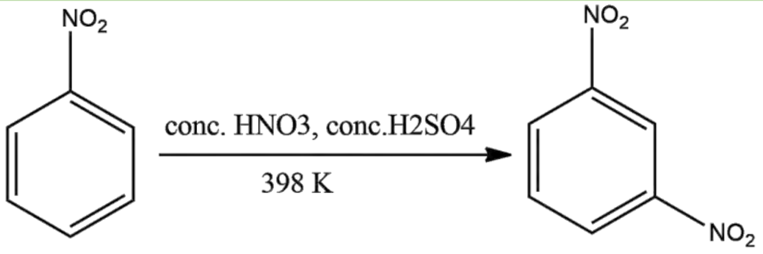


Fig. Resonance structures of nitrobenzene.

The above resonating structures show that the electrophile is substituted at meta position. In nitrobenzene, the -NO_2 group is electron-withdrawing due to both inductive and resonance effects. This makes the benzene ring less reactive towards electrophiles, compared to unsubstituted benzene. The nitro group pulls electron density away from the ring through: Inductive effect (–I): Pulls electrons through sigma bonds. Resonance effect: Delocalizes electrons from the ring, reducing electron density. The ring becomes deactivated. Electrophilic substitution is slower than with benzene. The reaction requires harsher conditions (e.g., higher temperature or stronger catalysts). The –NO_2 group is a meta-director. This means: Electrophiles are directed to the meta position (position 3 relative to –NO_2). Substitution at the ortho (2) and para (4) positions is less favorable due to resonance structures that destabilize the intermediate carbocation.

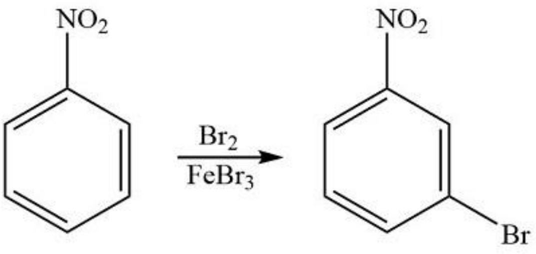
Some specific examples of electrophilic substitution reaction are given below.

a. Nitration

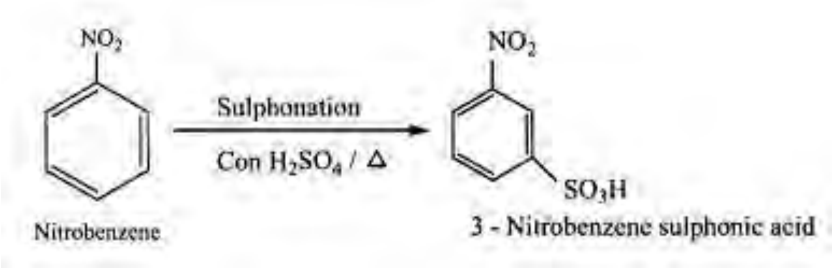


nitrobenzene meta-dinitrobenzene

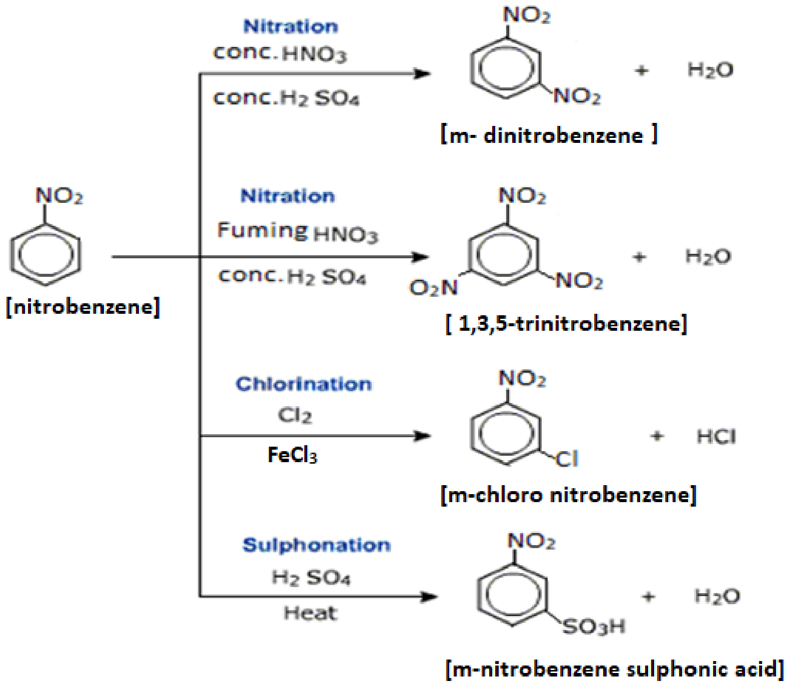
b. Halogenation



c. Sulphonation



These reactions can be summarized as follows.



Compare nitration, sulphonation and halogenation of nitrobenzene

Points to be compared	**Nitration**	**Sulphonation**	**Halogenation**
Reactants			
Conditions			
Products			

Uses of nitrocompounds

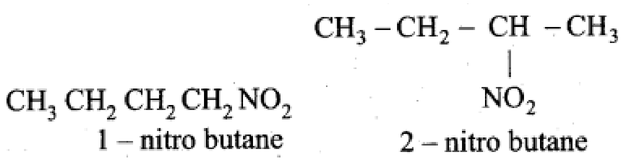
a. Nitroalkanes and nitrobenzenes are used as organic solvents
b. Used as chemical intermediates to prepare amines, carboxylic acids etc.
c. Nitromethane is used as fuel for internal combustion engines
d. Nitroalkanes are used in agriculture and medicines
e. Nitrobenzene is used in the preparation of aniline
f. Nitrobenzene is oxidizing agents in organic synthesis
g. Used for the manufacture of shoe polishes and other polishes.

Exercise

1. Which of the following is called as ambient group?

A. Amino B. Nitro C. aldehyde D. alcohol

2. What type of isomerism is shown in the following structures?



$CH_3CH_2CH_2CH_2NO_2$

1 – nitro butane

$$\underset{\displaystyle NO_2}{CH_3-CH_2-\underset{|}{CH}-CH_3}$$

2 – nitro butane

A. Chain isomerism C. Functional isomerism

B. Position isomerism D. Metamerism

3. What would be the product when; ethane is heated with concentrated nitric acid at about 430^0C?

A. Ethyl nitrite is obtained

B. Ethanoic acid is obtained

C. Ethanol is obtained

D. Nitroethane is obtained

4. What would be the product Z in the following reaction sequence?

$CH_3\text{-}CH_2\text{-}I + AgNO_2 \xrightarrow{Alcoholic\ /\Delta} Z + AgI$

A. Ethane silver C. Nitromethane

B. Ethyne D. Nitroethane

5. Study the following table and choose the correct alternative.

Reactants	**Condition/reagent**	**Major Products**
$CH_3CH_2NO_2$	Sn/HCl	P
Q	$AgNO_2$/heat	CH_3NO_2
$CH_3CH_2NO_2$	R	CH_3CH_2NHOH

A. P-N-ethylethanamine, Q- Ethyl iodide and R -Zn and NH_4Cl

B. P-ethanamine, Q- Ethyl iodide and R -Zn and NH_4Cl

C. P-N-ethylethanamine, Q- methyl iodide and R -Zn

D. P-ethanamine, Q- methyl iodide and R -Zn and NH_4Cl

6. Which of the following is secondary nitroalkane?

A. Nitropropane B. Nitroethane C. nitrobutane D. 2-nitropropane

7. Which of the following compound is used to convert nitroethane into ethanamine?

A. Li B. Sn C. $LiAlH_4$/heat D. Sn/heat

8. What could be the product X in the following reaction sequence?

$CH_3CH_2NO_2 \xrightarrow{LiAlH4\ /heat} X$

a. N-ethyl hydroxyl amine b. N-methyl hydroxyl amine

b. Ethanamine d. Propanamine

9. What is the process of addition of nitro group into benzene ring called?

A. Nucleophilic addition C. Nucleophilic substitution

B. Electrophilic addition D. Electrophilic substitution

10. What would be the product P on the following reaction sequence?

$$M \xrightarrow{\text{Conc.HNO3 and Conc H2SO4}} N \xrightarrow{\text{LiAlH4/heat}} O \xrightarrow{\text{Benzene diazonium chloride}} P$$

A. Aniline B. phenol

B. C. p-hydroxy diazobenzene D. p-amino diazobenzene

11. What are the required conditions for sulphonation of nitrobenzene?

A. H_2SO_4
B. H_2SO_4 and heat
C. conc. H_2SO_4
D. conc.H_2SO_4 and heat

12. Which of the following is correct about information given in the following table?

Reactants	**Condition**	**Major Products**
$C_6H_5NO_2$	Sn/HCl	P
$C_6H_5NO_2$	Zn/NaOH/Δ	Q
$C_6H_5NO_2$	R	C_6H_5NHOH

A. P-aniline, Q- azoxybenzene, R- Zn/NH_4Cl
B. P-hydroxylamine, Q- azoxybenzene, R- Zn/NH_4Cl
C. P-aniline, Q- hydrazobenzene, R- Zn/NH_4Cl
D. P-hydroxylamine, Q- hydrazoxybenzene, R- Zn/NH_4Cl

13. What would be the compounds M, N and O in the following reaction sequence?

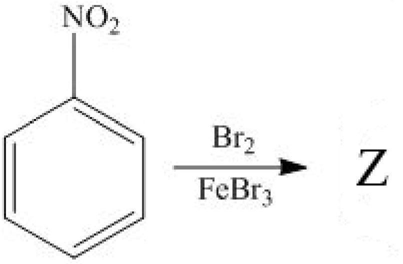
$M \xrightarrow{Conc.HNO3} N \xrightarrow{Sn/HCl} O$. The compound M is an aromatic hydrocarbon having molecular mass 78 amu.

A. M- ethyne, N- nitrobenzene, O- toluene
B. M- benzene, N- nitrobenzene, O- chlorobenzene
C. M- benezene, N- aniline, O- toluene
D. M- benzene, N- nitrobenzene, O- aniline

14. What is the nature of $-NO_2$ group during electrophilic substitution reaction?

A. o-director
B. m- director
C. p-director
D. o and p director

15. What is the compound Z ?



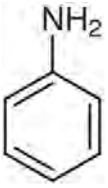
A. o-bromonitrobenzene
B. p-bromonitrobenzene
C. m-bromonitrobenzene
D. nitrobenzene

Short answer questions

16. Identify and write the compounds P, Q, R and S in the following reaction sequence.

$$\xrightarrow{\text{Conc.HNO3/Conc.H2SO4}} \text{P} \xrightarrow{\text{Sn/HCl}} \text{Q} \xrightarrow{\text{CHCl3 /KOH}} \text{R} \xrightarrow{\text{H2/Pd/heat}} \text{S.}$$

17. Identify A, B, C, D and E in the following reaction sequence.



$$\xrightarrow{NaNO2+HCl} \text{A} \xrightarrow{H2O/{-OH}} \text{B} \xrightarrow{Zn/heat} \text{C} \xrightarrow{conc.HNO3/ConcH2SO4} \text{D} \xrightarrow{Sn/HCl/heat} \text{E}$$

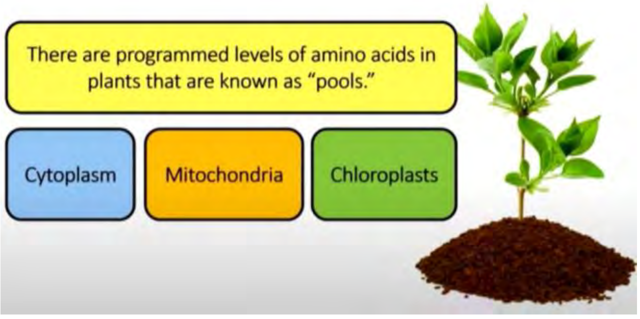
18. Convert nitrobenzene into phenol then treat it with ferric chloride solution. Write all the chemical equations involved.

19. Identify the unknown reagents, conditions and products

Reactants	Conditions	Products
Benzene	……………….	Nitrobenzene
Nitrobenzene	$NaNO_2$/dil HCl at low temperature	……………..
Nitrobenzene	Zn/CH3OH/heat	…………..
……………..	Zn/NH_4Cl	N-phenyl hydroxyl amine
Nitrobenzene	…………….	1,3,5-trinitrobenzene

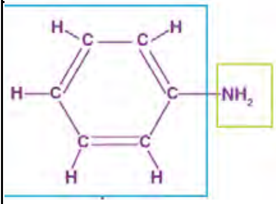
Unit 16
Amines

15.1 Introduction

Name of the substance	Use in
Amino acids	 There are programmed levels of amino acids in plants that are known as "pools." Cytoplasm Mitochondria Chloroplasts

❖ **Do you know that these things contain amino acids?**

Activity:
Study the following structures of organic compounds. Count the components (atoms) present in the compounds and write to the next column.

Molecular structure	Name of the molecules	Components (atoms) of the molecules
R- H	…………………………	……………………
R-NO_2	…………………………	………………………..
R-NH_2	……………………	………………………..
	………………….	…………………………………..

What are the differences that you find the above structures?

17. ………………………………
18. ………………………………
19. ………………………………
20. ………………………………

So, the amines are the amino derivative of alkane or alkyl or aryl derivative of ammonia. Amines may be aliphatic or aromatic.

(A) Aliphatic amines

16.1 Nomenclature, isomerism and classification of nitroalkane

Nomenclature:

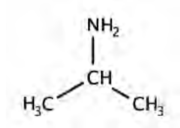
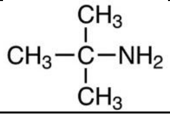
Common Naming system:

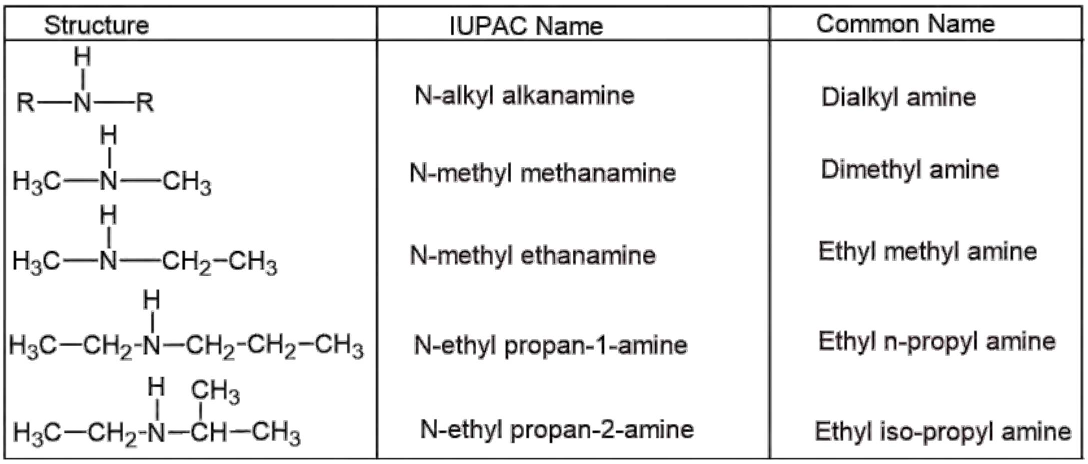
The common names for amines are derived by naming the alkyl or aryl groups attached to the nitrogen and adding the suffix "-amine".

IUPAC Naming System:

To write IUPAC name of amino compounds amino prefix is added in front of word root or amine suffix is added after word root. Rest of the other processes are same as other compounds.

Substituent +Prefix+ word root + amine

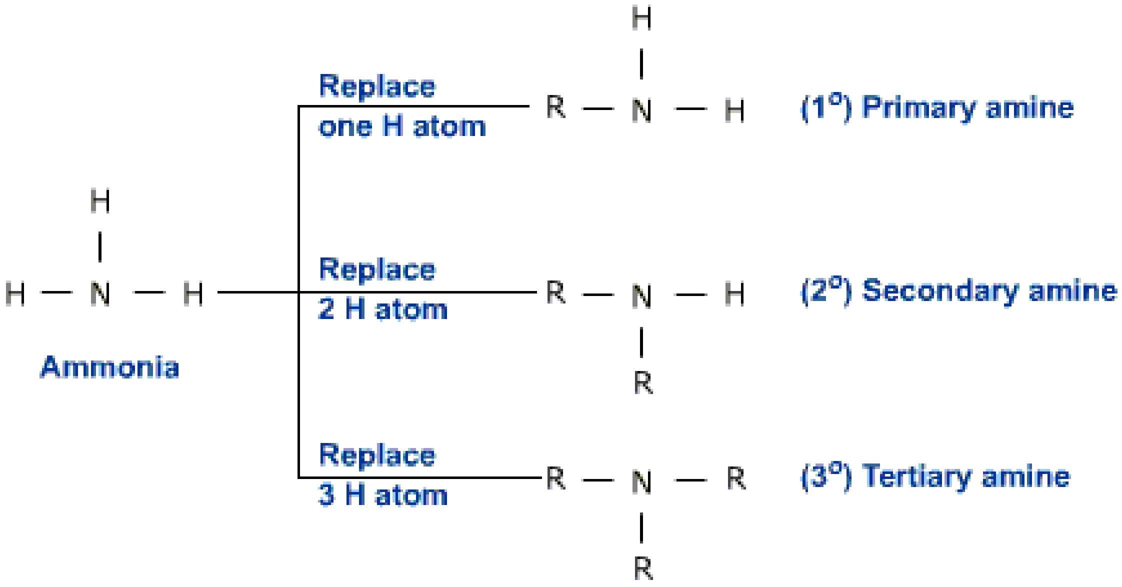
SN	Formula	IUPAC Name	Common Name
1.	$CH_3\text{-}NH_2$	Methanamine	Methyl amine
2.	$CH_3\text{-}CH_2\text{-}NH_2$	Ethanamine	Ethyl amine
3.	$CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_2$	Propanamine	Propyl amine
4.		2-aminopropane	Isopropyl amine
5.	 $CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-NH_2$	2-amino-2-methylpropane	Sec.butyl amine



Structure	IUPAC Name	Common Name
$R-\overset{\overset{H}{\vert}}{N}-R$	N-alkyl alkanamine	Dialkyl amine
$H_3C-\overset{\overset{H}{\vert}}{N}-CH_3$	N-methyl methanamine	Dimethyl amine
$H_3C-\overset{\overset{H}{\vert}}{N}-CH_2-CH_3$	N-methyl ethanamine	Ethyl methyl amine
$H_3C-CH_2\text{-}\overset{\overset{H}{\vert}}{N}-CH_2\text{-}CH_2-CH_3$	N-ethyl propan-1-amine	Ethyl n-propyl amine
$H_3C-CH_2\text{-}\overset{\overset{H}{\vert}}{N}-\overset{\overset{CH_3}{\vert}}{CH}-CH_3$	N-ethyl propan-2-amine	Ethyl iso-propyl amine

Classification of amines

On the basis of alkyl groups bonded with nitrogen amines are classified in the following classes



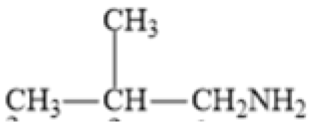
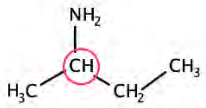
You can see in ammonia alkyl groups are substituted subsequently.

As it has mentioned that the primary amines are those compounds in which an alkyl group is bonded with nitrogen of ammonia by replacing one hydrogen atom. Similarly, if two hydrogen atoms of ammonia are replaced by two alkyl groups the amine is secondary amine. Furthermore, the compounds obtained by replacing three hydrogen atoms of ammonia by three alkyl groups or aryl groups is called tertiary amine. But when an alkyl halide is added to tertiary amine, a quaternary amine or ammonium salt is obtained.

Isomerism of aliphatic amines:

Study the pairs of compounds given in the following table. Write similarities and differences found in these pairs.

Table: 1

SN	Compounds	Similarity	Difference
1.	a. $CH_3-CH_2-CH_2-CH_2-NH_2$ b.  $CH_3-CH(CH_3)-CH_2NH_2$	....	....
2.	 a. b.$CH_3-CH_2-CH_2-CH_2-NH_2$	....	....
3.	a. $CH_3-CH_2-NH-CH_2-CH_3$ b. $CH_3-CH_2-CH_2-NH-CH_3$	....	....

Activity:

Study the pair of compounds given in table no. 1. Relate the following statements and fill in the following table.

Statements	Isomerism	Pair of compounds of table 1 (write S.N.)
- Same molecular formula but difference in chain.	Chain isomerism	……………………………
- Same molecular formula but difference in position of functional group.	Position isomerism	……………………………
- Same molecular formula but difference in functional group.	Functional isomerism	……………………………

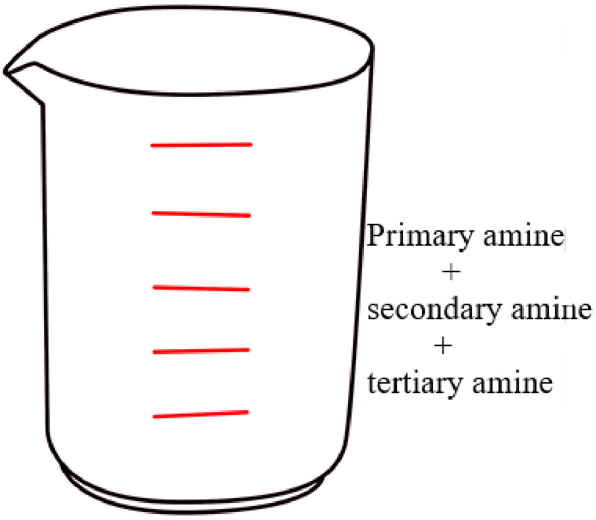
Test Yourself

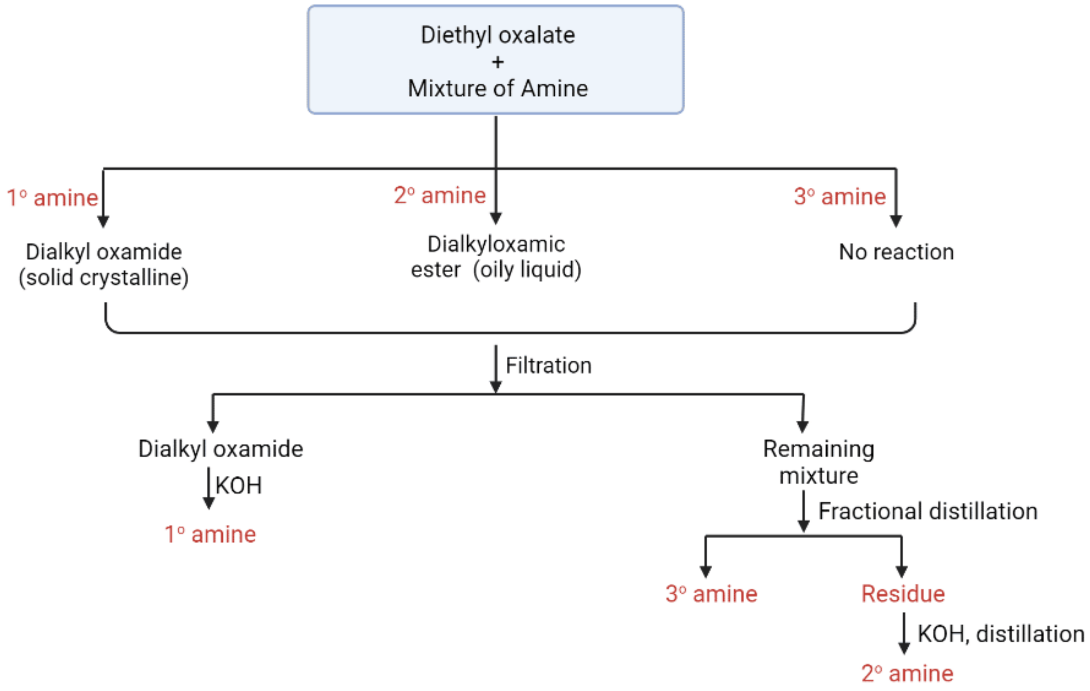
Write all types of isomers of the compound C_3H_7N.

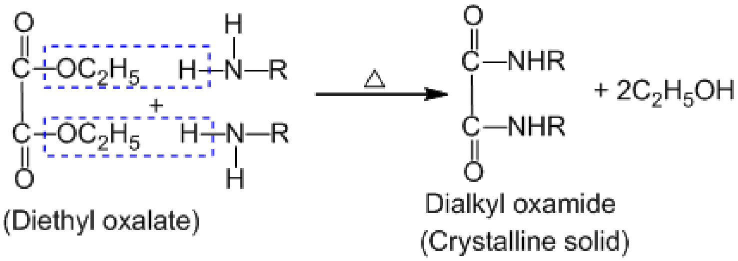
Separation of 1^0, 2^0 and 3^0 amines by Hoffmann's method.

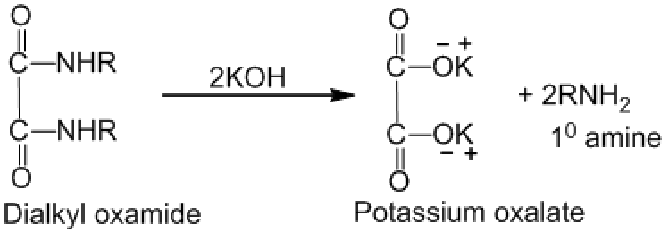
A mixture of primary, secondary and tertiary amine are given to you. How do you separate?

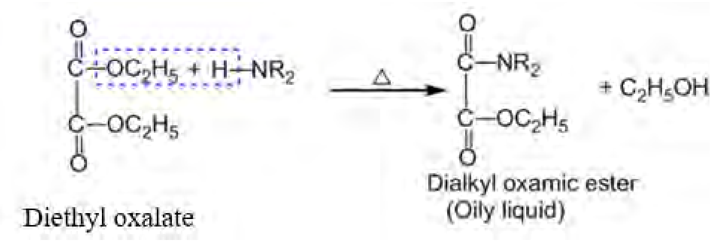
Please see the processes and compound used for the process.

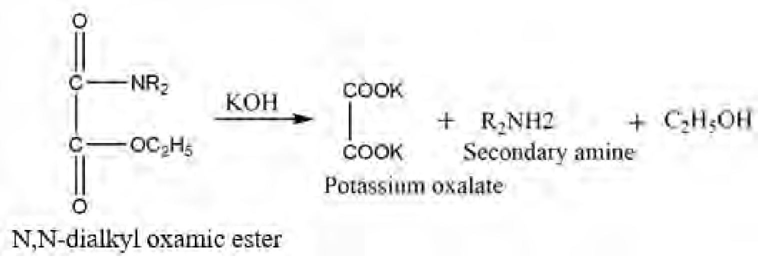



Diethyl oxalate
+
Mixture of Amine
1° amine
2° amine
3° amine
Dialkyl oxamide
(solid crystalline)
Dialkyloxamic
ester (oily liquid)
No reaction
Filtration
Dialkyl oxamide
KOH
1° amine
Remaining
mixture
Fractional distillation
3° amine
Residue
KOH, distillation
2° amine


(Diethyl oxalate)
Δ
+ $2C_2H_5OH$
Dialkyl oxamide
(Crystalline solid)


Dialkyl oxamide
2KOH
+ $2RNH_2$
1^0 amine
Potassium oxalate


Diethyl oxalate
Δ
+ C_2H_5OH
Dialkyl oxamic ester
(Oily liquid)


N,N-dialkyl oxamic ester
KOH
+ R$_2$NH2
+ C_2H_5OH
Secondary amine
Potassium oxalate

As you have seen the chemical equations for the separation of primary, secondary and tertiary amines. The process to be followed to obtain pure amines are described below.

But tertiary amine does not react with diethyl oxalate. So, it is purified by fractional distillation method. The solid which is obtained by the reaction between diethyl oxalate is again treated with potassium hydroxide and is distilled to obtain pure primary amine. Similarly, the oily yellow liquid which is obtained by the reaction between secondary amine and diethyl oxalate is distilled to gain the pure secondary amine. Thus the primary, secondary and tertiary amines are separated from their mixture.

Test yourself:

a. How do you separate the methanamine, N-methylmethanamine and N,N-dimethylmethanamine from their mixture by Hoffmann's method?

b. How do you separate the ethanamine, N-ethylmethanamine and N,N-diethylmethanamine from their mixture by Hoffmann's method?

Preparation of primary amines

a. By alkyl halide

If both the reagents are used in the ratio of 1:1, primary amine is obtained.

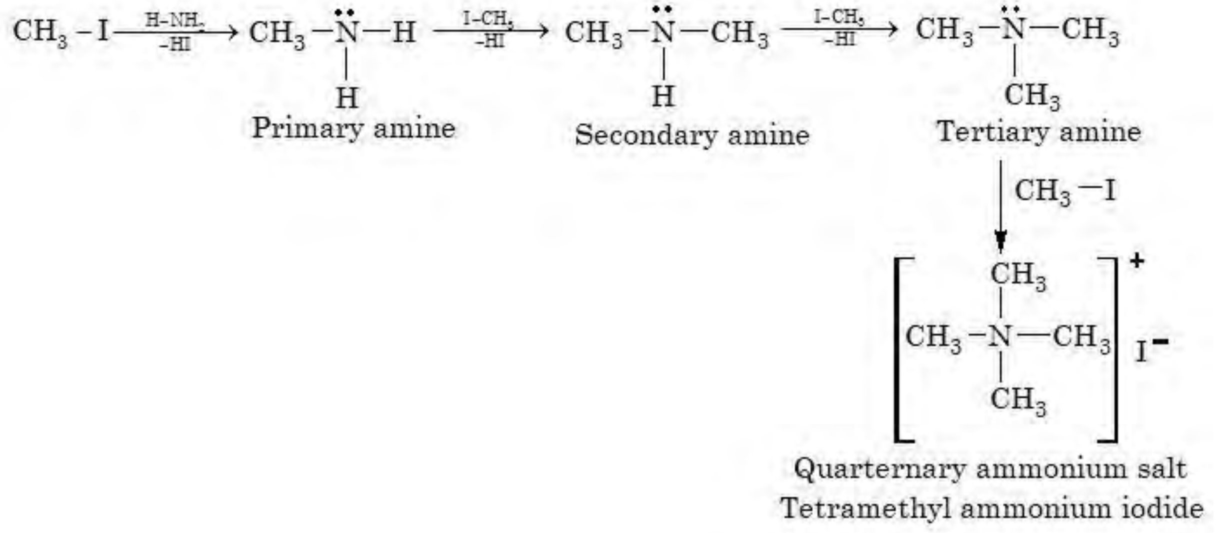
$$R\text{-}X + H\text{-}NH_2 \xrightarrow{\textit{Sealed tube+ethanol}/\Delta} R\text{-}NH_2 + HX$$

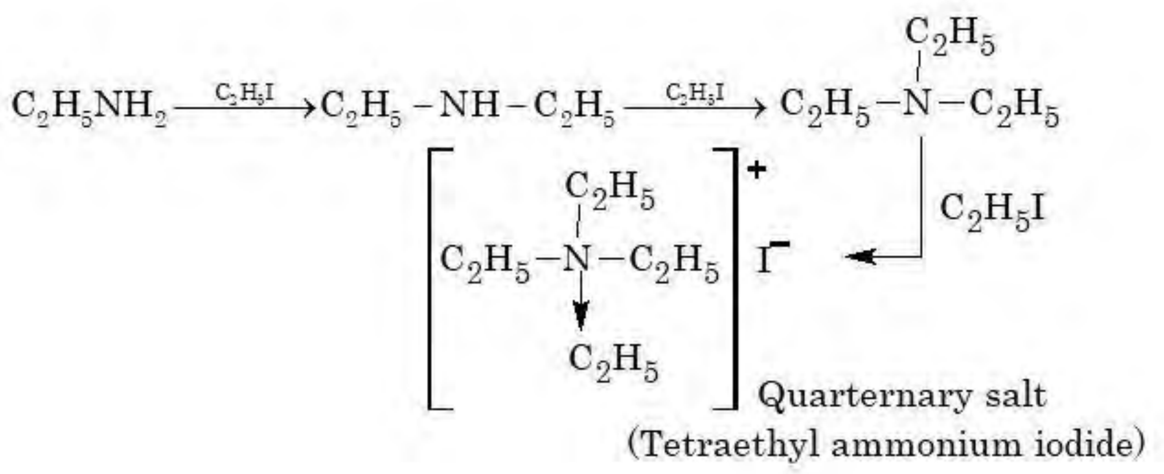
For example:

$$CH_3\text{-}Cl + H\text{-}NH_2 \xrightarrow{\textit{Sealed tube+ethanol}/\Delta} CH_3\text{-}NH_2 + HCl$$

When alkyl halide is heated with ammonia in sealed tube in presence of ethanol, alkanamine is obtained along with the byproduct hydrogen halide.

Note: if excess alkyl halide is used other hydrogen atoms are replaced by alkyl groups and secondary, tertiary and quaternary amines are obtained.



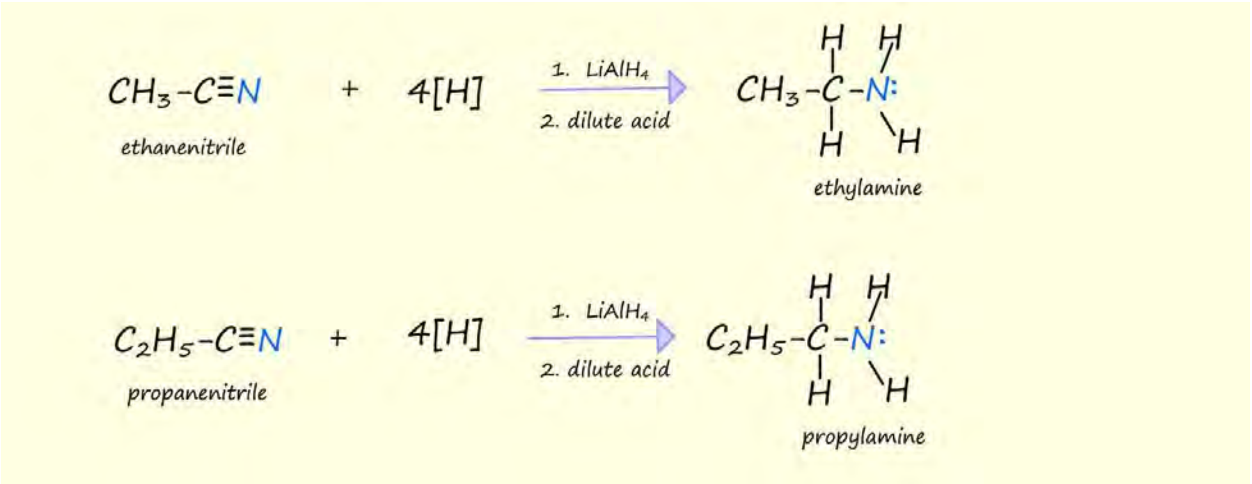


Quarternary salt
(Tetraethyl ammonium iodide)

b. By Nitriles

$$R-C\equiv N \xrightarrow[\text{2) } H_3O^+]{\text{1) } LiAlH_4} R-CH_2-NH_2$$

Nitrile **1° Amine**



As you have seen in the chemical equation when alkyl nitriles are reduced in acidic medium amines are obtained.

c. From Amides (R-CONH2)

i. By Hoffmann's bromamide degradation reaction (Hypobromite reaction)

Study the following chemical equation and write the conclusions

$$CH_3CONH_2 + Br + 4NaOH \xrightarrow{\Delta} CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

Acetamide Methanamine

$$CH_3CH_2CONH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} CH_3CH_2NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

Propanamide Ethanamine

You may find, the carbon number at the amides are decreased when amines are formed. When amides are heated with aq.bromine in presence of aq.alkali solutions, primary amines are obtained along with carbonate salt and bromide salt along with water.

ii. By reduction of amides

$$R\text{-}CO\text{-}NH_2 + [H] \xrightarrow{LiAlH4\ /\Delta} R\text{-}CH_2NH_2 + H_2O$$

For eg.

$$CH_3\text{-}CO\text{-}NH_2 + [H] \xrightarrow{LiAlH4\ /\Delta} CH_3\text{-}CH_2\text{-}NH_2 + H_2O$$

Ethanamide ethanamine

As you have studied the reduction of other organic compounds amines are obtained by reduction of amide in presence of metallic hydrides. The byproduct is water

Activity:

Write the difference between preparation of amine from Hoffman's bromamide degradation and reduction of amide.

Fill the following table about the difference that you find in these two methods of preparation of amines.

SN	Hoffmann's bromamide degradation	Reduction of amides
1.	…………………………….	………………………..
2.	……………………………	………………………..
3.	…………………………….	…………………………..
4.	……………………………	………………………...

d. From Nitroalkane

$$R\text{-}NO_2 + 6[H] \xrightarrow{Sn/HCl} R\text{-}NH_2 + 2H_2O$$

Nitroalkane Amine

$$CH_3CH_2NO_2 + 6[H] \xrightarrow{Sn/HCl} CH_3CH_2NH_2 + 2H_2O$$

Nitroethane Ethanamine

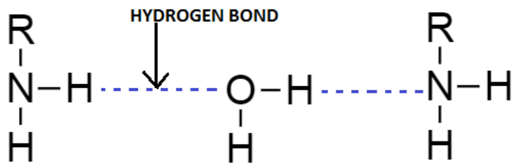
As you have discussed in chemical properties of nitrocompounds, amines are obtained by the reduction in acidic medium in presence of tin and conc. hydrochloric acid.

Test yourself:

What would be the product when nitromethane is reduced in acidic medium?

16.4 Physical properties of aliphatic amines

- Methanamine and ethanamines are colorless gas, few more are liquid and higher amines are in solid state.
- Upto carbon number three have ammoniacal odour, next upto carbon number six have fishy smell and higher amines do not have odor.
- They form weaker intermolecular hydrogen bond hence they have low density. Amines are lighter than water and other polar compounds.
- Lower members of amines are soluble in water and they form intermolecular hydrogen bonding but solubility decreases with the increase in molecular mass.



- Boiling point of amines is higher than the comparable hydrocarbons but lesser than that of alcohol and carboxylic acids. Primary amine has highest boiling point, then secondary amines and tertiary amines have the least boiling point.

Chemical properties of amines

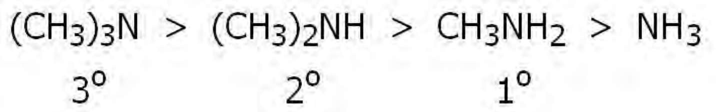
a. Basicity of amines (Comparative study of basic nature of primary, secondary and tertiary amines)

Due to the presence of lone pair of electrons at nitrogen, amines show basic in nature. Nitrogen of amines has sp3 hybridized. Due to electron donating nature of alkyl group electrons are intensified at nitrogen. So, the nitrogen can easily donate electron. Basic compounds have the tendency to loose electron. So it is basic in nature.

$$R - \ddot{N}H_2 + HX \rightleftharpoons R - \overset{+}{N}H_3 \ \overset{-}{X}$$

Basicity strength of 1^0, 2^0 and 3^0 amines

In gaseous state, tertiary amine is the most basic compound since it has three alkyl groups which donate more electrons at nitrogen through inductive effect which makes easier to donate electron from amines. Basic strength is arranged in gaseous state as following.



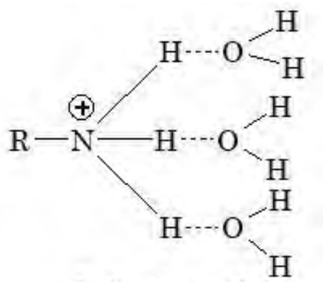
$$\underset{3^o}{(CH_3)_3N} > \underset{2^o}{(CH_3)_2NH} > \underset{1^o}{CH_3NH_2} > NH_3$$

But in aqueous state this sequence is not same due to following two factors

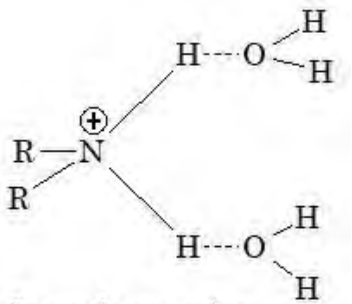
i. **Steric hindrance**
ii. **Hydration effect**

With the addition of alkyl group makes the nitrogen more crowded. Due to which electrons present at nitrogen are less available for other species.

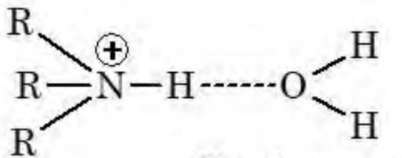
Due to hydration effect basicity is affected. Basicity order of primary, secondary and tertiary amines are based on +I effect, steric hindrance and hydration effect.



Primary amine



Secondary amine



Tertiary amine

b. Reaction with chloroform(carbylamines reaction)

$$\underset{\text{Primary amine}}{R-NH_2} + \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Potassium Hydroxide}}{3KOH(alc.)} \xrightarrow{\Delta} \underset{\text{Carbylamine}}{R-NC} + 3KCl + 3H_2O$$

For example,

$$\underset{\text{Methanamine}}{CH_3-NH_2} + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} \underset{\text{Methyl carbylamine or methyl isocyanide}}{CH_3-NC} + 3KCl + 3H_2O$$

As you have seen that, when amines are heated with chloroform in presence of alc. Potassium hydroxide alkyl isocyanides are obtained along with potassium chloride and water.
You may write the reaction of other amines of carbylamines reaction.

c. Action with conc. HCl

$R\text{-}NH_2 + HCl \longrightarrow RNH_3^+Cl^-$

$HCl + CH_3NH_2 \rightarrow CH_3NH_3^+ + Cl^-$

When amines are treated with concentrated hydrochloric acid, alkyl ammonium chloride salt is formed. This is an addition reaction.

Test yourself:
Write the reaction between ethanamine and concentrated hydrochloric acid.

d. Action with R-X

$R\text{-}NH_2 + X\text{-}R \longrightarrow R\text{-}NH\text{-}R + HX$

Other examples can be shown as follows.

$$\underset{\text{methylbromide}}{CH_3-Br} + \underset{\text{alc.}}{NH_3} \xrightarrow{\Delta} \underset{\text{methylamine}}{CH_3-NH_2} + HBr$$

$$\underset{\text{methyl amine}}{CH_3-NH_2} + CH_3-Br \xrightarrow{\Delta} \underset{\text{dimethyl amine}}{(CH_3)_2NH} + HBr$$

$$\underset{\text{dimethyl amine}}{(CH_3)_2NH} + CH_3-Br \xrightarrow{\Delta} \underset{\text{trimethyl amine}}{(CH_3)_3N} + HBr$$

$$\underset{\text{trimethyl amine}}{(CH_3)_3N} + CH_3-Br \xrightarrow{\Delta} \underset{\text{tetramethyl ammonium bromide (quaternary ammonium salt)}}{(CH_3)_4N^+Br^-}$$

In these chemical equations, you have seen that when alkanamine is heated with alkyl halide, secondary amines are obtained along with hydrogen halide. But in presence of excess alkyl halide tertiary and quaternary amines are obtained.

Try yourself:
What would be the products when ethanamine is heated with excess chloroethane?

e. Action with RCOX

Study the following chemical equations:

$R\text{-}NH_2 + XOC\text{-}R \longrightarrow R\text{-}NH\text{-}COR + HX$

For example:

$CH_3\text{-}NH_2 + Cl\text{-}COCH_3 \longrightarrow CH_3\text{-}NH\text{-}COCH_3 + HCl$

When amines are treated with acid chlorides amides are formed along with hydrogen halides.

f. Action with nitrous acid

$R\text{-}NH_2 + HNO_2 \longrightarrow ROH + H_2 + H_2O$

For example;

$$\underset{\text{Ethylamine}}{C_2H_5-NH_2} + \underset{\text{Nitrous acid}}{OH-N=O} \xrightarrow{NaNO_2\ +\ HCl} \underset{\text{Ethanol}}{C_2H_5OH} + N_2(g) + H_2O$$

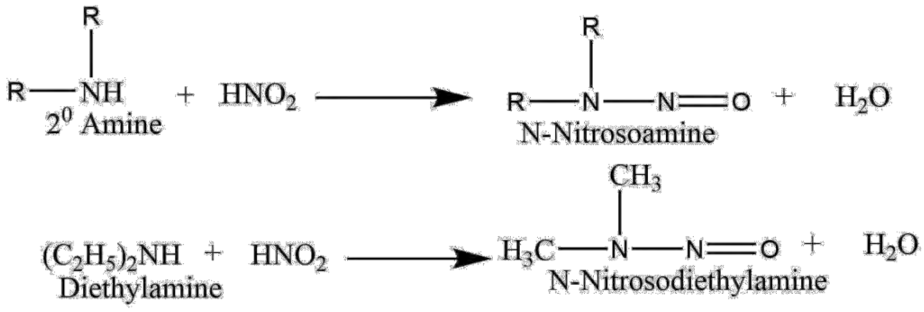
When primary amines are treated with nitrous acid, alcohol is formed. which is recognized by the smell and other test of alcohols.

g. Test of primary, secondary and tertiary amines

$RNH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O$

$$\underset{\text{Ethylamine}}{C_2H_5-NH_2} + \underset{\text{Nitrous acid}}{OH-N=O} \xrightarrow{NaNO_2\ +\ HCl} \underset{\text{Ethanol}}{C_2H_5OH} + N_2(g) + H_2O$$

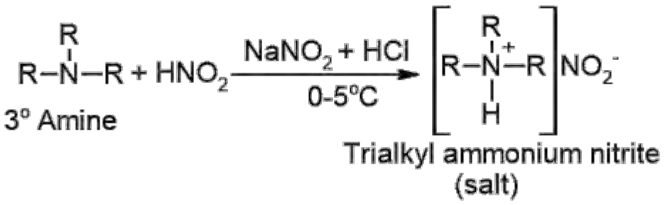
With primary amine nitrous acid gives alcohol, molecular nitrogen and water.

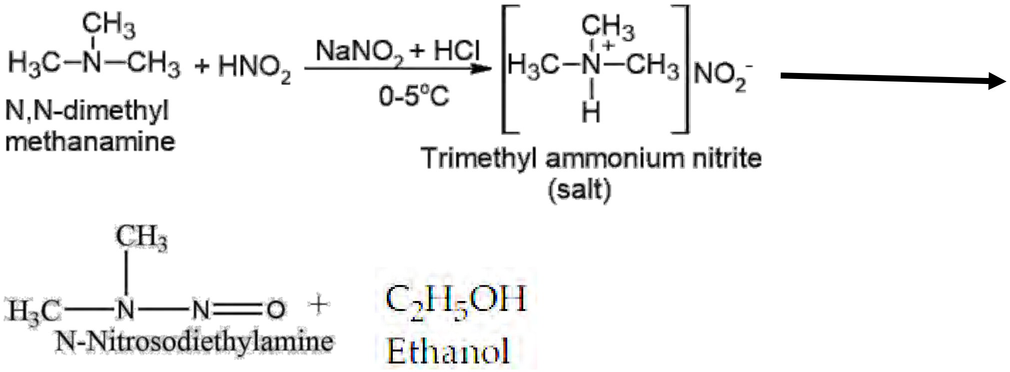


$$\underset{2^0\ \text{Amine}}{R-\overset{R}{\overset{|}{N}}H} + HNO_2 \longrightarrow \underset{\text{N-Nitrosoamine}}{R-\overset{R}{\overset{|}{N}}-N=O} + H_2O$$

$$\underset{\text{Diethylamine}}{(C_2H_5)_2NH} + HNO_2 \longrightarrow \underset{\text{N-Nitrosodiethylamine}}{H_3C-\overset{CH_3}{\overset{|}{N}}-N=O} + H_2O$$

Nitro group of nitrous acid makes bond with nitrogen of amine and forms nitroso group. So the product is N-nitrosoN-alkyl alkanamine



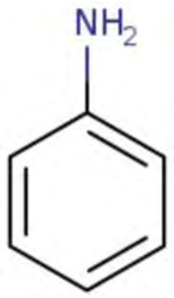


But with tertiary amine, nitrous acid gives trialkyl ammonium nitrite. Which is unstable in nature and gives N-nitrosoN-alkyl alkanamine and alcohol which are the products obtained from secondary and primary amines.

Uses of aliphatic amines

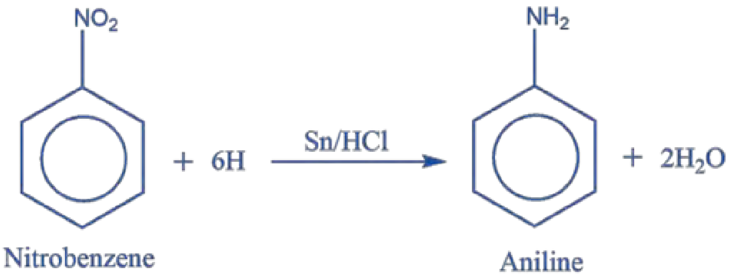
- Dimethylamine is used in vulcanization of rubber.
- Used as proteins, vitamins, alkaloids and hormones supplement which include polymers, dyestuffs and drugs.
- Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure.
- Novocain, a synthetic amino compound, is used as an anesthetic in dentistry.
- Benadryl, a well-known antihistaminic drug also contains tertiary amino group.
- Quaternary ammonium salts are used as surfactants.
- Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes.

Aromatic amines (Aniline)



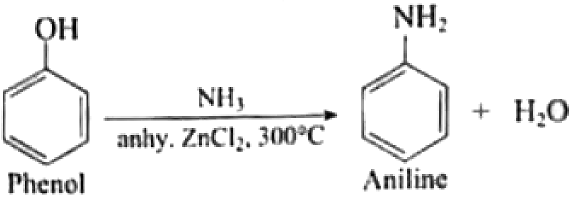
General methods of preparation of aniline

a. From nitrobenzene



As we have discussed in chemical properties of nitrobenzene, aniline is obtained by the reduction of nitrobenzene.

b. From Phenol



When phenol is heated with ammonia in presence of anhydrous zinc chloride, aniline is obtained along with water.

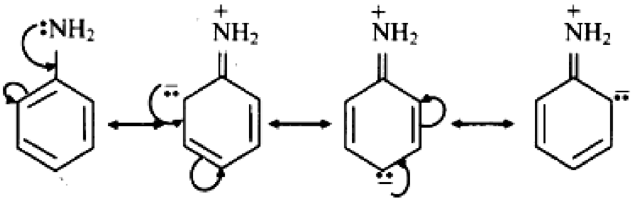
Physical properties of aniline (Aromatic amines)

i. It is colorless liquid
ii. Slightly heavier than water
iii. It has unpleasant odour
iv. Highly toxic in nature
v. Boiling point is 184^0C and it freezes at -6^0C

Chemical properties of aniline

a. Basicity of aniline comparison with aliphatic amine and with ammonia

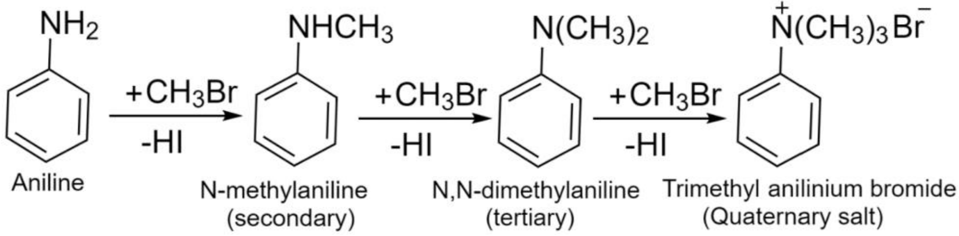
Compared to both ammonia and aliphatic amines, aniline is significantly less basic due to the delocalization of its lone pair of electrons through resonance with the benzene ring, making them less available for donation in a chemical reaction; therefore, aliphatic amines are more basic than ammonia, and both are more basic than aniline. Less basic because the lone pair on the nitrogen atom is delocalized across the benzene ring through resonance, reducing its availability for protonation.



Resonance structures of aniline

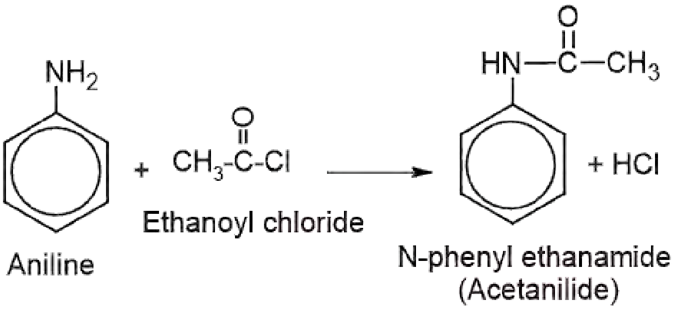
Ammonia is more basic than aniline because it’s lone pair is not involved in resonance and is readily available for donation. Aliphatic amines are generally more basic than both ammonia and aniline due to the electron-donating effect of alkyl groups attached to the nitrogen atom, increasing electron density and enhancing the ability to donate a lone pair.

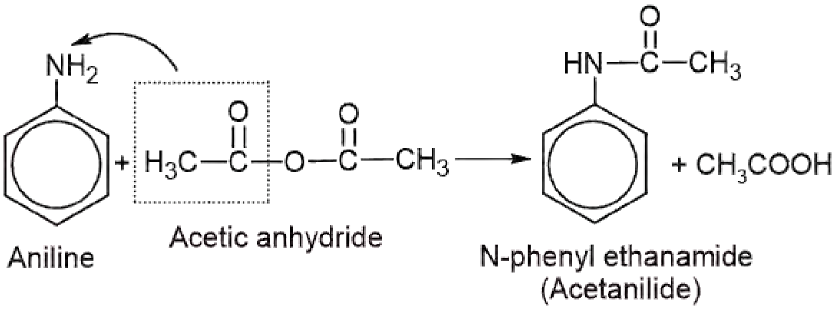
b. Alkylation of aniline



When aniline is alkylated directly, quaternary amine of ammonium salt is obtained along with hydrogen halide byproduct.

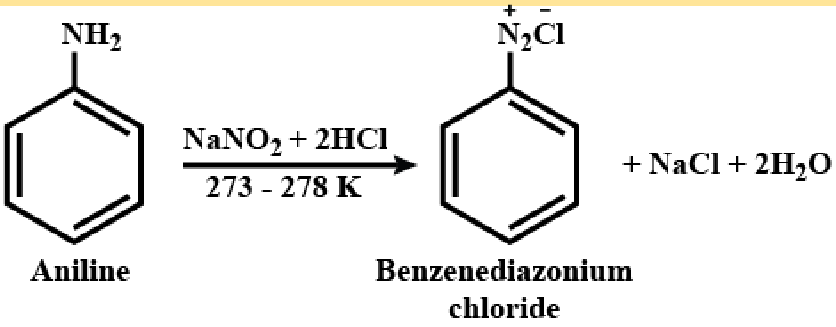
c. Acylation of aniline





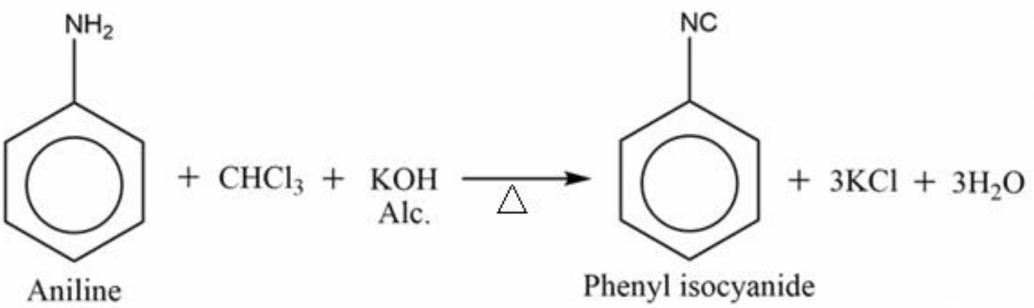
As in alkylation, in the acylation of aniline directly, acetanilide is obtained along with other byproducts.

d. Diazotization of aniline



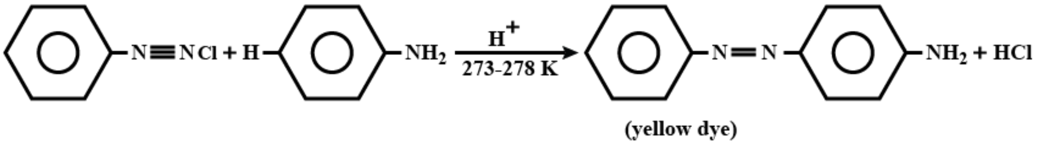
when aniline is treated with nitrous acid in presence of dil.hydrochloric acid at freezing temperature, benzene diazonium chloride(BDC) salt is obtained.

e. Carbylamines reaction



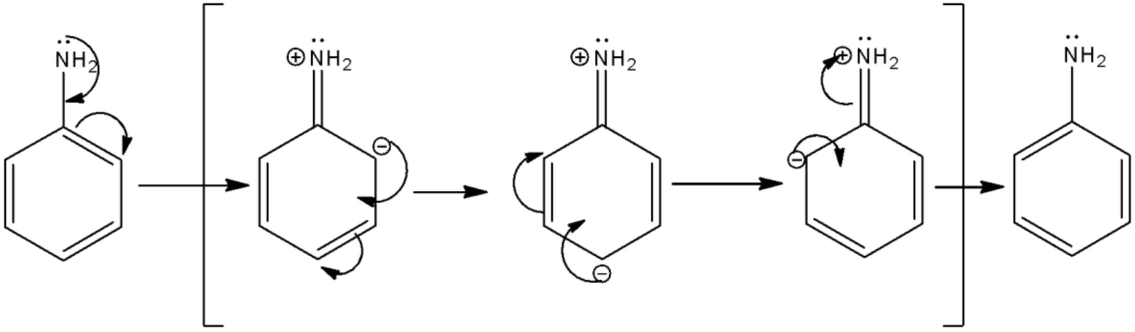
As in aliphatic amine, aniline gives phenyl isocyanide when heated with chloroform and alcoholic potassium hydroxide.

f. Coupling reaction of aniline



As there is a molecule of aniline and a molecule of benzene diazonium chloride, they get coupled to form yellow precipitate of p-amino diazobenzene along with hydrochloric acid.

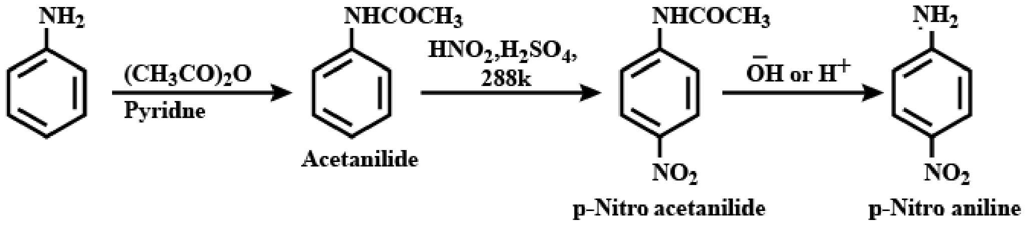
g. Electrophilic substitution reaction



Resonance strucutres of Aniline

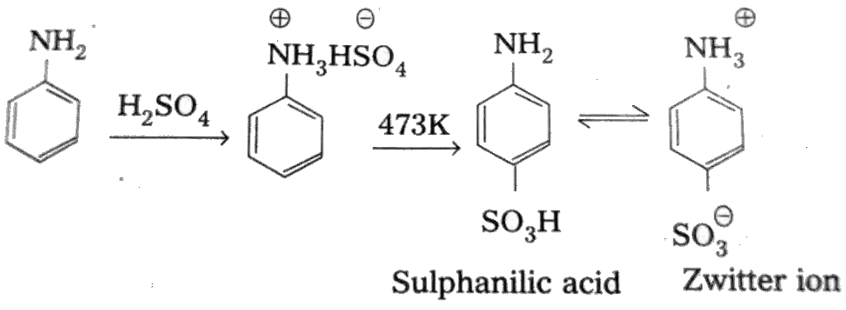
Due to electron releasing nature of –NH2 group and withdrawing nature of benzene ring, the lone pair of electrons of nitrogen are shifted towards the ring. The pi-electron gets repelled and carbanion is formed at ortho carbo. Due to declocalization of electron para carbon and another ortho carbon acquires negative charge (carbanion). The study of these resonating structure is for seeking the electron rich site within the benzene ring.

• Nitration



As in other aromatic hydrocarbons, aniline cannot be nitrated directly due to the possibility of oxidation of amino group. Without oxidizing amino group.

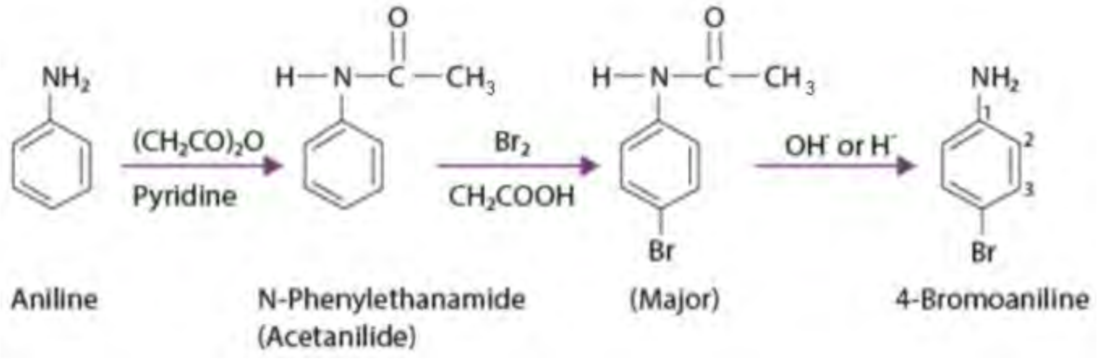
Sulphonation



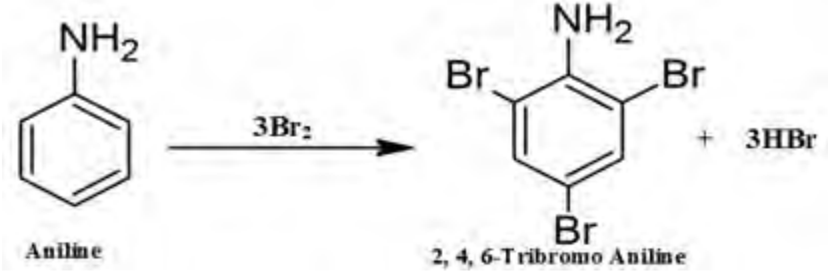
When aniline is treated with concentrated sulphuric acid in presence of pyridine, sulphanilic acid is formed. It becomes zwitter ion due to rearrangement of hydrogen ion.

Bromination

By protecting the



Without protecting the amino group



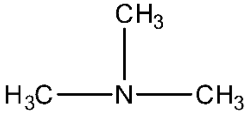
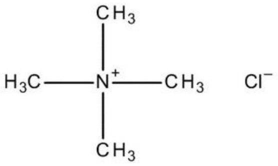
Exercise

Multiple choice questions

1. How many structural isomers of C_3H_9N can be formed?

   A. 2 B. 3 C. 4 D. 5

2. Which of the following is tertiary amine?

$CH_3CH_2CH_2NH_2$	$CH_3CH_2NHCH_3$	 $H_3C-\overset{CH_3}{N}-CH_3$	 $H_3C-\underset{CH_3}{\overset{CH_3}{N^+}}-CH_3\quad Cl^-$
A.	B.	C.	D.

3. Which of the following compound is used to separate the mixture of primary, secondary and tertiary amines from their mixture?

Nitrous acid	Nitrolic acid	Diethyl oxalic acid	Diethyl oxalate
A	B	C	D

4. What would be the product when excess chloroethane is treated with ammonia?

   A. Ethanamine C. N-ethylethanamine

   B. N,N-diethylethanamine D. N,N,N,N-tetraethyl ammonium chloride

5. What would be Z in the following reaction sequence?

   $CH_3CH_2NO_2 \xrightarrow{Sn/HCl} Z$

   A. Ethyl isocynide C. Ethanamine

   B. N-ethylethanamine D. N,N-ethylethanamine

6. Which of the following is the strongest base?

   A. NH_3 B. CH_3NH_2 C. $(CH_3)_2NH$ D. $(CH_3)_3N$

7. What would be the product when propanamine is treated with nitrous acid?

   A. Propanoic acid B. Propanal C. Propanol D. Propene

8. Which of the followings gives carbylamines test?

   A. NH_3 B. CH_3NH_2 C. $(CH_3)_2NH$ D. $(CH_3)_3N$

9. Which of the following would be the product when alkyl cyanides are reduced?

A. Alkanes B. alkene C. Amide D. Amine

10. Which of the following is correct sequence according to the basic strength in aqueous state.

A. 1°>2°>3°>NH_3 B. 1°>3°>2°>NH_3 C. 3°>2°>1°>NH_3 D. 2°>1°>3°>NH_3

11. Which of the following is correct about the given reaction sequence?

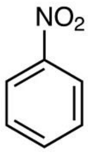
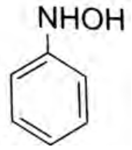
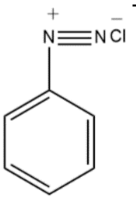
$P \xrightarrow{Conc.HNO3} Q \xrightarrow{Sn/HCl} R \xrightarrow{CHCl3/alc.KOH} S$. S gives a secondary amine having two carbon atoms when reduced.

A. P-nitroethane, Q-ethanamine, R- ethylisocyanide, S- ethylethanamine
B. P-nitromethane, Q-ethanamine, R- ethylisocyanide, S- ethylethanamine
C. P-nitroethane, Q-ethanamine, R- ethylisocyanide, S- ethylethanamine
D. P-methane, Q-nitromethane, R- methanamine, S- methylisocyanide

12. To which position does an electrophile direct during electrophilic substitution reaction of aniline?

A. Ortho B. para C. meta D. ortho and para

13. Choose the best alternatives from the followings

Reactant(s)	Conditions	Product
CH_3NH_2	alc.KOH/$CHCl_3$	M
	N	
O	HNO_2+HCl at freezing temperature	

A. M- Methanol, N- Sn/HCl, O- Nitrobenzene
B. M- ethylcyanide, N- Zn/NH_4Cl, O- aniline
C. M- Methyl isocyanide, N- Zn/NH_4Cl, O- aniline
D. M- Methanal, N- Zn/ NH_4Cl, O- aniline

14. Which of the following would be the product when aniline is treated with benzene diazonium chloride?

A. o- aminodiazobenzene C. p-aminodiazobenzene

B. Azobenzene D. Hydrazobenzene

15. An alcohol having molecular mass 46 amu is obtained by treating compound 'M' with nitrous acid, what could be 'M' ?

A. Ethanal B. Ethanamide C. Ethanoic acid D. Ethanamine

16. Which compound is possibly obtained by the reduction of methyl isocyanide?

A. N-methyl methanamine B. Ethanamide C. Methyl cyanide D. Ethanoic acid

17. Why do we need to protect aminogroup during nitration?

A. Amino group is meta-directing group

B. Amino group is reduced

C. Amino group is oxidized

D. Amino group is basic in nature

18. What is the compound to be used to separate methanamine, N-methyl methanamine and N,N-dimethyl methanamine?

A. Nitrous acid B.Diethyl oxalate C.Fehling's reagent D.Tollen's reagent

19. During the nitration of aniline why should acyl group is reacted with $–NH_2$ group or amino group is protected?

E. To make NH_2 active C. To make benzene ring less active

F. To make NH_2 group less reactive D. nitration is addition of acyl group

20. Which compound is possibly obtained by the reduction of methyl isocyanide?

a. N-methyl methanamine b.Ethanamide c.Methyl cyanide d.Ethanoic acid

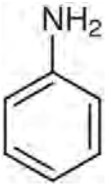
Short Questions

21. The compound 'V' is treated with sodium nitrite and dilute HCl at freezing temperature gives 'W'. The compound gives compound 'X' on hydrolysis of 'W'. 'X' gives violet coloration when treated with $FeCl_3$ forming a product 'Y' . 'W' and 'X' undergoes coupling reaction and gives 'Z' . The compound V can also be obtained when nitrobenzene is treated with Sn/HCl. Identify V, W, X, Y and Z with the pertinent reactions.

22. Identify the following compounds P, Q, R and S. Also write the name of the between P and S.

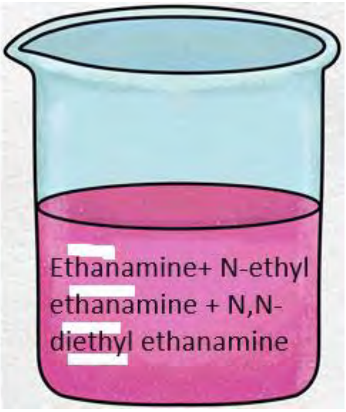
Reactant(s)	**Reagents/ conditions**	**Products**
P	Cu_2Cl_2/HCl	Q
Q	NH_3/Cu_2O	R
R	$NaNO_2$/dil HCl	P
P	S	P-amino diazobenzene

23. Identify A, B, C, D and E in the following reaction sequence.



$\xrightarrow{NaNO2+HCl} A \xrightarrow{H2O/-OH} B \xrightarrow{Zn/heat} C \xrightarrow{conc.HNO3/ConcH2SO4} D \xrightarrow{Sn/HCl/heat} E$

24. You are a chemistry student. Your teacher has given a task to submit the compounds given the beaker individually. How do you complete the task? Explain about the procedure and write all the reactions involved.



25. What happens when benzamide is heated with aq. KOH in presence of bromine to about 70^0C. Between ammonia and aniline which one is more basic? Explain. Convert ethanamine into methanamine.

26. Convert methanamine to ethanamine. Arrange the following compounds on the basis of increasing basicity order. Justify the order with proper explanation. [2+1+2]

$CH_3CH_2NH_2$, $C_6H_5NH_2$, CH_3NH_2

27. Identify A, B, C, D and E in the following reaction sequence.

$A \xrightarrow{NH3} B \xrightarrow{Br2/aq.KOH} C \xrightarrow{HNO2} D \xrightarrow{NaOH/I2/heat} E$, the compound C is an aliphatic primary amine having molecular mass 45 amu.

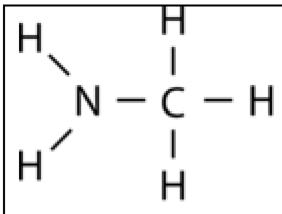
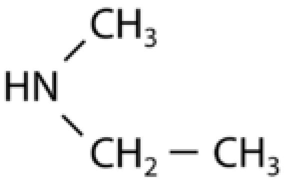
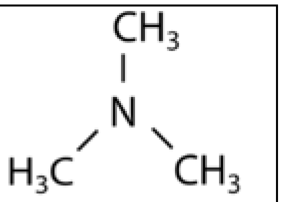
Long Questions

28. A. An aliphatic gaseous compound ‘L’ is passed into red hot iron tube under pressure and produces a compound ‘M’. ‘M’ is under nitration and gives ‘N’. By the reduction of ‘N’, ‘O’ is obtained. Again for the nitration of ‘O’, the active site is protected and the product ‘P’ is obtained in which major product is p-nitroaniline. Identify the L, M, N, O and P from the information given.

C. Give an example of each of the following.

i. Coupling reaction of aniline
ii. Separation of primary amine only from the mixture.
iii. Test of secondary amine

29. A. Write down the detail description of separation of the mixture of the following compounds.

B. What product would you obtain when nitrobenzene is treated with

a. $Zn/NH_4Cl/\Delta$
b. $NaOH/Na_3AsO_3$
c. Conc H_2SO_4 in presence of heat

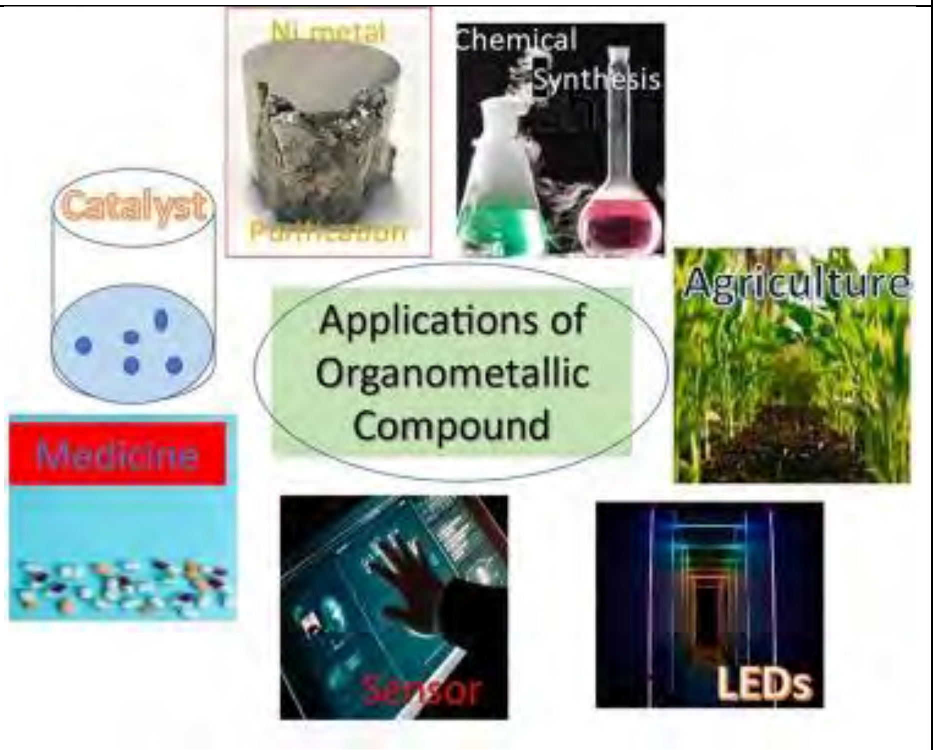
30. Two compounds A and B are given in the table. What would be the product when diethyl oxalate is treated with these two compounds individually? How would you obtain the compound B by using Hoffmann’s method? Show all the steps to obtain methanamine from ethanamine.
Write any three methods of preparation of aniline.

$A=(CH_3)_2NH$ and $B=CH_3NH_2$

Unit 17

Organometallic Compounds

17.1 Introduction

Name of the substance	**Uses**
Organometallic compounds	

- ❖ Have you ever seen the uses of compounds like R-Li, R-Cd and R-Cu?

Activity:

Study the following structures of organic compounds and do as indicated at the top.

Molecular structure	Difference	Use
R- Li	…………………………	………………………… ………………………… …………………………
R-Cu	…………………………	………………………… ………………………… …………………………
R-Cd	………………………..	……………………….. ……………………….. ………………………..

What are the differences in structure and differences in applications of the compounds?

21. ……………………………
22. ……………………………
23. ……………………………

So, these compounds have carbon atoms and these carbon atoms have made bond with metals like lithium, cadmium and copper. So, they are called organometallic compounds.

Organolithium Compounds

$$\text{R-X} + \text{Li} \xrightarrow{dry\ ether\ /\Delta} \text{R-Li} + \text{Li-X}$$

Alkyl halide Organolithium

$$CH_3\text{-Cl} + \text{Li} \xrightarrow{dry\ ether\ /\Delta} CH_3\text{-Li} + \text{Li-Cl}$$

Chloromethane methyllithium

$$CH_3\text{-}CH_2\text{-Cl} + \text{Li} \xrightarrow{dry\ ether\ /\Delta} CH_3\text{-}CH_2\text{-Li} + \text{Li-Cl}$$

Chloroethane ethyllithium

Organolithium compounds are a class of reactive organometallic reagents characterized by a direct bond between a carbon atom and a lithium atom, often represented as R-Li, where R is an organic group.

Organocopper compounds

$$2RLi + CuI \xrightarrow{ether} R_2CuLi + LiI$$

Eg.

$$2\,CH_3Li + CuI \xrightarrow{ether} (CH_3)_2CuLi + LiI$$

(methyl lithium) (Lithium dimethyl cuprate)

Monoorganocopper complex $CuX + RLi \longrightarrow RCu + LiX$

Lower-order organocopper species $CuX + 2\,RLi \longrightarrow R_2CuLi + LiX$

'Gilman reagent'

$CuX + R_TLi + R_RLi \longrightarrow R_TR_RCuLi$

Mixed lower-order organocuprate

$CuCN + RLi \longrightarrow RCu(CN)Li$

Lower-order cyanocuprate

Higher-order organocopper species $CuCN + 2RLi \longrightarrow R_2Cu(CN)Li_2$

$CuCN + R_RLi + R_TLi \longrightarrow R_TR_RCu(CN)Li_2$

Mixed higher-order cyanocuprate

Organocopper compounds are a class of organometallic compounds where copper is directly bonded to carbon. They are versatile reagents used in organic chemistry for various reactions, including coupling reactions and conjugate additions. Organocopper compounds are often prepared by transmetallation, a process where a metal is replaced in a complex with another metal.

Organocadmium Compounds

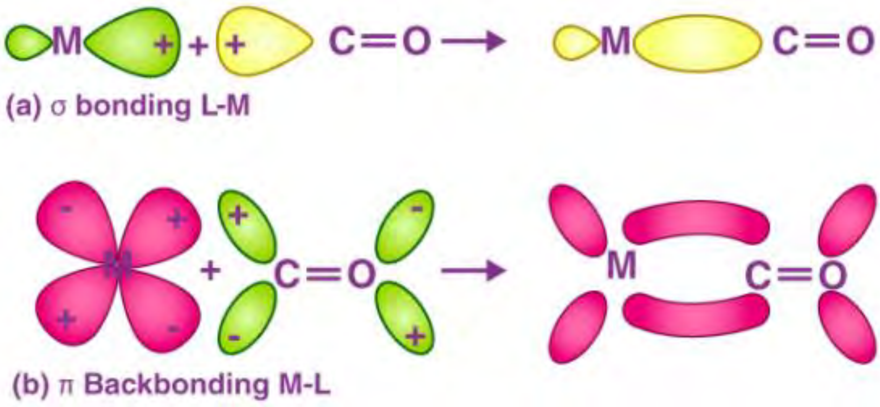
$$2RMgX + CdCl_2 \xrightarrow{ether} R_2Cd + 2MgXCl$$

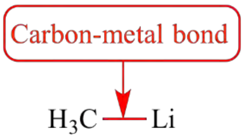
Eg.

$$2\,CH_3MgBr + CdCl_2 \xrightarrow{ether} (CH_3)_2Cd + 2MgBrCl$$

(methyl magnesium bromide) (dimethyl cadmium)

Metal-carbon Bond





A metal-carbon bond is a covalent bond that occurs between a metal and a carbon atom. Metal-carbon bonds are found in organometallic compounds.

Types of bond in metal and carbon.

Sigma bonds: A carbon atom donates a pair of electrons to an empty orbital of the metal

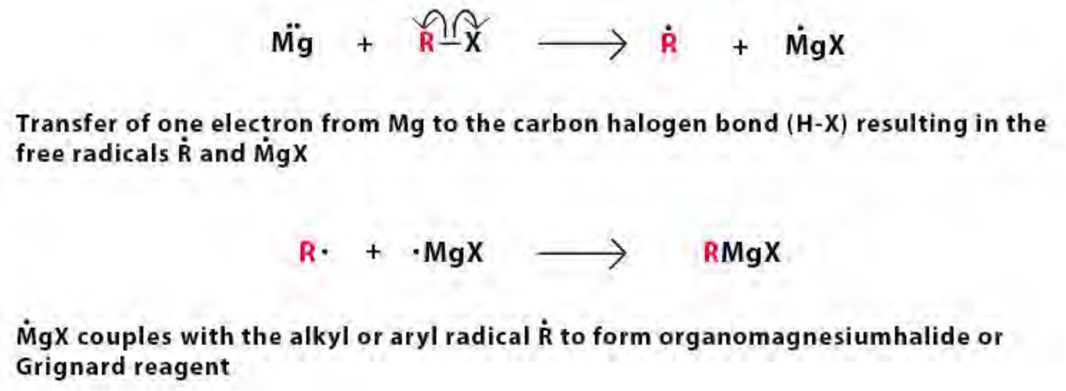
Pi bonds: A metal donates a pair of electrons from a filled d-orbital to an empty anti-bonding π orbital of carbon. Examples of metal-carbon bonds
Metal carbonyls: The metal-carbon bonds in metal carbonyls are formed when the carbon atom donates a pair of electrons to the metal's empty orbital.

Metal alkyls: These compounds feature a metal-carbon σ bond.

Grignard’s reagent:

Preparation:

For the preparation of Grignard’s reagent, magnesium metal is heated with alkyl halide in presence of dry ether. The product is alkyl magnesium halide; which is called Grignard’s reagent.



Transfer of one electron from Mg to the carbon halogen bond (H-X) resulting in the free radicals Ṙ and ṀgX

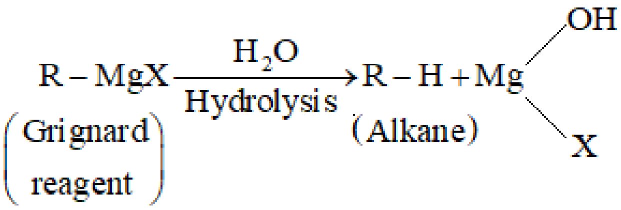
ṀgX couples with the alkyl or aryl radical Ṙ to form organomagnesiumhalide or Grignard reagent

$$\underset{\text{methyl iodide}}{CH_3I} + Mg \xrightarrow{\text{ether}} \underset{\text{methylmagnesium Iodide}}{CH_3MgI}$$

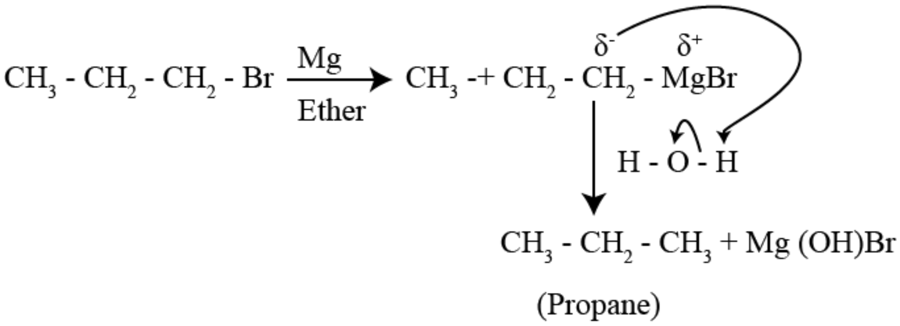
$$\underset{\text{methyl bromide}}{CH_3CH_2Br + Mg} \xrightarrow{\text{ether}} \underset{\text{ethylmagnesium bromide}}{CH_3CH_2MgBr}$$

Chemical properties of Grignard’s reagent

Action with water

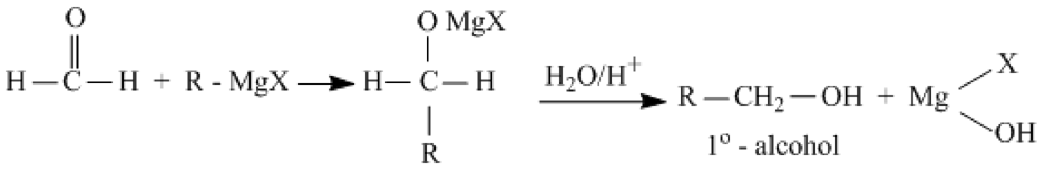


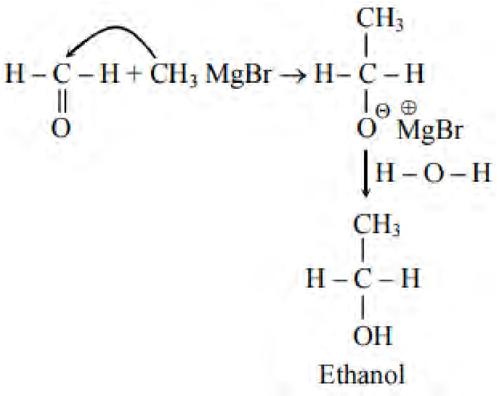
$$\underset{\left(\begin{array}{c}\text{Grignard}\\ \text{reagent}\end{array}\right)}{R-MgX} \xrightarrow[\text{Hydrolysis}]{H_2O} \underset{(\text{Alkane})}{R-H} + Mg\begin{array}{l}\diagup OH\\ \diagdown X\end{array}$$

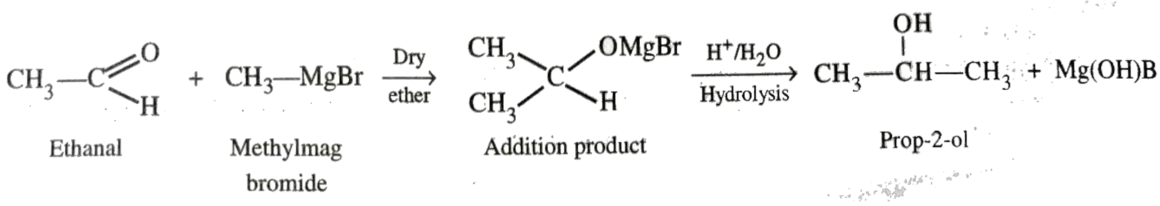


As the reaction is given above, when Grignard's reagent is dissolved in water (hydrolyzed) it gives alkane and magnesium hydroxylhalide as byproduct.

Action with aldehyde

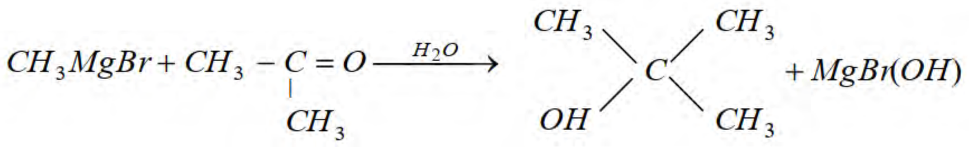






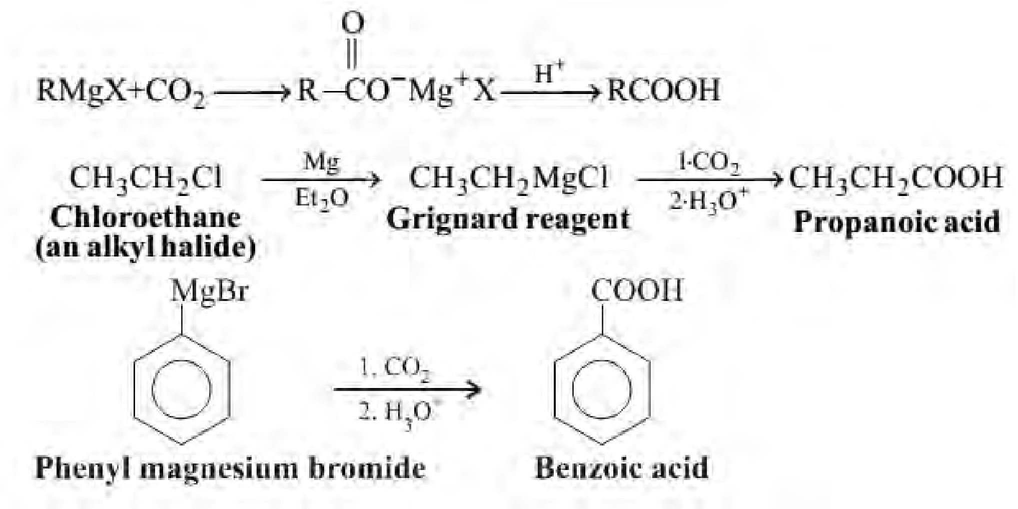
When formaldehyde is treated with Grignard's reagent, followed by hydrolysis, primary alcohol is obtained along with magnesium hydroxyl halide byproduct. But other aldehydes give secondary alcohol.

Action with ketone



When Grignard's reagent is treated with ketone, in presence of water, tertiary alcohol is obtained alongwith magnesium hydroxyl halide

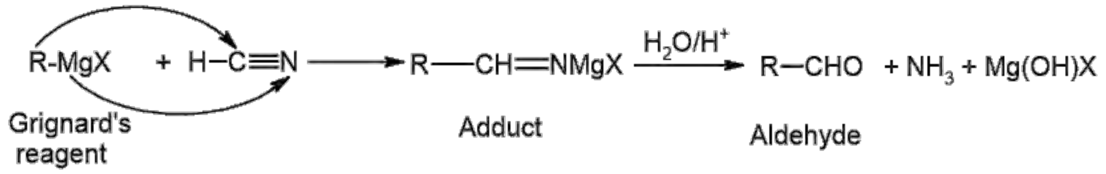
Action with carbondioxide

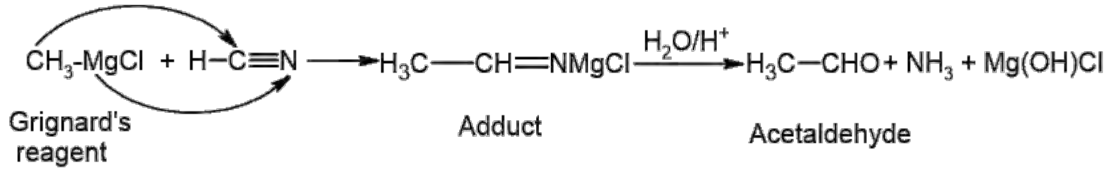


Can you explain the process of obtaining products when Grignard's reagent is treated with carbon dioxide?

When Grignard's reagent is treated with carbon dioxide followed by acidic hydrolysis carboxylic acid are formed. This reaction helps to increase the number of carbon atoms in the chain.

Action with HCN





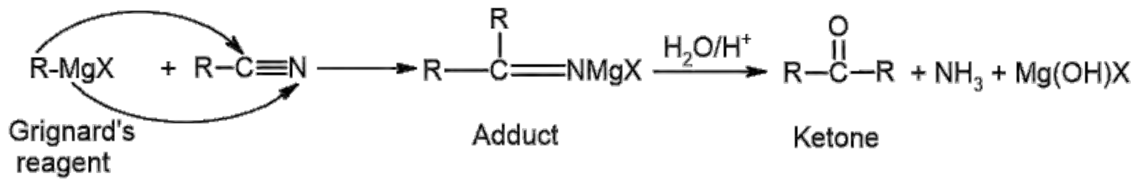
Fill the following table by studying the chemical equations given above.

General Reactants	General Products
…………………	……….+………..

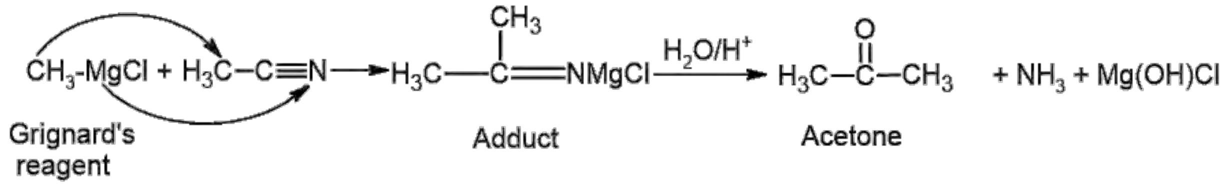
When a Grignard reagent reacts with hydrogen cyanide (HCN), it initially reacts with the acidic hydrogen in HCN to form a salt, followed by a nucleophilic addition reaction at the carbon atom of HCN. The overall result is the formation of an aldehyde (RCHO) after hydrolysis.

Action with RCN

Study the following chemical reacions and do the activities that follow.



$$R\text{-}MgX + R-C\equiv N \longrightarrow R-\overset{R}{\overset{|}{C}}=NMgX \xrightarrow{H_2O/H^+} R-\overset{O}{\overset{||}{C}}-R + NH_3 + Mg(OH)X$$



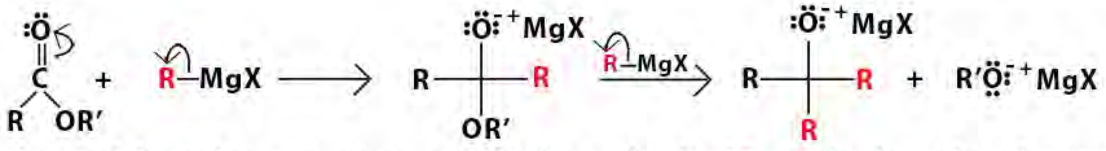
$$CH_3\text{-}MgCl + H_3C-C\equiv N \longrightarrow H_3C-\overset{CH_3}{\overset{|}{C}}=NMgCl \xrightarrow{H_2O/H^+} H_3C-\overset{O}{\overset{||}{C}}-CH_3 + NH_3 + Mg(OH)Cl$$

Grignard reagents react with nitriles (RCN) to form ketones through a two-step process: an initial addition reaction and a subsequent hydrolysis. The Grignard reagent attacks the nitrile's electrophilic carbon, forming an imine salt. This imine salt is then hydrolyzed in an acidic environment, yielding a ketone.

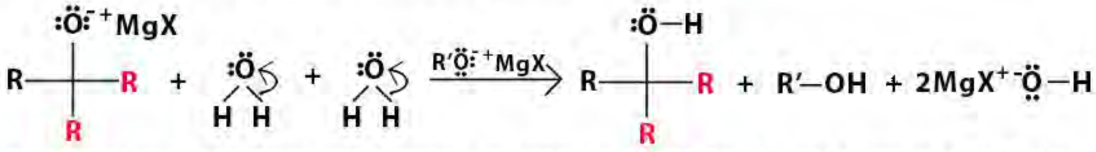
What are the differences between actions of Grignard's reagent with HCN and RCN?

SN	HCN+ RMgX	RCN + RMgX
1.		
2.		
3.		

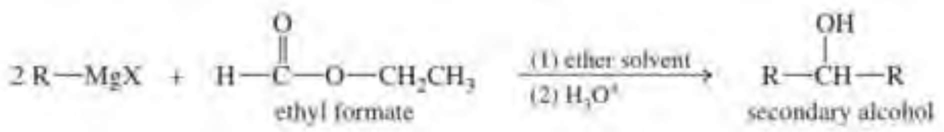
Action with ester

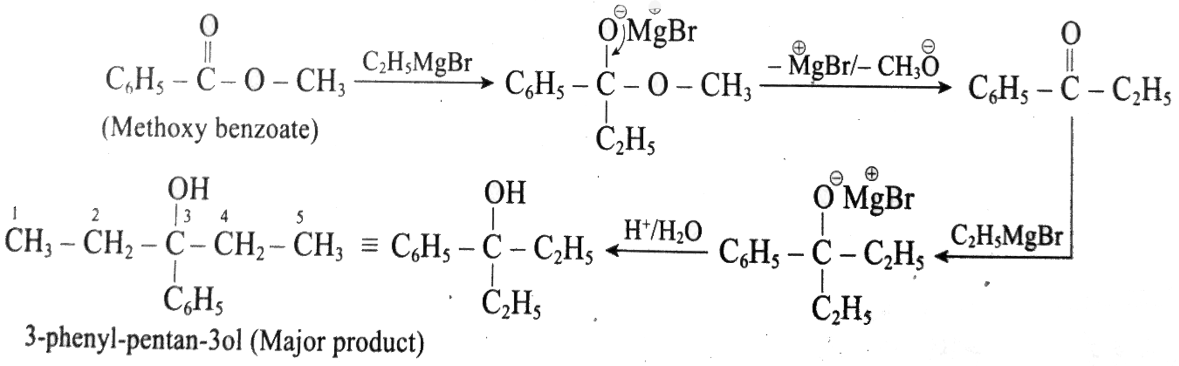


Nucleophilic carbon atom present in alkyl or aryl radical R attacks the carbonyl group (C=O) twice through single electron transfer

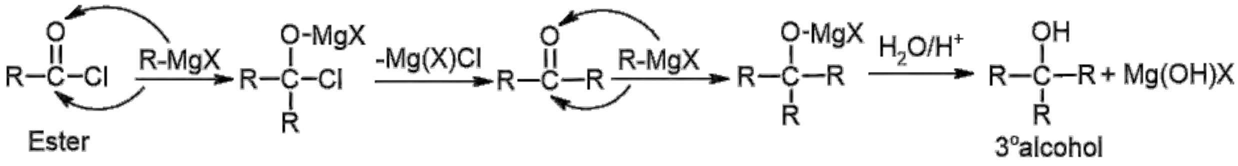


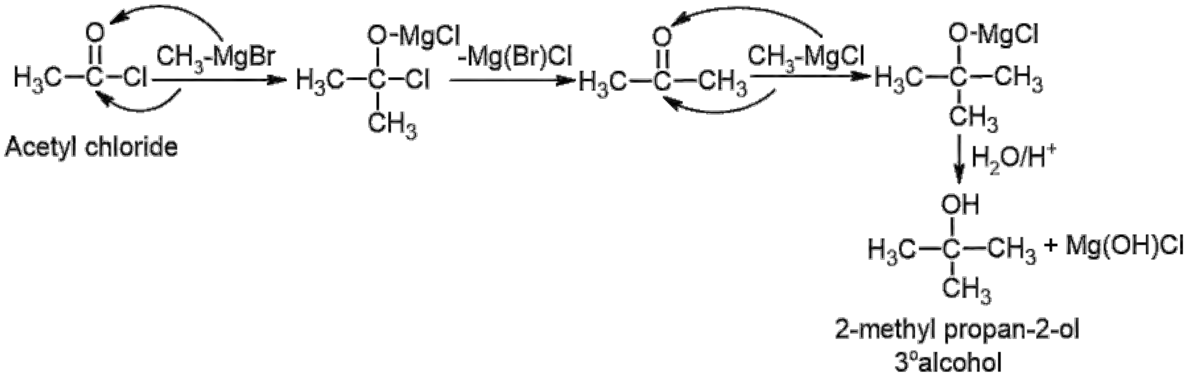
Protonation takes place in presence of water and acid producing tertiary alcohol as the main product





Action with acid chloride





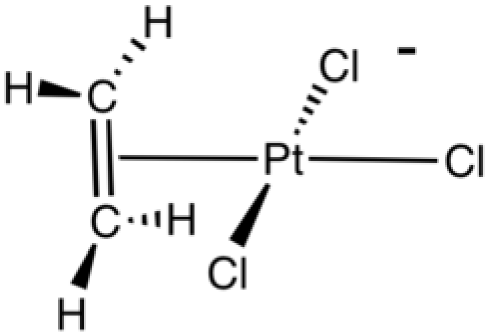
Tertiary alcohols are formed when acid chloride is treated with Grignard's reagent followed by acidic hydrolysis along with the byproduct magnesium hydroxyl halide.

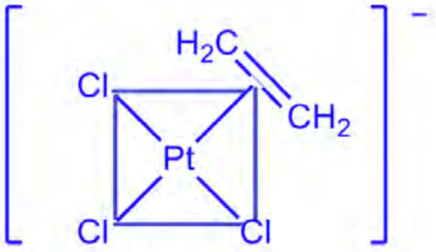
What are the differences between actions of Grignard's reagent with ester and acid chloride?

SN	RCOOR'+ RMgX	RCOCl + RMgX
1.		
2.		
3.		

Zeise’s salt

Zeise's salt, potassium trichloro (ethylene) platinate(II) monohydrate, is a pioneering organometallic compound with the formula $K[PtCl_3(C_2H_4)]\cdot H_2O$. It was discovered by William Christopher Zeise in 1830 and is significant in organometallic chemistry as one of the first examples of a transition metal alkene complex.





Structure of Zeise's Salt

Exercise

1. Which of the following reagent is suitable to obtain ethane from Grignard’s reagent?
   A. Ethanol B. Ethanal C. Ethanoyl chloride D. Ethyl magnesium bromide

2. What is Z in the following reaction sequence?
   $CH_3\text{-Mg-Br} + CH_3COCH_3 \xrightarrow{dry\ ether} Y \xrightarrow{H+/H2O} Z$
   A. 2-methyl Propan-2-ol C. 2-methyl Propanal
   B. 2-hydroxy propane D. 3-methyl propan-1-ol

3. Which of the following is the molecular formula of Ziese salt?
   A. $[PtCl_2(C_2H_4)]$ B. $[PtCl_3(C_2H_4)]$ C. $[PtCl_3(C_2H_6)]$ D. $[PtCl_3(C_2H_5)]$

4. What would be the product when methyl magnesium bromide is treated with HCN followed by hydrolysis?
   A. Methanoic acid B. Ethanoic acid C. acetaldehyde D. Formaldehyde

5. Choose the best alternative from the following.

Reactants	Condition	Products
M	Dry ether/Δ	$LiCH_3 + LiCl$
$CH_3COCl + CH_3MgBr$	H_2O/H^+	N
Ester + Grignard’s reagent	O	Secondary alcohol

A. M-Li+CH_3Cl, N-2-methyl-propan-2-ol, O- H_2O/H^+
B. M-LiCH_3+Cl_2, N-3-methyl-propan-2-ol, O- H_2O/H^+
C. M-Li+CH_3Cl, N-1-methyl-propan-1-ol, O- H_2O/H^+
D. M-Li+CH_3Cl, N-ethyl-propan-1-ol, O- H_2O/H^+

6. What is Z in the following chemical equation?

$$R\text{-}X + Mg \xrightarrow{dry\ ether/\Delta} Z$$

A. Alkyl magnesium
C. alkyl magnesium halide
B. Magnesium halide
D. Alkane

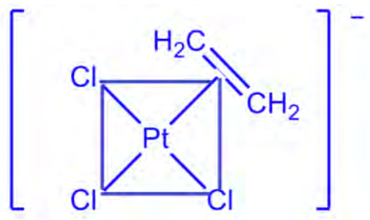
7. What is the chemical name of Zeise salt?
A. Potassium dichloro(ethylene) palatinate(I) monohydrate
B. potassium trichloro (ethylene) platinate(I) monohydrate
C. potassium trichloro (ethylene) platinate(II) monohydrate
D. potassium dichloro (ethylene) platinate(II) monohydrate

8. What happens when alkyl cyanide is treated with Grignard's reagent?
A. Aldehyde is formed
C. Ketone is formed
B. Alcohol is formed
D. Carboxylic acid is formed

Short Questions.

9. How is Grignard's reagent prepared? Explain with example. Can we prepare Grignard's reagent from ethane? Explain the process with suitable processes. Why can't we use water instead of ether?

10. Why the given compound is considered as organometallic compound? Writes its name and use. At which respect does it have similarities with Grignard's reagent?



11. What are organometallic compound? Give an example of each of organolithium, organocadmium and organocopper compounds. Explain the nature of bond formed in such compounds.

12. What happens when ;
    a. Grignard's reagent is treated with water?
    b. Ethyl ethanoate is treated with methyl magnesium chloride?
    c. Methyl magnesium chloride is heated with ethanoyl chloride?

13. Starting from Grignard's reagent (CH3MgBr), how would you prepare
    a. Methane
    b. Ethyl alcohol
    c. Acetic acid
    d. Isopropyl alcohol
    e. Propanol

14. How would you prepare Grignard's reagent from arylhalide? Write the structural formula with IUPAC name of each of the followings from C_3H_8O?
    a. Primary alcohol
    b. secondary alcohol
    c. Prepare these alcohols from Grignard's reagent.

Project Work:

Make a table in a chart paper, fill the following table based on the information given by the help of internet or other reference materials and present at your classroom then submit to your teacher.

Compounds	**Structure**	
Zeise Salt		
Tetraethyl lead		
Gilman reagent		
Zieglar-Natta catalyst		
Ferrocene		

Unit 18
Chemistry in the Service to Mankind

18.1: Introduction

1. Activity:
Observe the pictures of super market and answer the following questions based on your observation and knowledge-

Items in supermarket

a. List the name of some plastic items you observe in the super market and write their uses.
b. What is the role of chemistry in these plastic items you see in the market?
c. List the name of some common pesticides you can find in the supermarket.

a.	....
b.	....
c.	....

Chemistry plays a fundamental role in shaping human civilization by transforming raw materials into practical goods that impact our daily lives. By understanding chemical processes and principles, human has been able to create revolutionary breakthroughs. For instance, **polymers** are the fundamental components of innumerable goods, ranging from packaging materials to plastics and apparel. Similarly, chemical-based **medications** have dramatically improved health, extending life expectancy and saving lives. The development of synthetic **dyes** has transformed the **textile** business and added vivid colors to art, food, and other media.

Additionally, **pesticides** control the pests and have contributed to the security of food for expanding populations by boosting agricultural productivity. In addition to driving technological progress, chemistry also tackles real-world problems, improving the environment and our quality of life, as demonstrated by these examples.


Daily use polymer items


Use of Pesticide in agriculture


Drugs to cure disease

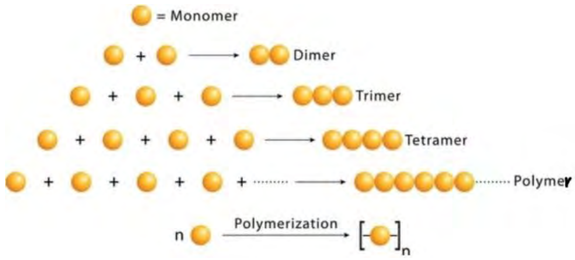

Dyes to provide color

18.2: Polymers

2. Activity:
Observe the items shown in the pictures and answer the following questions based on your observation and knowledge:
a. What do all items have common in them?
b. List the name of some polymer based items found in your classroom.

a.	....
b.	....

You are all familiar with the texture, flexibility, and appearance of everyday objects like plastic bottles, nylon ropes, woolen sweaters, and even switchboards. But do you know that all these materials are made up of long chains of repeating units? These repeating units are called **monomers**, and when they link together, they form long chains known as **polymers**. This process of linking monomers to create polymers is called **polymerization**. Polymers are everywhere around us, from the materials we use to the clothes we wear!



For, example,

$$n\text{CH}_2\text{=CH}_2 \xrightarrow{\textit{Heat, pressure of catalyst}} [\text{-CH}_2\text{-CH}_2\text{-}]_n$$

Ethene Polyethene

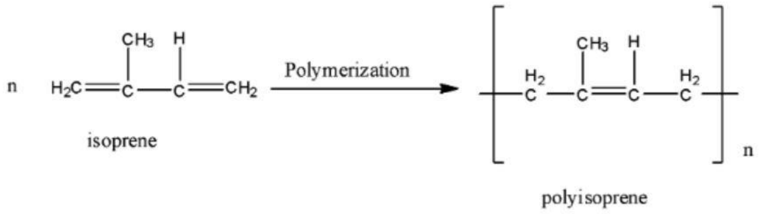
18.2.1: Classification of Polymers

Polymers can be classified in several ways based on their origin, structure and behavior. Some of them are discussed below:

A. Polymers on the basis of origin

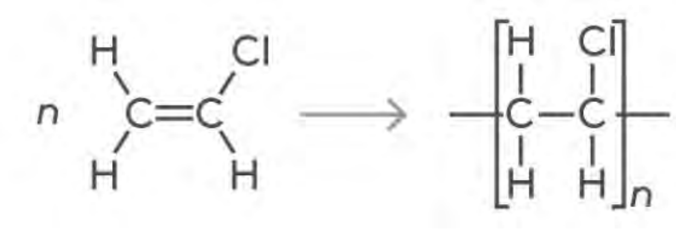
On the basis of origin, polymers are of two types. They are

i. Natural polymers: Polymers that are naturally found in plants and animals are called natural polymers. Starch, cellulose, protein, nucleic acid, natural rubber, etc. are some examples of natural polymers.



Natural rubber consists of polyisoprene

ii. Synthetic polymers: Polymers that are synthesized artificially in laboratory from different compounds are called synthetic polymers. They are designed to have specific properties and widely used in daily life. Polyvinyl chloride (PVC), Polystyrene, Nylon, Teflon, Bakelite, etc. are some examples of synthetic polymers.



Vinyl chloride **Polyvinylchloride (PVC)**

PVC pipe

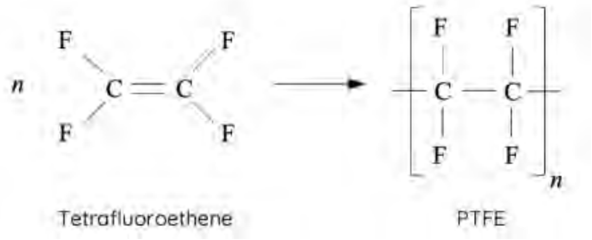
Test yourself

Q. Write the monomers of protein and nucleic acids.

B. Polymers on the basis of synthesis:

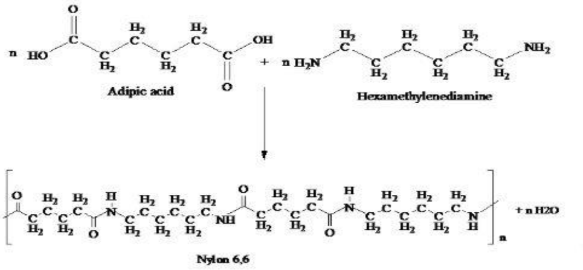
On the basis of synthesis polymers are of two types. They are

i. Addition polymers: The polymers formed by repeated addition of large number of same or different unsaturated monomers are called **addition polymers** and the process is called **addition polymerization**. These polymers are generally obtained from monomers containing double bond like alkenes. Polyethene, PVC, Polytetrafluoroethene (Teflon), Polystyrene, etc. are some examples of addition polymers.



Teflon (PTFE) products

ii. Condensation polymers: Polymers formed by the repeated condensation reaction between **two different functional groups** of monomers are called **condensation polymers** and the process is called **condensation polymerization**. In this process, each step of polymerization involves the **elimination of small molecules** such as water, carbon dioxide, ammonia, HCl, alcohol, etc. **Nylon-6,6,** Polyethylene terephthalate (PET) or **Terylene** and **Bakelite are some common examples of condensation polymers.**



Nylon rope

C. Polymers on the basis of molecular force:

On the basis of molecular force, polymers are of two types. They are-

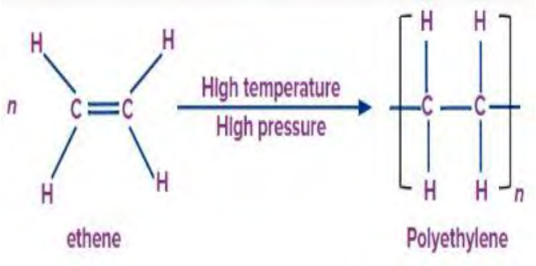
i. Elastomers: Polymers that readily stretch when force is applied and regain their original shape without deformation when a force is released are called **elastomers.** This is due to the fact that their polymer chains are flexible due to their loose coiling and a few cross-links. Neoprene, Buna-S, and natural rubber are some examples of elastomers.

ii. Fibers: Polymers having strong, thread-like structures, low elasticity, and great tensile strength are called **fibers**. They are stiff and long-lasting due to tightly packed, crystalline arrangement of their chains. Rayon, acrylic, polyester, and nylon are some examples of fibers.

18.2.2: Some synthetic polymers

Synthetic polymers are man-made materials produced chemically, in laboratories or in industries. These polymers are made to have certain qualities, such as durability, strength, flexibility, and resistance to heat or chemicals. From apparel and packaging to household goods and building materials, they are widely used in daily life. The monomers and applications of a few typical synthesized polymers are listed below.

1. Polythene (Polyethylene): The monomer of polyethne is ethene (also known as ethylene).



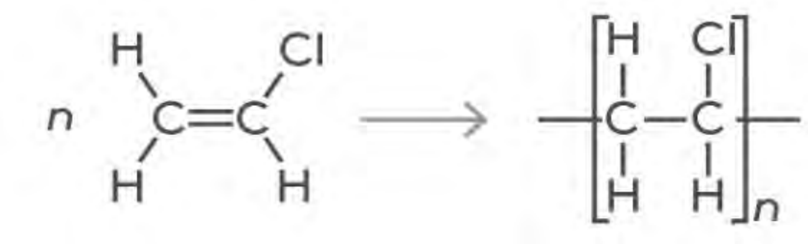
Polyethene bag

Uses: It is widely used in the manufacturing of household items like dustbins, carpet, buckets, packaging materials, cable insulations and various types of containers.

Test yourself

Q. What type of polymer is polyster?

2. PVC (Polyvinyl chloride): The monomer used to form PVC is chloroethene (also known as vinyl chloride).

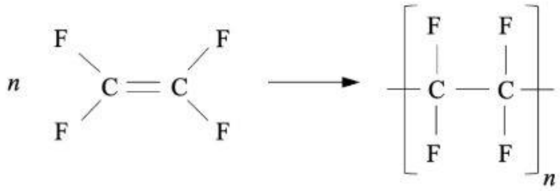


Vinyl chloride

PVC

Uses: It is widely used in plumbing pipes, cable insulation, window and door frames, flooring, medical equipment like IV bags, raincoats, synthetic leather, packaging materials, and even credit cards due to its strength, durability, and resistance to chemicals.

3. Polytetrafluoroethene (Teflon or PTFE): The monomer used to form Teflon is tetrafluoroethene.

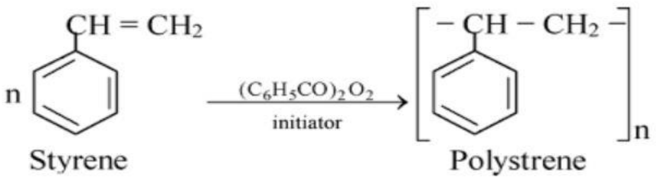


Tetrafluoroethene PTFE

Teflon coated cookware

Uses: It is used as a non-stick coating on cookware, and in electrical insulation and chemical-resistant clothing due to its heat resistance and low friction.

4. Polystyrene: The monomer used to form polystyrene is styrene.



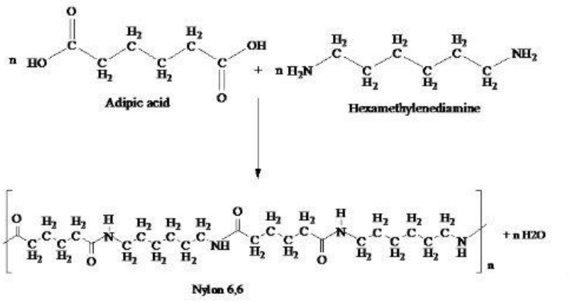
Polystyrene scale

Uses: It is used for making disposable cutlery, foam packaging, insulation materials, and lightweight containers due to its rigidity and insulating properties.

Polystyrene cutlery items

Polystyrene keyboard

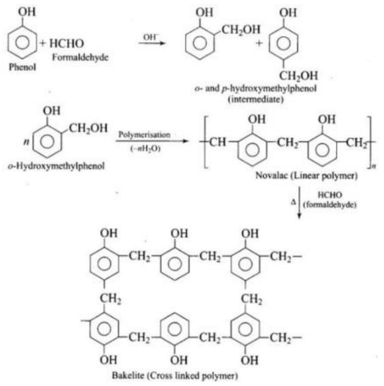
5. Nylon-6,6: The monomer used to form nylon-6,6 are hexanedioic acid (i.e, Adipic acid) and hexane-1,6-diamine (i.e, hexamethylenediammnie).



Nylon rope

Uses: It is used in making textiles, ropes, parachutes, seat belts, carpets, and mechanical parts due to its high strength, elasticity, and resistance to abrasion and heat.

6. Bakelite: The monomers used to form bakelite are formaldehyde and phenol.



Switch board

Uses: It is used for making electrical switches, combs, plugs, handles of cooking utensils, telephone casings, and other heat-resistant and non-conductive items due to its hardness and insulating properties.

18.3: Dyes

3. Activity:

Observe the picture of different color shown below and answer the following questions based on your knowledge.

a. Do all the colors come from same source?

b. What materials do these colored items is made up of?

a	**...**
b	**..**

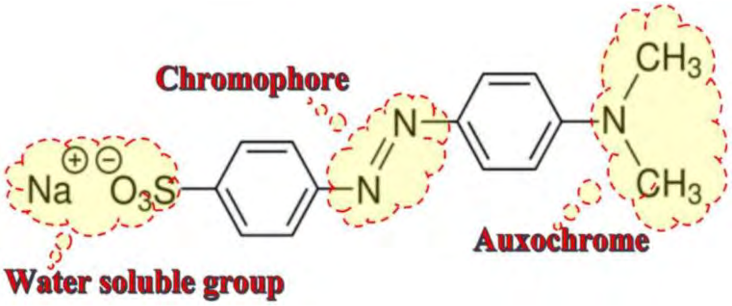
Various materials, including food, paper, and textiles, can be colored using dyes. These coloring agents can be derived from natural sources like plants, animals, or minerals, such as cochineal from insects or indigo from plants or artificially created in laboratories. These coloring substances are known as **dyes**, which are chemicals that impart color to the material they are applied to. For ages, various cultures have utilized natural dyes to color textiles and food products. On the other hand, because of their vibrant hues, affordability, and durability, synthetic dyes are made artificially in laboratories and are widely utilized in industries today. The process of applying dye to a material is known as **dying** which is important in the sectors like fashion, arts and food production. Cost, color brilliance, and environmental concerns are some of the variables that frequently influence the choice between using natural versus synthetic dyes. Indigo, Turmeric, Cochineal, Henna, Madder, etc are some examples of natural dyes and Aniline Blue, Methyl Orange, Azo dyes, Crystal violet, Rhodamine B, Acid Red 1 etc, are some examples of synthetic dyes.

18.3.1: Structural Features of Dyes

Structural features of dyes: A dye consists of two main constituents. They are-

1. Chromophore: A chromophore is the part of the dye molecule which is responsible for the color of the dye. It usually contains conjugated double bonds or other function groups. For example, p-quinoid group, -CO-(carbonyl group), >C=C< (alkene), -N_2-(azo group), -NO_2 (nitro group), etc.

2. Auxochrome: An auxochrome is a functional group which does not produce color on its own but when present along with chromophore, enhances the intensity or shifts the color of the dye. For example, -OH, -COOH, -SO_3H, -NH_2, -NHR etc.



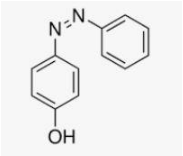
Methylorange

18.3.2: Classification of Dyes

There are several ways to categorize dyes, including by their chemical composition (structure), mode of application, or affinity for particular fibers. The following is a standard classification of dyes according to their chemical structure and mode of application:

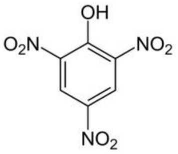
1. Classification of dyes based on structure (Chemical constituent): On the basis of chemical constitution, dyes are classified into different classes. Some of them are-

i. Azo dyes: These are the synthetic dyes characterized by the presence of one or more azo group (-N=N-), which are responsible for their bright colors. Azo group acts as chromophore in these types of dyes. These dyes are used in dying textiles, leather, food and cosmetics. For example, p-Hydroxyazobenzene, p-Aminoazobenzne, Methyl Orange, Congo Red etc.



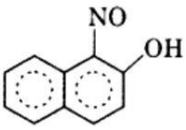
p-Hydroxyazobenzene

ii. Nitro dyes: These are the synthetic dyes characterized by the presence of one or more nitro group (-NO_2), which are responsible for their bright colors. Nitro group acts as chromophore in these types of dyes. These dyes are used in dyeing wool, silk and paper. For example, Picric acid (2,4,6-trinitrophenol), Martius Yellow (2,4-dinitro-1-naphthol), Naphthol Yellow S etc.



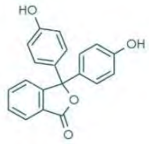
Picric acid

iii. Nitroso dyes: These are the synthetic dyes characterized by the presence of one or more nitroso group (-NO), which are responsible for their bright colors. Nitroso group acts as chromophore in these types of dyes. These are used in dying textiles but more commonly used in analytical applications due to their sensitivity to metal ions. For example, Nitroso Green B, Fast Green O (Dinitrosoresorcinol), Gambine Y (α-nitroso-β-naphthol), Cupferron,etc.



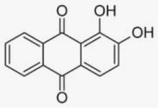
Gambine Y

iv. Phtahlein dyes: These are the synthetic dyes formed by condensing phthalic anhydride with phenols. Their **chromophore** is a conjugated **quinonoid structure** that develops under basic conditions. These dyes are coomonly used as pH indicator, bioogical staining and dye tracing. For examples- Phenolphthalein, Fluorescein, Thymolphthalein etc.



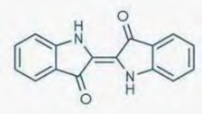
Phenolphtahlein

v. Antraquinone dyes: These are synthetic dyes derived from anthraquinone, containing a conjugated system of aromatic rings and carbonyl groups that act as the chromophore. These dyes are commonly used in textile dyeing, ink production, and biological staining due to their bright colors and excellent stability.
For examples-Alizarin, Indanthrene Blue, Quinizarin, etc.



Alizarin

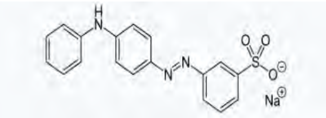
vi. Indigo dye: These are natural or synthetic dye with a deep blue color, historically obtained from the plant *Indigofera*, and characterized by a conjugated double bond system responsible for its color. These dyes are commonly used in dyeing denim fabrics, especially for blue jeans, as well as in textile printing and traditional fabric arts. For examples- Indigo, Tyrian Blue (historical variants), etc.



Indigo

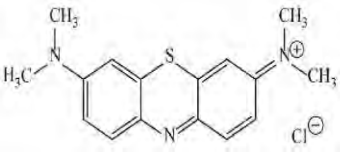
2. Classification of dyes based on mode of application: On the basis of mode of applications, dyes are classified into different classes. Some of the major classes include-

i. Acid dyes: These are the anionic dyes containing azo or anthroquinone chromophore groups, which works in acidic medium to produce bright water soluble colors with good fastness. They are used for dyeing protein fibers like wool, silk and nylon. For example, Acid Metanil Yellow, Acid orange 7, Acid Red 88, etc.



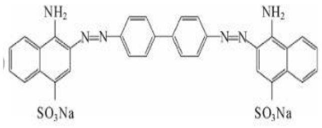
Acid Metanil Yellow

ii. Basic dyes: These are the cationic dyes that usually contain amino group as a chromophore, which works in basic or neutral medium to produce bright intense color. They are used for dyeing acrylic fibers as well as silk, wool, paper and leather. For example, Malachite Green, Methylene Blue, Crystal Violet, etc.



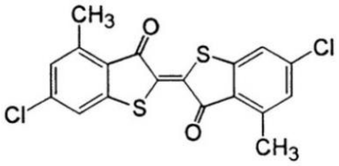
Methylene Blue

iii. Direct dyes: These are the anionic dyes that typically contain azo group or anthroquinone as chromophore, which works in neutral or slightly alkaline medium to produce bright color with moderate fastness. They are applied directly to cellulose fibers like cotton and rayon without the need for mordant. For example, Congo Red, Direct Blue 1, Direct Red 28, etc



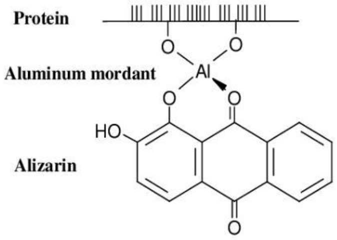
Congo Red

iv. Vat dyes: These are insoluble dyes that contain azo, anthroquinone or other chromophores. They are typically **reduced to a soluble form** in an alkaline medium, applied to fibers, and then **oxidized back to their insoluble form** to produce **bright, fast colors.** They are used for dyeing cellulose fibers like cotton and denim. For example, Vat Red 1, Vat Blue 1, Indigo, etc



Vat Red 1

v. Mordant dyes: These are the dyes that require mordant (a metallic salt) to help fix onto the fabrics. Salts of metals such as Al, Cr, Fe, Ba etc are common mordants. The metal ion binds to the fabric first and then dyes coordinate to the metal ions resulting in the coloring of fabrics. The same dye can give different color with different metal ions. For example, Alizarin gives red rose color with Al but blue color with Ba. They are used for dyeing wool, cotton and nylon. If the dye is basic then acidic mordant is used and vice versa. For example, Alizarin, Cochineal, Madder, etc



Alizarin with Al salt

vi. Disperse dyes: These are water insoluble, non ionic dyes that typically contain azo, anthroquinone or other similar chromophores. They primarily applied to synthetic fibers such as polyster, nylon and acetate. Since they are insoluble in water, disperse dyes are applied in the form of a colloidal dispersion. When fabric is immersed in colloidal form of dyes fine particles are absorbed in the crystal structure of fabrics imparting color to the fabrics. For example, Disperse Blue 1, Disperse Yellow 3, Disperse Orange 25, etc.

Other dyes are- reactive dyes, azoic dyes, sulphur dyes, natural dyes etc.

Summary Table for Modes of Application:

Dye Type	**Fiber Type**	**Mode of Application**	**Example(s)**
Acid Dyes	Protein fibers	Applied in **acidic medium**	**Acid Blue 9**, **Acid Red 88**
Basic Dyes	Synthetic fibers	Applied in **alkaline/neutral medium**	**Methylene Blue**, **Malachite Green**
Direct Dyes	Cellulose fibers	Applied directly to fibers (no mordant needed)	**Direct Blue 1**, **Congo Red**
Vat Dyes	Cellulose fibers	Reduced to soluble form, then oxidized	**Indigo**, **Vat Blue 1**
Mordant Dyes	Protein & Cellulose fibers	Requires **mordant** (metallic salt) to fix the dye to fibers	**Alizarin**, **Cochineal**, **Madder**

Disperse Dyes	Synthetic fibers	Applied in **dispersed form** in an aqueous bath	**Disperse Yellow 3, Disperse Blue 1**
Reactive Dyes	Cellulose fibers	**React chemically** with the fiber	**Procion**, **Reactive Blue 19**
Sulfur Dyes	Cellulose fibers	Reduced and oxidized for application	**Sulfur Black 1, Sulfur Brown 6**
Natural dyes	Various fibers	Requires **mordant** (metallic salt) to fix the dye to fibers	**Alizarin**, **Cochineal**, **Madder**
Azoic dyes (Ingrain Dyes)	Cellulose fibers	Applied by **coupling reaction** in **alkaline medium**	**Fast Yellow 2G**, **Orange 2G**

18.4: Drugs

4. Activity:

Observe the pictures of pharmaceutical items (i.e, drugs) carefully and answer the following questions based on your observation and knowledge:

a. What are the drugs shown in the figure 1 and 2 used for?
b. What do you mean by the term "drugs"?
c. Every medicine is drug but the reverse is not true, why?

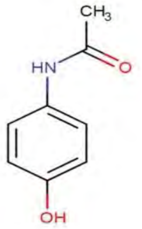
Fig(1): Insecticide

Fig(2): Cetamol

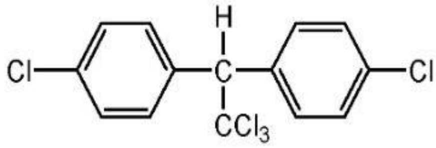
a.	**..**
b.	**..**
c.	**..**

Imagine you're feeling unwell—perhaps with a headache, a cold, or even an infection. What do you do? Most likely, you reach for a **medicine** to help you feel better. But have you ever wondered how these medicines actually work inside your body? How can something like a **pill** or **liquid** help relieve your pain or cure an infection? These substances are called **drugs**, and they are carefully designed to interact with our bodies in specific ways. Thus, drug is a substance used for prevention, diagnosis and treatment of disease. The **World Health Organization (WHO)** defines a drug as- **"any substance or product that is used or intended to be used to modify or explore physiological systems or pathological states for the benefit of the recipient".** Every medicine is drug but not every drug is medicine.

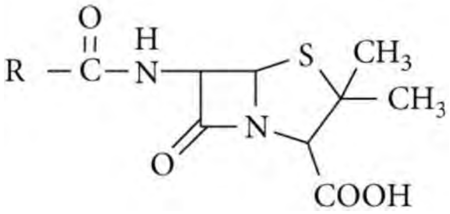
There are numerous ways to take drugs, including tablets, capsules, liquids, and even injections. Whether the goal is to combat infection, lessen pain, or manage a chronic illness like diabetes, each one is designed to address a particular issue. They know what to do, but how? The secret is in the active chemical components of the medication, which are carefully chosen and made according to **chemistry principles**. **Painkillers**, such as **acetaminophen**, contain chemicals that block the brain signals that cause pain, whereas **antibiotics**, such as **penicillin**, are composed of chemical structures that can kill hazardous germs.



Paracetamol



DDT



Penicillin

18.4.1: Characteristics of Drugs

A perfect drug that is meant for medication should have following characteristics:

i. The drug should have localized and systemic effect.
ii. The drug should be effective and efficient.
iii. The drug should be non-toxic and non-irritant.
iv. The drug should have no or minimum side effect.
v. The drug should not disturb the physiology of the host.
vi. The drug should not cause the host cell to become resistant to it after its prolonged use.
vii. The drug should not cause any harm to the host tissue.
viii. The drug should be cost effective and easily available.

Test yourself

Q. What do you mean by medication?

18.4.2: Natural and Synthetic drugs

5. **Activity:**

Observe the given two pictures and answer the following questions based on your knowledge-

a. What are the differences between these drugs?
b. Discuss the advantages and disadvantages of these drugs.

a.	....
b.	....

On the basis of source of origin drugs are broadly classified into two main categories. They are-

1. Natural drugs: Drugs that are derived naturally from plants, animals and minerals are called natural drugs. These drugs are frequently used in daily life to cure common illnesses. For example, some people use **peppermint** to treat digestive problems, **aloe vera** to treat skin disorders, **turmeric** to reduce inflammation, and **ginger** to relieve nausea etc. In addition to their everyday uses, many natural drugs serve as the foundation for modern prescription medications and play a vital role in healthcare systems around the world.

Atropine

Atropa belladonna

Morphine

Papaver somniferum

Honey

Honey bee

Saline solution

Sodium chloride

Test Yourself

Q. How can ginger and garlic, both commonly found in kitchen, can be used as natural remedies?

Q. Can you write the traditional importance of cumin (jeera)?

List of some plant based drugs-

Drug name	Plant source	Therapeutic use
Morphine	*Papaver somniferum* (Opium poppy)	Pain relief (analgesic)
Quinine	*Cinchona officinalis* (*Cinchona* bark)	Treatment of malaria
Atropine	*Atropa belladonna* (Deadly nightshade)	Dilates pupils, treats bradycardia (smooth muscles, relaxant)
Caffeine	*Coffea arabica* (Coffee plant), *Camellia sinensis* (Tea)	CNS (Central Nervous System) stimulant
Castor Oil	*Ricinus communis* (Castor bean plant)	Laxative, skin moisturizer, anti-inflammatory
Pilocarpine	*Pilocarpus jaborandi* (Jaborandi plant)	Treatment of glaucoma and dry mouth, uterine atony

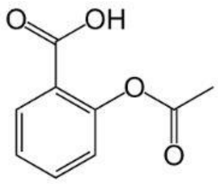
List of some animal based drugs-

Drug name	Animal source	Therapeutic use
Cod Liver Oil	Liver of cod fish (*Gadus* species)	Source of vitamins A and D, used in bone and eye health
Antivenoms	Antibodies produced in horses or sheep	Treatment of venomous bites and stings
Hirudin	Salivary glands of leeches (*Hirudo medicinalis*)	Anticoagulant (inhibits thrombin)
Lanolin (Wool Fat)	Sebaceous secretions from sheep wool	Emollient in skin ointments, creams, and cosmetics
Honey	*Apis mellifera* (Bees)(from nectar of flowers)	Antibacterial, wound healing, soothing sore throat, cough relief
Gelatin	Collagen from animal bones and skin	Used in capsules, wound dressings, and drug delivery
Thyroxine (T4)	Thyroid glands of animals (historically pigs)	Treatment of hypothyroidism

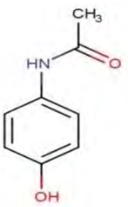
List of some mineral based drugs-

Drug name	Mineral source	Therapeutic use
Epsom Salt	Magnesium sulfate (mineral)	Laxative, muscle relaxation, and foot baths for sore muscles
Sodium Chloride	Salt (mineral)	Used in saline solutions for hydration and nasal irrigation
Sodium Bicarbonate	Sodium carbonate (mineral)	Antacid for heartburn, treatment for metabolic acidosis, and as a systemic alkalizer
Magnesium Hydroxide	Magnesium (mineral)	Antacid for heartburn and indigestion, laxative
Alum	Potassium alum (mineral)	Used as an astringent, in water purification, and in some cosmetics

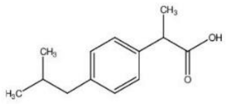
2. Synthetic drugs: In contrast to natural sources, synthetic drugs are produced artificially in laboratories using chemical methods. The purpose of these medications is to treat particular medical disorders or to replicate or intensify the effects of natural compounds. For example, **aspirin**, a widely used pain reliever and anti-coagulant, was developed to imitate the pain-relieving effects of compounds found in **willow bark**. Several illnesses, including as infections, chronic illnesses, and mental health issues, are frequently treated with synthetic drugs. Unlike natural drugs, which often come from plants, animals, or minerals, synthetic drugs are specifically engineered for targeted therapeutic action, making them an essential part of modern medicine. Often more reliable, powerful, and simpler to produce, they make a substantial contribution to healthcare systems around the world. Some examples of synthetic drugs are given below-



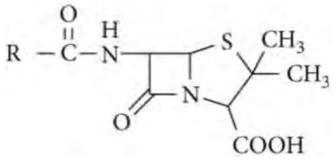
Aspirin



Paracetamol



Ibuprofen



Penicillin

Test yourself

Q. Write the name of any two synthetic drugs that are commonly used in your home, especially by elder family members.

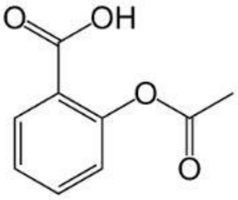
18.4.3: Classification of some common group of drugs:

Drugs are systematically classified into various groups based on their source of origin, therapeutic effects, mechanism of action, chemical structures, or anatomical targets. Some common groups of drugs are-

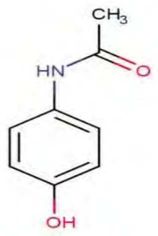
1. NSAIDs (Non-Steroidal Anti-inflammatory Drugs): Non-steroidal anti-inflammatory drugs, or NSAIDs, are a class of drugs that lower fever, inflammation, and pain without the use of non steroidal nucleus. Three main therapeutic effects of NSAIDs are as follows:

- **Pyrexia (Fever):** Fever refers to rise in body temperature greater than normal body temperature (i.e, 37 ^{0}C or 98.6 ^{0}F).
- **Pain:** Pain is sensory or emotional experience associated with potential and actual tissue damage.
- **Inflammation:** Inflammation is protective response to tissue damage and is characterized by pain, inflammation, redness, hot and loss of function.

i. Antipyretics: The drugs that are used to lower the body temperature during high fever are called antipyretics or antipyretic drugs. Common antipyretics include paracetamol, aspirin, etc.

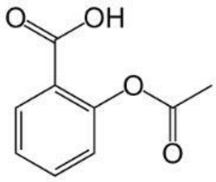


Aspirin

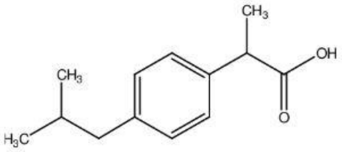


Paracetamol

ii. Analgesics: The drugs that are used to relieve pain without causing loss of consciousness are called analgesics or analgesic drugs. Common analgesics include aspirin, ibuprofen, paracetamol, etc.



Aspirin



Ibuprofen

iii. Anti-inflammatory drugs: The drugs that are used to lessen inflammation, which is the body's reaction to irritation, infection, or injury, are called anti-inflammatory drugs. These drugs are commonly used to treat conditions such as arthritis, muscle injuries, and inflammatory diseases. Common anti-inflammatory drugs are ibuprofen, aspirin etc.

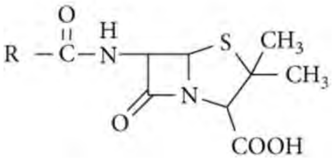
Do you know?

- All NSAIDs generally possess antipyretic, analgesic and anti-inflammatory properties. But the drugs under this are chosen on the basis of their major action. For example, paracetamol has good antipyretic effect but poor inflammatory action. Similarly ibuprofen is known for its strong anti-inflammatory action rather than antipyretic effect.
- **Analgesic drugs** are primarily focused on **pain relief**, while **anti-inflammatory drugs** not only relieve pain but also reduce the underlying **inflammation**. Many drugs, like **ibuprofen** and **aspirin**, serve both purposes as they have both **analgesic and anti-inflammatory properties**.

2. **Antibiotics:** Antibiotics are a class of drugs used to treat infection caused by bacteria. These drugs are chemical substances produced from microorganism (fungi, bacteria, & actinomycetes) and are used to kill or inhibit the growth of microorganisms when used in small concentrations. Common antibiotics include penicillin, streptomycin, chloramphenicol, vancomycin, etc.

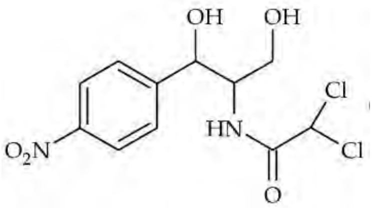
   On the basis of spectrum of activity, antibiotics are of two types. They are-

a. Narrow spectrum antibiotics: Antibiotics that are effective against limited range of bacteria (**either gram positive or gram negative**) are called narrow spectrum antibiotics. Such antibiotics target only specific group of bacteria**.** Common narrow spectrum antibiotics include penicillin, streptomycin, vancomycin, etc.



Pinicillin

b. Broad spectrum antibiotics: Antibiotics that are effective against wide range of bacteria (both gram positive and gram negative bacteria) are called broad spectrum antibiotics. Commonly used broad spectrum antibiotics include chloramphenicol, tetracycline, etc.



Chloramphenicol

Do you know?

Penicillin, the first widely used antibiotic, was discovered by **Alexander Fleming** in 1928 when he noticed that the mold *Penicillium notatum* (now *Penicillium chrysogenum*) inhibited bacterial growth. This discovery revolutionized medicine, marking the beginning of the antibiotic era and saving millions of lives from bacterial infections.

3. Antiseptics and Disinfectants: Antiseptic and disinfectant are the drugs used to kill or suppress the growth of microorganisms. Although they have similar antimicrobial action, they differ primarily in their application.

- **Antiseptics** are applied on living tissues such as skin, wound, cuts to control the infection caused by microorganisms. Common antiseptics include alcohol (iso-propyl alcohol), Povidone iodine (Iodine solution), hydrogen peroxide, 1% $KMnO_4$, phenolic compounds (like phenol, thymol, picric acid, p-chloro-m-xylenol) etc.

p-chloro-m-xylenol (Dettol)

Povidone iodine (Betadine)

- **Disinfectants** are applied on non-living (inanimate) objects like floor, instruments and swimming pool, etc. to reduce the risk of contamination or infection. Common disinfectants include bleach (sodium hypochlorite), formaldehyde, chlorine, bithinol, 1% phenol, etc.

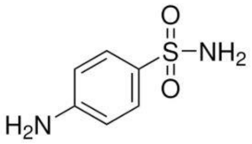
Chlorine

Test yourself

Q. Can you use dettol as an antiseptic and a disinfectant?
Q. What is the purpose of adding chlorine to drinking water?

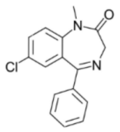
4. Other important class of drugs:

i. Sulpha Drugs (Sulfonamides): **Sulpha drugs are synthetic drugs used to treat bacterial infection. Actually they were the first antibiotics used before development of penicillin.** For example, sulfanilamide, sulfadiazine, sulphagunadine etc.



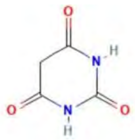
Sulphanilamide

ii. Tranquilizers: Tranquilizers are psychoactive drugs used to lower the stress, anxiety and mental disorder. For example, diazepam, equanil, etc.



Diazepam

iii. Sedatives & Hypnotics: Sedatives are the drugs that cause drowsiness and calm the brain activity without causing sleep whereas hypnotics are the drugs that calm an individual inducing normal sleep. For example, barbiturates (like phenolbarbitone), benzodiazepines (like Diazepam, Alprazolam, Lorazepam, Nitrazepam), etc.

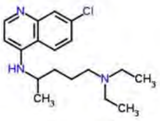


Barbituric acid

Do you know?

The sedatives and hypnotics action can differ mainly by dose, rather than by drug class. For example, Diazepam, when given in low dose, acts as sedative, while, in higher dose, it produces hypnotic effect.

iv. Antimalerial drugs: Antimalerial drugs are used to prevent or treat malaria disease caused by plasmodium parasite transmitted by mosquitoes. For example, chloroquine, quinine, artemisinin, mefloquine etc.



Chloroquine

v. Antacids: Antacids are weak bases that neutralize hyperacidity. For example, $NaHCO_3$, $Mg(OH)_2$, $Ca(OH)_2$ etc.

Antacid ($NaHCO_3$)

18.4.4: Habit-forming drugs and drug addiction

Repetitive use of medications that cause physical or psychological dependence is referred to as habit-forming or addictive. These include stimulants (like cocaine and methamphetamine), sedatives (like benzodiazepines), opioids (like heroin and prescription painkillers), nicotine, alcohol, and some prescription drugs. The signs of addiction, commonly referred to as substance use disorder, include compulsive drug-seeking, tolerance development (requiring larger dosages to have the same effect), and withdrawal symptoms when the drug is stopped. Complex interplay between psychological, environmental, and hereditary factors, play a role in the development and progression of addiction. For instance, individuals with a family history of addiction or those with underlying mental health conditions may be at higher risk. The effects of addiction are profound, impacting not only the individual but also their families and communities. Health consequences can range from chronic diseases, such as liver or heart disease, to mental health disorders like anxiety and depression. In order to address the psychological as well as the physical components of addiction, treatment usually consists of a mix of counseling, support groups, and medicinal intervention. Drug addiction is less common when preventive measures including education, early intervention, and community support are implemented.

Drug addiction

18.4.5: Pesticides (Insecticide, herbicide and fungicide)

Use of pesticides in agriculture

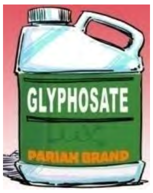
Many living organisms such as insects, weeds, herbs, fungi, rodents etc, that is harmful to human, animals and crops. These organisms are called **pests.** In order to manage them certain chemicals used which are called **pesticides**. Pesticides are designed to kill, repel or control the pests and play a crucial role in agriculture and public health. For example, DDT, Malathion, BHC, Parathion, Zinc phosphide, ANTU etc.

Categories of pesticides include:

- Insecticides (for insects),
- Herbicides (for weeds),
- Fungicides (for fungi),
- Rodenticides (for rodents) etc.

- **Insecticides:** Insecticides are those pesticides that are used to kill or control insects. They are commonly applied to protect crops from insects and also used to control insects borne diseases like malaria, dengue etc. Some examples of insecticides are- DDT, BHC, Malathion, Parathion, etc.

- **Herbicides:** Herbicides are those pesticides that are used to kill or control the growth of unwanted plants that are harmful to the crops. They are widely used in fields, garden and lawns to improve crop productivity. They are also used to reduce the competition for nutrients, sunlight and water. Some examples of herbicide are- Glyphosate, 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-Trichlorphenoxyacetic acid (2,4,5-D),etc.



- **Fungicides:** Fungisides are those pesticides that are used to kill or control the growth of fungi. They are mainly used to protect plants from diseases like mildew, rust, and blight. They are also used to stop spoilage of stored fruits, foods, vegetables and grains. Some examples of fungicides are- Trichloronitromethane (Chloropicrin), Aluminium phosphide, copper sulphate soliution, Bordeux mixture etc.

Bordeux mixture ($CuSO_4$ + Lime)

Test yourself:

Q. What is Bordeux mixture? Why is it used?
Q. List one example of insecticide, herbicide and fungicide.
Q. What are the environmental effects of pesticides?

Exercise

A. Multiple choice questions

1. Which of the following is addition polymer?
   a. Bakelite b. Nylon-6,6 c. Protein d. Polyethne

2. What type of polymer is Nylon-6,6?
   a. Addition polymer b. Natural polymer c. Condensation polymer d. Homopolymer

3. Pick out the natural polymer.
   a) Cellulose b) Teflon c) PVC d) Nylon

4. Name the monomers present in Nylon-6,6.
   a. Tetrafluoroethene b. Phenol and formladehyde
   c. Adipic acid and hexamethylene diamine d. Hexamethylene diamine and phenol

5. Which of the following property is suitable for classifying fibers?
   a. Tensile strength b. Elasticity c. Rigidity d. Crystallinity

6. Which of the following chromophore is present in azo dyes?
   a. -OH b. -N=N- c. $-NO_2$ d. Anthraquinone

7. Which of the following dye is applied in acidic medium to protein fibers such as silk and wool?
   a. Vat dyes b. Mordant dyes c. Basic dyes d. Acid dyes

8. Pick out the vat dye.
   a. Crystal violet b. Congo red c. Indigo d. Malachite green

9. Which class of following dye requires salts of metals to fix the dye onto the fabrics?
   a. Reactive dye b. Mordant dye c. Disperse dye d. Acid dye

10. Which of the following is an example of basic dye?
    a. Methylene blue b. Eosin c. Alizarin d. Congo red
11. Which dye form covalent bond with fabrics during application?
    a. Vat dye b. Reactive dye c. Disperse dye d. Acid dye

12. Which of the following is true for drugs?
    a. Drugs are highly toxic
    b. Drugs are chemically unstable
    c. Drugs are expensive and hard to produce
    d. Drugs should selectively act on target cell

13. Which of the following is a natural drug?
    a. Paracetamol b. Morphine c. Penicillin d. Aspirin

14. Which of the following drug is used to get relieve from pain and fever?
    a. Ibuprofen b. Diazepam c. Aspirin d. Amoxicillin

15. Which of the following drug is used to treat bacterial infection?

a. Antacids b. Tranquilizer c. Antipyretics d. Antibiotics

16. Which of the following can result from long term drug abuse?

a. Support of family b. Increase learning ability

c. Liver and brain damage d. Improved immune system

17. Which of the following pesticide is used to kill cockroach?

a. Fungicide b. Insecticide c. Germicide d. Weedicide

18. Which chemical is commonly used as herbicide?

a. DDT b. Bordeaux mixture c. 2,4-D d. Permethrin

19. Which of the following is an example of insecticide?

a. Sulphur b. DDT c. Captan d. ANTU

B. Short answers questions:

20. Give reason,
    a. Polyethene is adition polymer whereas bakelite is condensation polymer..
    b. PVC is homolpolymer whereas Nylon is copolymer.

21. Define pest and pesticides with example.

22. What are elastomers and fibers? Give example of each.

23. Write the monomers of- PVC, polyethene, teflon, bakelite and nylon.

24. Differentiate between-
    a. Addition polymer and condensation polymer
    b. Natural dyes and synthetic dyes
    c. Natural drugs and synthetic drugs

25. What are insecticides and fungicides? Give example of each.

26. What do you mean by chromophore and auxochrome? Give example of each.

27. Write the uses of each-

a. PVC b. Mordant dye c. Herbicide d. Nylon-6,6

28. Draw the structure of paracetamol and aspirin.

29. Define-
   a. Antibiotics b. analgesics c. Pesticides d. Azo dyes d. Antabase

30. What are dyes? Give any two examples of natural dyes.

31. What are broad and narrow spectrum antibiotics? Give example of each.

32. How do antiseptics differ from disinfectants?

33. What are sulpha drugs? Give example.

34. Write the distinction between direct dye and mordant dye.

C. Long answer question:

35. What are drugs? Write the characteristics of drugs.

36. Write a note on drug addiction and suggest some preventive measures.

37. What are dyes? Discuss various types of dyes on the mode of their applications.

38. What is polymer? Classify polymers on the basis of monomer units.

39. "All medicines are drugs but all drugs are not medicines". Justify the statement.

PROJECT WORK

1. Make a poster showing classification of Polymers and dyes.
2. Conduct an interview with a local pharmacist and prepare a project report on the common drugs used in your area.
3. Conduct an interview with a local agriculture officer and prepare a project report on the common pesticides used in your area. Also list the pros and cons of using pesticides.
4. Visit a food industry and prepare a project report on the common dyes used in food products.

Unit 19
Cement

19.1: Introduction

1. Activity:
A part of construction site is shown in the picture. Observe it carefully and answer the following questions based on your observation and knowledge-
a. What material is used to hold the bricks together?
b. What natural resources or raw materials are used to make this material?
c. List some industries of Nepal that produce this material.

a	………………………………………………………………………………
b	………………………………………………………………………………
c	………………………………………………………………………………

Have you ever wondered how long-lasting highways and tall skyscrapers are maintained? The bricks in the image you just saw are held firmly together by a unique substance that is used practically everywhere in building; it is not magic. It is gray and powdery when dry, and when combined with water, it solidifies into rock. You might have spotted it near your school, by the side of the road, or perhaps at a building site. This essential substance is **cement**. Hence, **cement** is a fine, gray powder composed of limestone, clay, and other mineral that works as a powerful binder in construction when mixed with water.

19.2: Raw materials for cement production

The production of high-quality cement relies on a precise combination of calcium-rich materials (primarily limestone), silica, alumina, and iron-bearing materials (typically clay or shale), a setting regulator (gypsum). Smaller amounts of corrective materials are also used to fine-tune the chemical composition and enhance the specific property of the cement. These raw materials are broadly classified as-

1. Calcareous materials: These are lime rich component abundant in calcium carbonate, such as limestone, chalk, marl etc.

2. **Argillaceous materials:** These are clay rich component that supply silica and alumina such as clay, shale, slate, etc.

3. **Corrective materials:** These are minor components that are used to adjust the chemical composition of raw mix to ensure the desire clinker formation such as iron ore and bauxite.

4. **Alternative raw materials:** These are added to cement to improve some qualities, recycle industrial waste, and lessen its negative effects on the environment. They include gypsum, slag and fly ash.

The detail of raw materials are presented below-

i. Lime stone (Calcium carbonate- $CaCO_3$): (60-67)%

Its primary purpose is to supply calcium which is necessary for the production of calcium silicate during cement making process. This is the most important raw material for the production of cement.

ii. Clay (or Shale): (20-25)%

Its primary purpose is to supply silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3), all of which are essential for the formation of clinker.

iii. Gypsum ($CaSO_4.2H_2O$): (3-5)%

Its primary purpose is to regulate the setting time of cement by controlling the rate of hydration.

iv. Bauxite (Alumina- Al_2O_3): (0-2)%

Its primary purpose is to keep the amount of alumina in a particular kind of cement. It can impact the properties of cement.

v. Magnesium oxide (MgO): (0.1-4)%

It improves hardness and strength but kept low as its excess amount can cause expansion and cracking in the hardened cement.

vi. Alkali oxide (Na_2O, K_2O): (0.3-1.5)%

They help in **reducing the melting temperature** during clinker formation but are generally kept low as excess amounts can cause **efflorescence** and affect cement durability.

vii. Alternative raw materials (Fly ash, slag etc): (5-10)%

Its primary goal is to recycle industrial waste, lessen the influence on the environment, and enhance the quality of cement by improving certain characteristics like strength and durability. Blast furnace slag falls under this category due to its latent hydraulic properties.

Lime stone

Gypsum

Shale

Bauxite

Test yourself

Q. Provide two examples of alternative raw materials used in cement production.

19.3: Steps involved in cement production

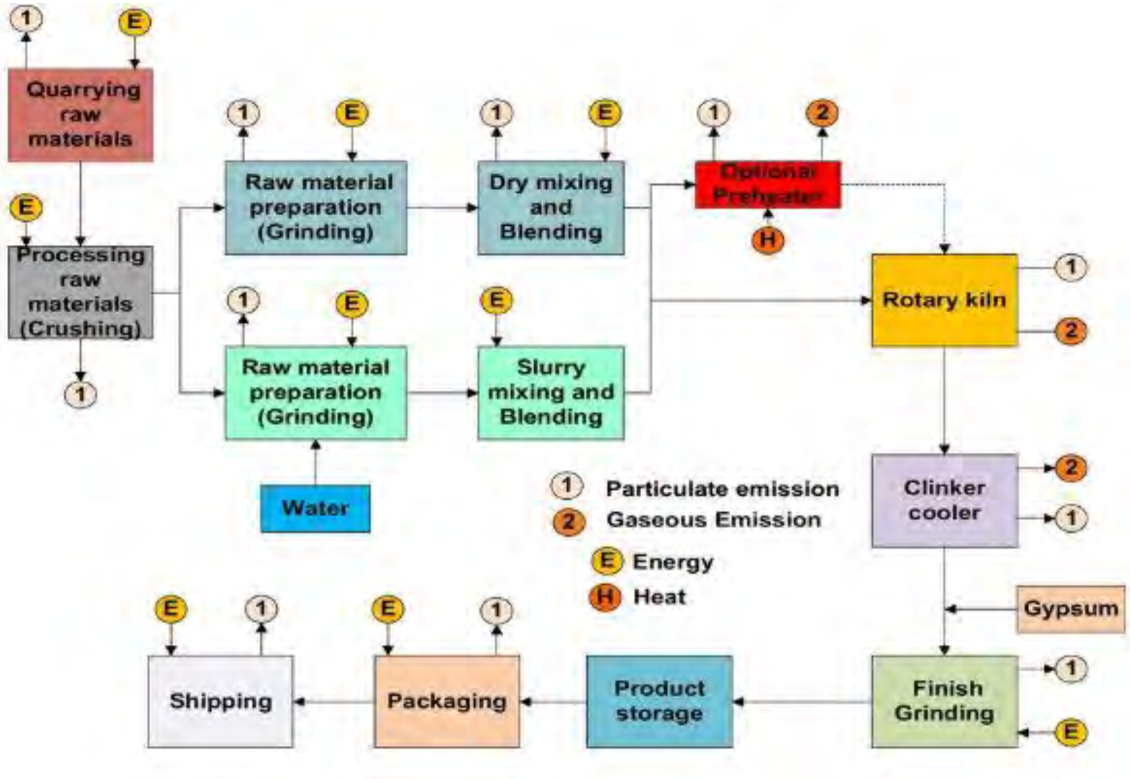


Fig: Sequential steps involved in production of cement

The production of cement in general involves following four steps-

1. Crushing and grinding:

The raw materials such as limestone, clay, and sometimes iron ore are extracted from quarries, and then crushed into smaller pieces using crushers. After crushing, these materials are ground into fine powder using grinding mills. The resulting powdered mixture is called **raw meal**, and is **stored in silos** before being sent to the kiln for heating.

2. Blending:

This procedure makes sure that the raw material has the right chemical makeup, which is necessary to produce cement of superior quality.

Compressed air or mechanical mixing systems are used in silos or blending units to properly combine the powdered raw materials. During this step, any changes in the ratio of important oxides such as CaO, SiO_2, AlO_3, and FeO_3 are corrected.

3. Burning (Calcination or clinker formation):

After blending, the **raw meal** is fed into a large, rotating furnace called a **rotary kiln**, where it undergoes strong heating at very high temperatures, typically between **1400°C to 1500°C**.
Inside the kiln, several changes take place:

- Moisture evaporates from the raw meal.
- **Calcium carbonate ($CaCO_3$)** from limestone breaks down into **calcium oxide (CaO)** and **carbon dioxide (CO_2)** which is called **calcination**.
- The **calcium oxide (CaO)** then reacts with **silica (SiO_2)**, **alumina (Al_2O_3)**, and **iron oxide (Fe_2O_3)** to form new compounds like:

$$2CaO + SiO_2 \longrightarrow Ca_2SiO_4 \text{ (dicalcium silicate or } C_2S \text{)}$$

$$3CaO + Al_2O_3 \longrightarrow Ca_3Al_2O_6 \text{(tricalcium aluminate or } C_3A\text{)}$$

$$3CaO + SiO_2 \longrightarrow Ca_3SiO_5 \text{ (tricalcium silicate or } C_3S\text{) and}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow Ca_4Al_2Fe_2O_{10}$$

$$\text{(tetra calcium aluminoferrite or } C_4AF\text{)}$$

These compounds form small, hard nodules called **clinker**, which is the intermediate product of cement.

4. Final grinding (Finish Grinding):

The clinker formed is allowed to cool down and sent to a grinding mill for the final stage of cement production where it is mixed with 3% to 5% of gypsum.

The gypsum is essential because it controls the setting time of cement. Without gypsum, cement would set too quickly when mixed with water, making it difficult to work with during construction.

This final powder is the **finished cement**, which is then stored in **silos** and later packed into bags or transported in bulk for use.

Flow sheet diagram for the production cement -

Cement (Raw Materials: Limestone, Clay, etc.)

↓
Crushing and Grinding
↓
Blending (Raw Mix Homogenization)
↓
Burning in Rotary Kiln (Clinker Formation)
↓
Cooling of Clinker
↓
Finish Grinding (Clinker + Gypsum)
↓
Cement Storage in Silos
↓
Packaging or Bulk Transport
↓
Finished Cement

19.3: OPC and PPC cement

2. Activity:
Observe the given picture carefully and answer the following questions based on your observation and knowledge-
a. What are OPC and PPC cements?
b. Which type of cement would you prefer to use building your house-OPC or PPC, why?
c. Can you name some brand or companies that produce OPC and PPC cement in Nepal?

a.	**...**
b.	**...**
c.	**...**

You might have observed construction sites and the use of cement in building walls, houses, and roads. But not all cement is the same. Depending on their composition and properties, cement is classified into different types. Among them, the two most commonly used in constructions are Ordinary Portland Cement (OPC) and Portland Pozzolana Cement (PPC). Each type has its own features and is selected based on the need of the project.

1. OPC (Ordinary Portland Cement) cement:

The most widely utilized kind of cement in building is Ordinary Portland Cement (OPC). It is mostly composed of clay and limestone, and when combined with water, it sets and hardens rapidly. Because of its great strength and quick setting time, OPC is perfect for general construction projects involving pavements, buildings, bridges, and other structures where early strength is crucial. It comes in a variety of grades, including 33, 43, and 53, which represent the cement's compressive strength.

Fig: OPC

2. PPC (Portland Pozzolana Cement) cement:

PPC is a variant of OPC. Ordinary Portland Cement (OPC) and pozzolanic ingredients, such as fly ash or volcanic ash, are combined to create Portland Pozzolana Cement (PPC). Over time, these substances combine with calcium hydroxide to create compounds that improve the cement's strength and resilience. PPC is perfect for big building projects like foundations, bridges, and dams since it generates less heat during setting. It is a wonderful option for long-lasting constructions because it is also more resistant to chemicals, moisture, and cracks.

Fig: PPC

Features of OPC and PPC:

Features	OPC	PPC
Raw materials	Made from limestone, clay and gypsum.	Made from OPC clinker, gypsum, and pozzolanic materials (e.g., fly ash, slag).
Composition	Mainly Portland clinker (rich in calcium silicates) with gypsum.	Contains less clinker OPC along with gypsum.
Properties	High early strength, higher heat of hydration, potentially lower long-term durability in harsh conditions, faster setting time.	Lower early strength, lower heat of hydration, improved long-term durability, better resistance to chemical attack, often better workability, and slower setting time.
Common Use	Suitable for structures needing early strength like high-rise buildings, bridges, roads, etc.	General construction, mass concreting (dams, foundations), hydraulic structures, marine works, plastering, masonry, areas with aggressive environmental conditions.
Cost	Generally more expensive due to higher clinker content.	Often more economical due to the use of pozzolanic materials (industrial by-products).
Manufacture	More energy is required due to higher clinker production.	Less energy is required as it utilizes industrial waste, reducing clinker production.
Eco-friendly	Less eco-friendly due to higher emission of CO_2 from clinker production and greater reliance on natural resources.	More eco-friendly as it utilizes industrial by-products, reduces CO_2 emissions, and conserves natural resources.

Strength	Has high early strength (especially in higher grades like OPC 53).	Lower early strength but often achieves comparable or higher long-term strength over time.
Setting time	Generally faster setting time.	Generally slower setting time.
Durability	Good in general conditions, but can be less resistant to certain chemical attacks compared to PPC.	Generally more durable, especially against sulfate and chloride attacks, and has reduced permeability.
Workability	May require more water to achieve same smoothness.	Usually has better workability due to finer pozzolanic particles.
Heat of hydration	Produce more heat while setting which can cause crack in mass concrete.	Produces less heat, making it more suitable for mass concrete mass.
Grades	Available in different grades like, OPC 33, OPC 43, OPC 53.	Has no specific grade.

Do you know?

There are two verities of cement based on how they set and harden-

1. Hydraulic cement: This form of cement sets and hardens by reacting with water, even when submerged.

2. Non-hydraulic cement: It sets only in dry air and cannot harden in wet or underwater conditions.

19.4: Manufacture of Portland Cement with Flow sheet diagram

Portland cement (specifically known as OPC) is the most widely used type of cement in the world. It serves as the **basic ingredient in concrete, mortar, plaster,** and many other construction materials. It gets its name, **"Portland"** from its similarity in color to **Portland stone**, a type of building stone found in England. Typical composition of ordinary Portland cement is-

Compound	Chemical Formula	Proportion(%)	Function
Tricalcium silicate	$3CaO.SiO_2$ (C_3S)	45-60	Provide high strength, responsible for initial setting
Dicalcium silicate	$2CaO.SiO_2$ (C_2S)	15-30	Contributes to strength gain at later stages, improves long term durability
Tricalcium Aluminate	$3CaO.Al_2O_3$ (C_3A)	6-12	Reacts rapidly, responsible for initial setting and heat of hydration
Tetracalcium Aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$ (C_4AF)	6-10	Contributes to cement's color and minor strength, improves resistance to sulphate attack
Gypsum	$CaSO_4.2H_2O$	3-5	Regulates the setting time, prevents immediate hardening (flash setting).
Minor compounds	MgO, Na_2O, K_2O etc	<2	Influences soundness and other physical properties.

Portland cement is manufactured through two main techniques: the dry process and the wet process. Both methods aim to produce **clinker**, which is then ground with gypsum to form the final cement. In the **dry process**, raw materials such as limestone and clay are crushed, dried, and ground into a fine powder known as **raw meal**. This powder is then preheated and fed into a rotary kiln, where it is heated to high temperatures to form clinker. In contrast, the **wet process** involves mixing the raw materials with water to create **slurry**, which is then thoroughly blended and fed into the kiln. Although both processes follow similar steps of clinker formation and grinding, the dry process is more energy-efficient and widely used today due to lower fuel consumption and environmental benefits.

Flow sheet-Dry process: The dry process is the most common method used today because it saves energy.

1. Raw material crushing: Limestone, clay and other materials are crushed in to smaller pieces using crusher.

2. Drying and grinding: The crushed raw materials are dried and ground in to ball mill to obtain fine powder called raw mill.

3. Blending (Raw mill homogenization): The raw mill is tested and blended to ensure the correct chemical composition required for quality cement.

4. Preheating: The blended raw mill is preheated in a pre-heater tower where it absorbs heat from the klin's exhaust gas, increasing energy efficiency.

5. Clinker formation (Rotary klin): The preheated raw mill enters the rotary klin and is heated about 1450^{0}C, where it undergoes chemical changes to form small, hard pellets called clinker.

6. Clinker cooling: Thus obtained hot clinker is rapidly cooled using cooler to stabilize its properties.

7. Grinding with Gypsum: The cooled clinker is mixed with 3-5 % gypsum and ground in to fine powder to obtain Portland cement.

8. Storage and packaging: The finished cement is stored in silos and then packed in bags for distribution.

Raw Materials (Limestone, Clay)
↓
Crushing & Dry Grinding
↓
Raw Mill Homogenization
↓
Preheater
↓
Rotary Kiln
↓
Clinker Formation
↓
Clinker Cooling
↓
Clinker + Gypsum
↓
Cement Grinding
↓
Storage, Packing & Distribution

Flow sheet-Wet process: An older technique for making cement is the wet process. It combines raw ingredients with water to create slurry, which enhances blending but takes more energy for evaporation.

1. Raw material crushing: Limestone, clay and other materials are crushed in to smaller pieces using crusher.

2. Slurry formation: The crushed raw materials are mixed with water in a wash mill to form a semi liquid mixture called slurry that contains 30-40% water.

3. Grinding: The slurry is further grounded in a ball mill to ensure fine and uniform particle size improving chemical reaction during burning.

4. Homogenization (Blending): The slurry is stored in a large tank and stirred continuously so as to obtain uniform chemical composition.

5. Clinker formation (Rotary klin): The slurry is passed into a rotary klin and is heated about 1450^0C, where it undergoes chemical changes to form small, hard pellets called clinker.

6. Clinker cooling: Thus obtained hot clinker is rapidly cooled using cooler to stabilize its properties.

7. Grinding with Gypsum: The cooled clinker is mixed with 3-5 % gypsum and ground in to fine powder to obtain Portland cement.

8. Storage and packaging: The finished cement is stored in silos and then packed in bags for distribution.

Raw Material Crushing

↓

Mixing with Water (Slurry Formation)

↓

Grinding (Slurry Ground in Ball/Tube Mill)

↓

Homogenization (Slurry Tank Blending)

↓

Clinker Formation in Rotary Kiln

↓

Clinker Cooling

↓

Grinding with Gypsum

↓

Storage and Packaging

Test yourself:

Q. How does the presence of water in wet process affect energy consumption?
Q. What is slurry? Why is it used?

19.5: Cement Industry in Nepal:

The cement sector in Nepal has grown significantly as of 2024, both in terms of export performance and production capacity. With a total yearly production capacity of 22 million tons, the nation currently has more than 50 cement companies in operation, supporting an estimated Rs 300 billion in investment and employing about 15,000 people. Exports of cement and clinker increased to Rs 3.85 billion in the fiscal year 2023–2024, almost tripling that of the year before. Government programs, such as an 8% cash incentive for exporting mine-based products and power tariff waivers ranging from 1 to 15% for high-consuming manufacturers, are responsible for this impressive development.

Despite these developments, large-scale infrastructure projects are expected to drive Nepal's cement demand, which is expected to reach 26 million tons annually by the fiscal year 2024–2025. Despite having a 22 million-ton manufacturing capacity, actual output has typically lagged, requiring imports to make up the difference. But according to current data, Nepal is becoming more self-sufficient in its cement production, which would lessen its dependency on imports and establish it as a possible exporter in the regional market.

Fig: Hetauda Cement Industry

Fig: Udaypur Cement Industry

List of some cement industries established in the public and private sectors-

Public Sectors- Himal cement company, Hetauda cement industry, Udaypur cement industry.

Private sectors- Arghakhanchi cement, Sagarmatha cement, Maruti cement udhyog, Agni cement industry, Jagdamba cement industry, Triveni cement udhyog, Balaji cement udhyog, Butwal cement, Koshi cement, Pashupati cement, Ambe cement, Hongshi shivam cement, Mittal cement industry, Surya cement udhyog, Kanak cement Pvt. Ltd., Dang cement Industry Pvt. Ltd., Suprim cement Pvt. Ltd., Bishwokarma cement Pvt. Ltd., Buddha cement Industry, Siddhartha cement udhyog, Reliance cement Pvt. Ltd., etc.

Challenges during cement production in Nepal:

i. Energy Shortages: Operations are disrupted by frequent power outages and insufficient supply.

ii. Outdated Equipment: As machinery ages, it becomes less efficient and requires more maintenance.

iii. High Costs of Raw Materials: Profitability is strained by the rising costs of imported coal and clinker.

iv. Regulatory Barriers: Operations and development are hampered by stringent environmental and licensing requirements.

v. Export Restrictions: Nepali cement's access to markets is restricted by trade barriers, especially those with India.

vi. Infrastructure Deficiencies: Inadequate logistics and transportation raise prices and delay delivery.

vii. Market Oversupply: Price competition and financial distress are caused by excess production capacity.

viii. Labor shortages: Lack of labor shortage has an impact on quality assurance and productivity.

ix. Environmental Impact: The manufacture of cement has a major impact on both environmental deterioration and CO_2 emissions.

x. Financial instability: The expansion of the industry is hampered by economic difficulties and restricted access to financing.

Test yourself:

Q. What strategies can put to cope up the challenges faced by cement industry in Nepal?
Q. Write the impact of cement industry on environment?

Exercise

A. Multiple choice questions

1. Which of the following is primary ingredient in the production of Portland cement?
   a. Limestone b. Clay c. Gypsum d. Alumina

2. What is the function of gypsum in the production of cement?
   a. It acts as binder
   b. It increases fineness
   c. It controls setting time
   d. It improves strength

3. Which of the following is not a primary raw material for cement?
   a) Sand b) Gypsum c) Limestone d) Clay

4. Which of the following cement contains fly ash and volcanic ash?
   a. Hydraulic cement b. Ordinary Portland cement
   c. Pozzolana Portland cement d. Portland cement

5. Which grade of cement is generally used for construction work?
   a. 35 b. 43 c. 53 d. 57

6. Which of the following type of cement is most suitable for mass concrete work like dams?
   a. OPC b. OPC 43 grade c. OPC 53 grade d. PPC

7. Which of the following is responsible for the early strength of cement?
   a. Dicalcium silicate b. Tricalcium aluminate
   c.Tetra calcium aluminoferrite d. Tricalcium silicate

8. Which manufacturing process of cement is more energy-efficient and used commonly today?
   a. Wet process b. Dry process c. Semi-wet process d. Semi-dry process

9. What should be the minimum percentage of lime in OPC?
   a. 35 b. 42 c. 54 d. 60

10. Which of the following is not a raw material used in cement production?
    a. Limestone b. Fly ash c. sand d. Clay

B. Short answers questions:

11. Give reason,
    a. Wet process of cement manufacturing is not used nowadays.
    b. Gypsum is added to clinker during grinding.
    c. OPC is not suitable for mass concrete work.
    d. PPC is preferred for the construction in marine environment.

12. Define cement. Write any two uses of cement.

13. What are the raw materials of cement?

14. What is the function of gypsum in the production of cement?

15. Differentiate between-

    a. OPC and PPC
    b. Dry process and wet process of cement production

16. What is clinker? Write its use.

17. What are the stages in the production of cement?

18. Give a flow sheet diagram for the production of cement.

19. What are the challenges faced by cement industry in Nepal?

20. Write one advantage and one disadvantage of OPC.

21. What are the merits and demerits of PPC?

22. What is the function of pozzolanic material in PPC?

C. Long answer question:

23. Describe the stages in the production of cement. Draw flow sheet diagram showing different stages of cement production.
24. Explain the flow sheet diagram for the manufacture of Portland cement by dry process.
25. Describe the entire process flow for manufacturing Portland cement using the wet process.
26. Differentiate between OPC and PPC.
27. Write a note on- Cement industry in Nepal.

PROJECT WORK

1. Prepare a project work on, " Sources of raw materials for the production of cement".
2. Make a poster showing different stages in the production of cement along with flow sheet diagram.
3. Visit nearby construction site and identify the type of cement used with its advantages.
4. Prepare a chart paper showing flow sheet diagram for the manufacture of Portland cement by dry and wet process.
5. Prepare a chart or poster on the current status of cement industry in Nepal, including key facts such as production capacity, challenges faced, and the contribution to the economy.

Unit 20

Paper and Pulp

20.1: Introduction

1. Activity:

Observe the picture carefully and answer the following questions based on your observation and knowledge-

a. What is shown in the picture?

b. Which natural resources do you think are used in making paper?

c. List some paper industry of Nepal.

a.	....
b.	....
c.	....

Whether it's the book you immerse yourself in, the notebook you write in, or the packaging that safeguards your online buys, we deal with paper on a daily basis without really thinking about it. However, have you ever pondered how this vital component is made? ***Paper*** is a thin, flexible material created by pressing together moist fibers, typically derived from wood or other plants, and drying them into sheets. At the center of it all is ***pulp***, the fibrous substance made from plant sources that forms the basis of each sheet of paper. Wood is the main raw material used to make pulp; hardwood trees like eucalyptus provide smoothness, while softwood plants like pine provide strength. To make paper production more sustainable, non-wood fibers like bamboo, cotton, and even recycled paper are also utilized. Different chemicals and additives are added to these fibers to change their texture, toughness, and brightness, creating the multipurpose paper goods that are essential to our everyday existence.

20.2: Raw materials and their sources

Pulp is the primary raw material used in the production of paper, consisting mainly of cellulose fibers derived from wood, recycled paper, or other plant sources. In addition to pulp, water and various chemicals are also essential in the papermaking process to improve paper quality and processing efficiency. The raw materials used in paper production can be broadly categorized into two types: fibrous materials, which provide the structural fibers needed to form paper, and non-fibrous materials, such as fillers, sizing agents, and additives, which enhance properties like smoothness, brightness, strength, and printability.

i. Fibrous raw materials: Pulp is obtained from following fibrous raw materials.

a. Softwood: They are the source of long fibers and are used to provide strength in paper. For example, eucalyptus, poplar etc.

b. Hardwood: They are the source of short fibers and are used to provide smoothness and printability. For example, eucalyptus, poplar etc

c. Bamboo: They are fast growing plants with strong and long fibers and are used to provide good strength in paper.

d. Bagasse: They are the agriculture waste obtained from sugarcane, contain good source of fibers.

e. Straw: They are the farm residues that contain cellulose with short fibers. For example, wheat, rice, barley, maize etc. Some grasses like, lemon grass, kush (कुश), babiyo (बाबियो), reeds, siru(सिरु) etc can also be good source of pulp.

f. Jute: They are the source of long, strong and coarse fibers. They are less commonly used in paper making.

g. Cotton rags: They are the source of long, strong and almost pure cellulose fibers. They are used to produce high quality of handmade paper. For example, old clothes, manufacturing left over, towels, bed linens, fabric scrap, blankets etc.

h. Lokta: They are the source of strong, durable and flexible bast fibers. They are used to produce eco-friendly, strong and durable handmade paper.

i. Recycled paper: They are already processed fibrous materials obtained from used or discarded paper products.

 **Pine**	 **Eucalyptus**	 **Bamboo**
 **Rice straw**	 **Bagasse**	 **Desmostachya *bipinnata* (Kush)**
 **Eulaliopsis *binate* (Babiyo)**	 **Recycled paper**	 **Eulaliopsis *binate* (Babiyo)**
 **Daphne *bholua* (Lokta)**	 **Reeds**	 **Banana**

ii. Non-fibrous raw materials: Followings are some of the common non-fibrous raw materials mixed with pulp during paper production to meet specific quality of the paper. They are

A: Inorganic raw materials: These include-

a. Sodium hydroxide: It is used to breakdown lignin and separate cellulose fibers during pulping.

b. Alum (Aluminium Sulphate): It is used for sizing and pH control.

c. Kaolin clay: It is used to enhance smoothness and brightness.

d. Calcium carbonate: It is used to improve whiteness, opacity and brightness.

e. Titanium dioxide: It is used to increase opacity and brightness in high quality paper.

f. Other: Other chemicals are Na_2S, Na_2CO_3, Na_2SO_3, $Mg(OH)_2$, H_2O_2, Cl_2, $NaHClO$, Soda ash, talc etc.

B: Organic raw materials: These include-

a. Starch: It is used to improve surface strength and printability.

b. Rosin: It is used to provide water resistant to the paper.

c. Dyes and pigments: They are used to provide color to the paper.

d. Optical Brightening Agnets (OBAs): They are used to make paper appear white and bright.

e. Synthetic binders: They are used to bond fibers and fillers for better strength of paper.

f. Glycerol: It is used as a plasticizer to increase flexibility, softness and moisture retention.

g. Wax: It is used to provide water resistant, surface smoothness and coating quality.

Test Yourself

Q. Why are bast fibers preferred over leaf fibers in handmade paper production?
Q. Non-wood plants like bagasse and bamboo are considered as sustainable source for paper making, why?

20.3: Stages in paper production

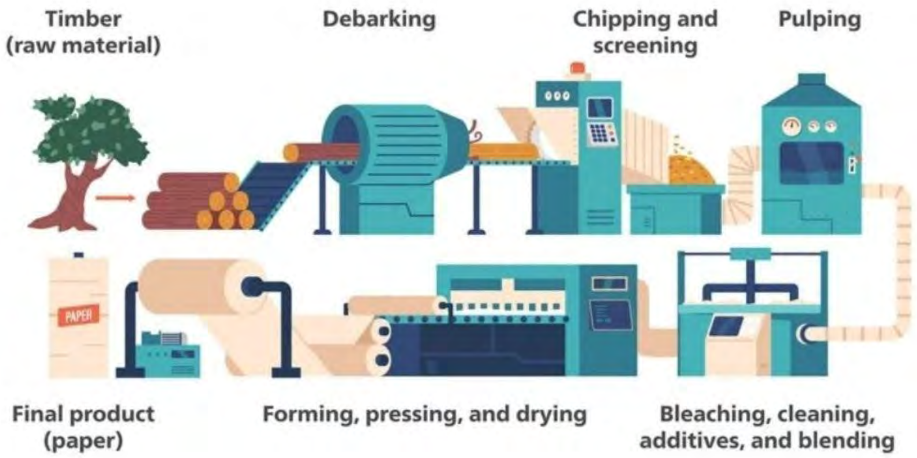


Fig: Illustration of stages in paper production

Production of paper is a systematic process that includes multiple steps, starting from raw material preparation to the final finishing of the product. The different stages in the production of paper are-

1. Timber (Raw Material): Timber is the main ingredient for paper making. Trees are harvested and logs are transported to the paper mill for processing.

2. Debarking: The outer bark of the logs is removed using machines. This step is important because bark contains impurities that can affect the quality of paper.

3. Chipping and Screening: The logs that have been debarked are chopped into uniformly sized wood chips. The chips are then filtered to get rid of any fragments that are too big or inappropriate.

4. Pulping: The wood chips are transformed into pulp using chemical or mechanical technique. Pulp is a soft and fibrous raw material that serves as basis for making paper.

5. Bleaching, Cleaning, Additives and Blending: The pulp is thoroughly cleansed to get rid of any remaining particles or debris. To make the paper better, pulp is bleached to improve whiteness and mixed with additives like fillers, dyes, or sizing agents to enhance paper quality. In some cases, different types of pulp may be blended to produce paper with specific properties.

6. Forming, Pressing and Drying: The treated pulp is spread onto moving screens to form thin sheets. Excess water is removed by pressing and the sheets are then dried off using heated rollers.

7. Final Product (Paper): The dried paper is rolled, cut, and packed for use. This is the finished product which is now ready for writing, printing, packaging etc.

Do you know?

Mechanical Pulping	**Chemical Pulping**
1. Wood is physically shredded or grounded into pulp using machine.	1. Wood chips are cooked in chemical solution to dissolve lignin in order to obtain pulp.
2. No chemical or minimal chemical is used.	2. Chemical is used.
3. High yield of pulp.	3. Low yield of pulp.
4. Fibers are shorter and weaker.	4. Fibers are longer and stronger.
5. Paper is less durable.	5. Paper is more durable.

20.4: Flow sheet diagram for paper production

Timber (Raw Material)
↓
Debarking
↓
Chipping and Screening
↓
Pulping
↓
Bleaching, Cleaning, Additives, Blending
↓
Forming, Pressing, and Drying
↓
Winding Roll
↓
Series of Pressure Rolls
↓
Finished Paper

Test yourself:

Q. How can paper production impact the environment?
Q. What is the purpose of pulping?

20.5: Quality of paper:

Fig: Use of Lokta kagaz for official record

In the accompanying figure, Nepali paper is used for the registration of birth certificates. Can you infer why this specific paper is chosen for such official records?

Paper quality matters significantly because it affects printed goods' readability, durability, and overall attractiveness of printed materials. Higher-quality paper is crucial for documents that need to be presented professionally since it guarantees superior print performance, longevity, and a polished finish. The qualities that affect how well a paper operates for its intended function are referred to as **paper quality**. It encompasses elements like finish, absorbency, strength, brightness, thickness, and texture. High-quality paper is appropriate for essential documents, publications, packaging, and promotional items because it provides superior print clarity, durability, and a polished appearance.

The quality of paper is influenced by:

- **Type of pulp used** (mechanical vs. chemical)
- **Paper weight and thickness (GSM)**
- **Surface finish** (glossy, matte, coated, uncoated)
- **Brightness and whiteness**
- **Sizing** (affects ink absorption and surface strength)

Based on these features, paper is classified into different grades such as:

1. **Premium/High-quality paper:** Used for certificates, resumes, brochures, magazine etc.

2. **Standard-quality paper:** Commonly used in office printing and everyday use. For example, book, novel, workbook and writing sheets etc.

3. **Low-quality paper:** Used in newspapers, short term materials, flyers etc.

4. **Specialty paper:** Used for hygiene, delicate wrapping or decoration, rather than for printing such as tissue paper and wrapping paper.

5. **Nepali paper (Lokta paper):** Lokta paper is a durable, handmade paper from Nepal used in government offices, as well as for journals, crafts, packaging, and traditional documents.

Do you know?

Traditionally produced Lokta paper is chosen for the preservation of official government documents and holy religious texts, due to its exceptional durability, resistance to deterioration and pests, and inherent archival properties that guarantee lifetime.

मालपोत कार्यालय, [redacted]

जग्गाधनी दर्ता प्रमाण पुर्जा

Exercise

A. Multiple choice questions

1. Which of the following is primary raw material for paper production?
   a. Glass b. Wood c. Plastic d. Cotton

2. What is the purpose of the pulping process in paper production?
   a. To shape the paper
   b. To make the paper glossy
   c. To add color to the paper
   d. To separate fibers from the wood.

3. Which type of paper is commonly used for writing and copying in school and offices?
   a) Standard quality paper b) Specialty paper
   c) Newsprint d) High quality paper

4. Which process is used to make paper brighter (whiter)?
   a. Sizing b. Chemical pulping c. Bleaching d. Mechanical pulping

5. What is the final step in paper production?
   a. Sizing b. Drying c. Pulping d. Pressing

6. What type of paper is used for magazine and brochure?
   a. Premium b. Specialty paper c. Standard paper d. Low quality paper

7. Which of the following is not commonly used as a raw material for making paper?
   a. Cotton b. Wood c. Rice husk d. Plastic

8. Which part of tree is primarily used for paper production?
   a. Bark b. Flowers c. Wood d. Bark

9. Which of the following is non-wood material used for paper production?
   a. Pine b. Banana c. Eucalyptus d. Birch

10. Which fiber is commonly used for making high quality of paper?
    a. Hemph b. Bagasse c. Cotton d. Bamboo

B. Short answers questions:

11. Give reason,
    a. Soft wood is preferred over hard wood in paper production.
    b. Lokta paper is preferred for keeping official document records.

12. What are the raw materials of paper production?

13. Explain the qualities of paper.

14. What are fibrous raw materials used for making paper?

15. Differentiate between-
    a. Paper and pulp
    b. Mechanical pulping and chemical pulping

16. What are non- fibrous raw materials of paper and pulp?

17. What are the stages in the industrial preparation of paper?

18. Give a flow sheet diagram for the manufacture of paper production.

C. Long answer question:

19. Describe the stages in the manufacture of paper. Draw flow sheet diagram showing different stages of paper production.

20. Write a note on- Raw materials for pulp and qualities of paper.

PROJECT WORK

1. Create a categorized chart listing various paper industries in Nepal**,** detailing their specialties and locations.
2. Design a poster illustrating the stages of paper production, accompanied by a flow sheet diagram.

Unit 21

Nuclear Chemistry and Applications of Radioactivity

21.1: Introduction

1. Activity:
Observe changes shown in figure 1 & 2 and answer the following questions-
a. What type of reactions do the figure 1 & 2 represent?
b. Can you write the basic difference occurring in them?

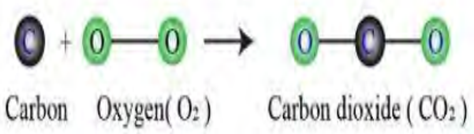


Figure 1

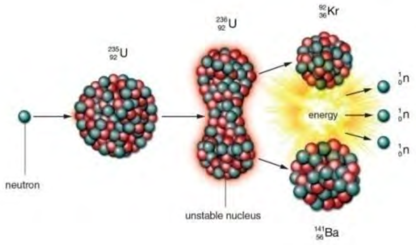


Figure 2

a.	**...**
b.	**...**

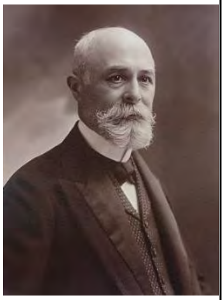
The atoms of certain elements such as uranium, plutonium, thorium, radium, polonium etc are unstable and continuously emit invisible radiations. During this process, these atoms undergo transmutation, meaning they are transformed into atoms of different elements. Unlike ordinary chemical reactions, where changes occur in the electrons surrounding the nucleus, here the nucleus itself changes. This type of transformation is called **nuclear reaction** or **nuclear transformation** and it is studied under a specialized branch of chemistry known as **nuclear chemistry.**

21.2: Radioactivity

2. Activity:
Observe the given picture of waste kept in barrels and answer the following questions-
a. What kind of waste is this?
b. What does the symbol on the barrel indicate?
c. Can you name some places where you can see such symbol?

a.	....
b.	....
c.	....

Antoine Henri Becquerel (15 December 1852- 25 August 1908), a French physicist, discovered something revolutionary in 1896 while researching minerals that illuminated when exposed to sunlight. He discovered by chance that uranium salts could release invisible rays that could penetrate solid surfaces and fog photographic plates—even in the absence of sunlight—while he was researching phosphorescent materials. This surprising finding showed that the energy was not originating from an outside source but rather from inside the atom itself. By discovering **radioactivity**, Becquerel's work paved the way for a whole new branch of research. Becquerel is regarded as the father of radioactivity since he was the first to identify and record this characteristic of atoms.



Antoine Henry Becquerel

Marie Curie (1867-1934)

Inspired by Becquerel's discovery, **Marie Curie** and her husband **Pierre Curie** carried out extensive research on radioactive substances. They discovered two new radioactive elements—**polonium** and **radium**—and helped deepen our understanding of atomic structure and nuclear energy. For their pioneering work in this field, **Henri Becquerel, Marie Curie, and Pierre Curie were jointly awarded the Nobel Prize in Physics in 1903**. Later on, in **1911 Marie Curie** was awarded **Nobel Prize in chemistry** in recognition of her services to the advancement of chemistry by the discovery of element **polonium and radium**.

You might have seen **universal radiation hazard** symbol in hospitals, industries, and research laboratories, as shown on the barrel in the picture above. The items in the picture are radioactive wastes produced as a byproduct of nuclear reaction.

Imagine atoms to be little building blocks composed of protons and neutrons with a dense core known as the nucleus. Most elements have a stable nucleus, but certain atoms have an imbalance that makes the nucleus unstable, such as too many protons, too many neutrons, or both. These atoms emit invisible particles or rays of energy from their nucleus to increase stability. This natural process is referred as **radioactivity**. The unstable nucleus gradually decomposes or disintegrates during this process, evolving into a new, more stable nucleus or occasionally into an entirely new element. **Nuclear disintegration** is the term used to describe this breakdown of the nucleus. The elements which show radioactivity are called **radioactive elements**. Generally heavier elements like uranium, radium, thorium, and polonium, etc are radioactive. Radiations emitted by radioactive elements are **α (alpha) particles**, **β (beta) particles** and **γ (gamma) electromagnetic radiations (wave)**.

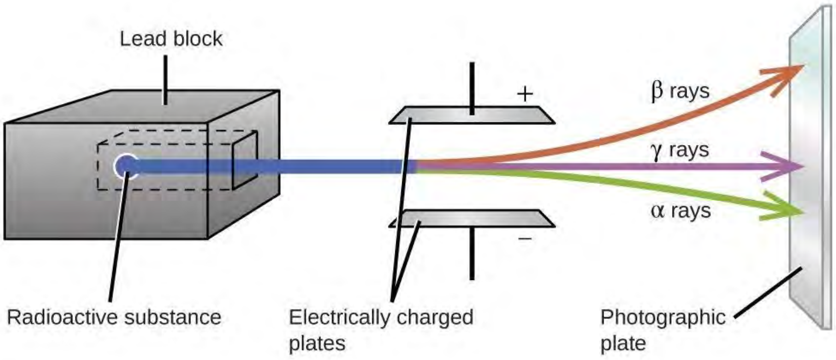


Fig: Radioactive radiations

Properties of α, β, & γ rays

Properties	**α**	**β**	**γ**
Nature	Particle	Particle	Radiation
Charge	+2 unit	-1 unit	0
Mass	4 amu	about 1/1840 of H atom	0
Symbol	${}_2^4He^{2+}$ or **α**	${}_{-1}^0e$ or **β**	**γ**
Ionizing power	Maximum	100 times lesser than **α**	Very low (10^4 times lesser than α)
Penetrating power	Least	Less	Very high
Velocity	1/10 th of velocity of light	Velocity is nearly same as that of light	Travel with velocity of light

Units of Radioactivity:

Units of radioactivity are-

Becquerel (Bq)	**Curie (Ci)**	**Rutherford (Rd)**
One disintegration per second is one Becquerel	3.7×10^{10} disintegration per second is one Curie.	10^6 disintegration per second is one Rutherford.
1 Bq = 1 dps	1 Ci = 3.7×10^{10} dps	1 Rd =10^6 dps

Becquerel is the SI unit of radioactivity.

Ways of writing nuclear equation:

Nuclear equations can be written in two main ways: the **symbolic format** and the **word format**. In the symbolic format, we use atomic symbols with mass number (A) and atomic number (Z), such as ${}_{92}^{238}U \rightarrow {}_{90}^{234}Th + {}_2^4He$, which shows uranium-238 undergoing alpha decay to form thorium-234 and an alpha particle.

In the word format, the same reaction is described as "Uranium-238 decays to thorium-234 by emitting an alpha particle." Common symbols used include α **or** ${}_2{}^4He^{2+}$ for alpha particles, β **or** ${}_{-1}{}^{0}\mathbf{e}$ for beta particles, and γ for gamma rays. If neutron is used or emitted then it is written as ${}_{0}{}^{1}\mathbf{n}$. In all nuclear equations, both the **mass number** and the **atomic number** are conserved. Some examples are-

$\mathbf{{}_{13}{}^{27}Al + {}_0{}^1n \rightarrow {}_{11}{}^{23}Na + {}_2{}^4He}$ **(or,** $\mathbf{{}_{13}Al^{27} + {}_0n^1 \rightarrow {}_{11}Na^{23} + {}_2He^4}$**)**

$\mathbf{{}_{11}Na^{23} \rightarrow {}_{12}Mg^{24} + {}_{-1}e^0}$

$\mathbf{{}_{92}U^{235} + {}_0n^1 \rightarrow {}_{56}Ba^{139} + {}_{36}Kr^{94} + 3\,{}_1n^0}$

Test Yourself

Q. Write the nuclear equation for the beta decay of carbon-14 into nitrogen-14.
Q. Write the nuclear equation for the alpha decay of radium-226.

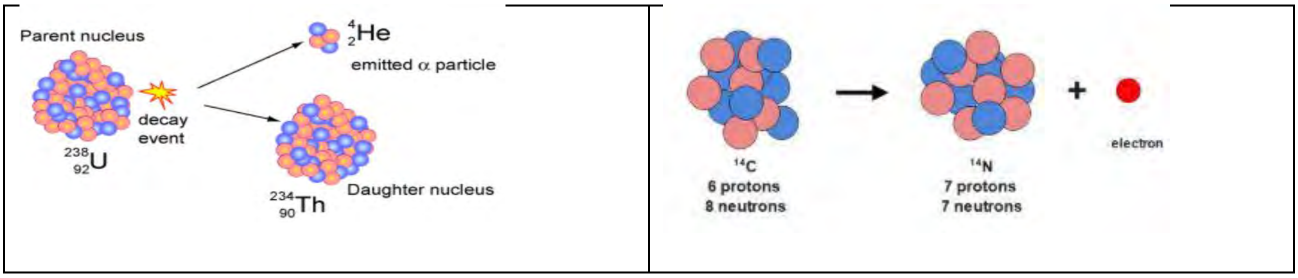
21.3: Natural and artificial radioactivity

Radioactivity is broadly classified in two types. They are-

1. Natural Radioactivity: Uranium-238 is a naturally occurring radioactive element which continuously undergoes alpha decay giving transforming into thorium-234. This disintegration happens on its own without any external trigger. This kind of spontaneous breakdown of an unstable atomic nucleus, accompanied by the emission of radiations is known as **natural radioactivity**. It occurs naturally in certain elements found in the earth crust like-uranium-238, thorium-232, radium-226, polonium-210, carbon-14, etc. Some examples of natural radioactivity are,

$\mathbf{{}_{92}U^{238} \rightarrow {}_{90}Th^{234} + {}_2He^4}$

$\mathbf{{}_6C^{14} \rightarrow {}_7N^{14} + {}_{-1}e^0}$



Applications of Natural Radioactivity: Natural radioactivity is used in carbon dating of fossils, uranium dating of rocks, medical imaging, smoke detectors, and tracing groundwater movement.

2. Artificial Radioactivity:

Aluminiu-27 has a stable nucleus and it does not undergo radioactive decay on its own. However, when it is bombarded with a neutron, it can transform into radioisotope such as sodium-24 or phosphorous-30. This shows that when a stable nucleus is bombarded (hit) by slow moving neutron (or high energy particles), it can start to disintegrate by emitting radiations. This man made process is called **artificial radioactivity or induced radioactivity** as it requires human intervention to trigger the decay.

$${}_{13}\mathbf{Al}^{27} + {}_{0}\mathbf{n}^{1} \rightarrow {}_{12}\mathbf{Na}^{24} + {}_{2}\mathbf{He}^{4}$$

$${}_{12}\mathbf{Na}^{24} \rightarrow {}_{12}\mathbf{Mg}^{24} + {}_{-1}\mathbf{e}^{0}$$

Here, **sodium-24** shows artificial radioactive decay.

Other examples that show artificial radioactivity are-

Stable element	Bombarded with	Radioactive isotope	Type of radiation
Aluminium-27	Neutron	Sodium-24 or phosphorous-30	Beta
Nitrogen-14	Alpha particle	Oxygen-17 + proton	Beta, Gamma
Phosphorous-31	Neutron	Sulphur-32	Beta
Iodine-127	Neutron	Iodine-131	Beta, Gamma

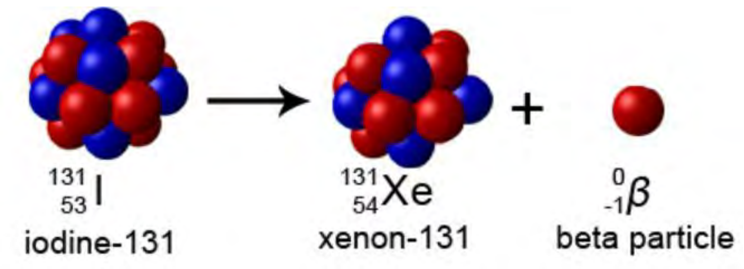


Fig: The beta particle emitted by iodine-131 has high energy and can kill cancerous cells.

Applications of Artificial Radioactivity: Artificial radioactivity is widely used in medicine, agriculture, research, industry, nuclear power plant etc. some of its applications are-

i. Iodine-131is used to diagnose and treat thyroid disorder.
ii. Cobalt-60 is used in radiotherapy to destroy cancerous cell.
iii. Plutonium-239 is used as a fuel in nuclear reactor to generate electricity.

21.4: Nuclear Reaction:

3. Activity:

Observe the given picture showing a nuclear reaction occurring in the sun and answer the following questions-

a. What is the source of energy coming from the sun?

b. Write the nuclear equation represented by the given picture.

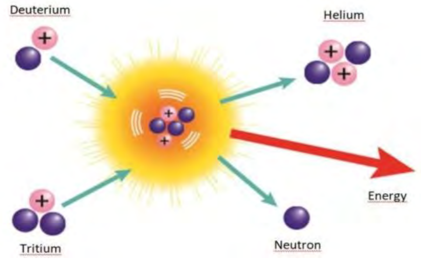


Fig: Nuclear reaction occurring in the sun

a.	………………………………………………………………
b.	………………………………………………………………

In the activity above, a new element, **helium** is produced from the nuclear fusion of **deuterium** and **tritium,** the two isotopes of hydrogen. This process is an example of **nuclear reaction**. A **nuclear reaction** is a process in which the nucleus of one element is transformed into the nucleus of another element, often accompanied by the emission of **radiation and energy**. Unlike chemical reactions, which involve the outer electrons of atoms, nuclear reactions involve changes in the atomic nucleus and release far more energy. The source of the Sun's energy is **nuclear fusion**, which can be represented by the following nuclear equation:

$${}_{1}\mathbf{H}^{2} + {}_{1}\mathbf{H}^{3} \rightarrow {}_{2}\mathbf{He}^{4} + {}_{0}\mathbf{n}^{1} + \textbf{Energy}$$

Types of nuclear reaction:

Fusion and fission are the two primary types of nuclear processes. In fission, a heavy nucleus splits into two lighter nuclei, each of which releases a significant amount of energy, whereas in fusion, light nuclei merge to form a heavier nucleus as shown in the figures below.

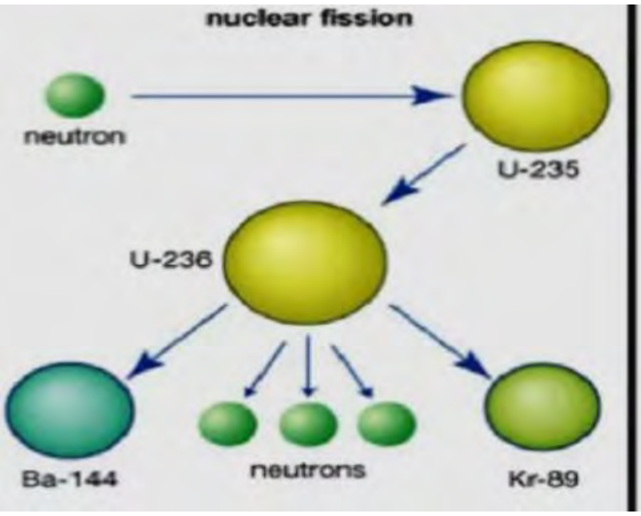


Fig: 1

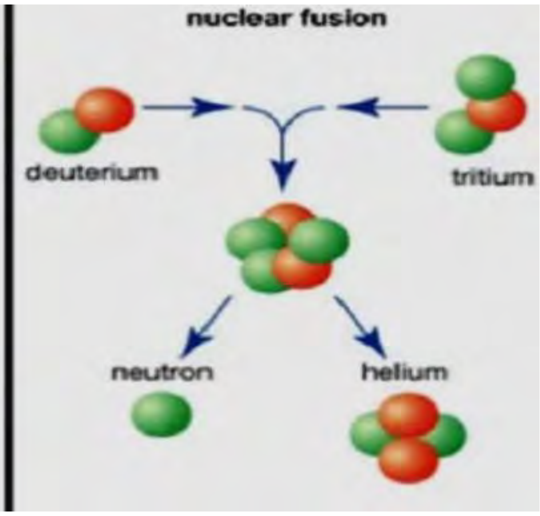


Fig: 2

Figure 1 represents a **nuclear fission reaction**, where, a heavy nucleus like, uranium-235 breaks into two lighter nuclei, barium-144 and krypton-89 along with release of energy and three neutrons. Thus a nuclear reaction where a heavy atomic nucleus splits into two or more lighter atomic nuclei with release of large amount of energy and radiations is called **nuclear fission.** This nuclear reaction that does not normally occur in nature can proceed in a chain. Some other examples, of fission are-

$${}_{92}\mathbf{U}^{235} + {}_{0}\mathbf{n}^{1} \rightarrow {}_{38}\mathbf{Sr}^{95} + {}_{54}\mathbf{Xe}^{139} + \mathbf{2}\ {}_{0}\mathbf{n}^{1}$$

$${}_{92}\mathbf{U}^{238} \rightarrow {}_{90}\mathbf{Th}^{234} + {}_{2}\mathbf{He}^{4}$$

Figure 2 shows a **nuclear fusion reaction**, where the isotopes of hydrogen, deuterium and tritium, fuse to give a single heavier nucleus of helium and a neutron, releasing tremendous amount of energy. Thus a nuclear reaction where two or more light atomic nuclei fuse together to produce a single large atomic nucleus with release of huge amount of energy and radiations is called **nuclear fusion.** The energy released during nuclear fusion is significantly greater than that of nuclear fission. This type of nuclear reaction naturally occur in nature like in star, sun etc., and unlike fission, does not proceed in a chain reaction. Some other examples of fusion are-

$$_1H^2 + {}_1H^2 \rightarrow {}_2He^4$$

$$_1H^3 + {}_1H^3 \rightarrow {}_2He^4 + 2\,{}_0n^1$$

Test yourself:

Q. Write the nuclear equation shown in figure 1 & 2.

Applications of nuclear fission: Nuclear fission is employed in the manufacturing of atomic weapons, nuclear electricity, medicinal isotopes, and naval propulsion systems.

Do you know?

The system that propels and moves a naval vessel, like an aircraft carrier or submarine, is known as a naval **propulsion system**. Heat from nuclear fission is utilized in nuclear naval propulsion to create steam, which powers turbines and moves the ship forward. It makes ideal for military use.

Applications of nuclear fusion: Nuclear fusion has the potential to provide a clean, virtually limitless source of energy, as demonstrated by experimental fusion reactors and the Sun's energy production. The primary objective of current fusion research is to produce power in a sustainable, safe, and clean manner.

Test yourself:

Q. What do you mean by controlled and uncontrolled nuclear fission?

21.5: Nuclear Power and Nuclear Weapons:

Fig: Nuclear power station

Fig: Nuclear weapon

4. Activity:

Observe the two pictures given above and answer the following questions-

a. Write the purpose of each item shown in the picture.

c. What are the dangers of nuclear energy used in each item?

d. Name the two nuclear weapons that were used in World War II.

a.	....
b.	....
c.	....

The energy generated by nuclear reactions, mainly nuclear fission, in which the nucleus of a heavy atom, such as uranium, splits into smaller nuclei and releases a significant amount of energy, is called as **nuclear power**. This energy is utilized to generate electricity in nuclear power plants, which are a major global power source. Nuclear reactors use uranium-235 and plutonium-239 as a primary fuel to generate electrical energy through the release of thermal energy. Nuclear power is the second largest low carbon source of energy in the world.

On the other hand, the same nuclear technology can also be used in the creation of by **nuclear weapons**. These are explosive device that cause massive destruction as result of nuclear reaction. The destruction occurs either through nuclear fission or nuclear fusion. Fusion-based weapons, like the **hydrogen bomb** or **thermonuclear bomb**, release enormous amounts of energy by fusing light atomic nuclei, whereas fission-based weapons, like the **atomic bombs**, depend on the splitting of heavy atomic nuclei.

Do you know?

"Little Boy" was the first nuclear weapon ever used in combat, a fission bomb dropped on Hiroshima in 1945. By the end of the year, an estimated 140,000 people had been killed and vast destruction had been caused by the tremendous energy released by the fission of uranium-235. World War II came to an end when Japan surrendered after a second fission bomb, known as "Fat Man," was dropped on Nagasaki a few days later. These bombings remain the only use of nuclear weapons in war to date

Advantages of Nuclear Power	Disadvantages of Nuclear Power
➢ It is an energy source that is both sustainable and safe.	➢ Nuclear accident can cause long term harm to people and environment.
➢ It is environment friendly as it emits very little carbon.	➢ It creates hazardous nuclear waste that poses long term environmental risk.
➢ A small nuclear fuel is enough to produce large amount of energy.	➢ The establishment and maintenance of nuclear power plants are very costly.

21.6: Industrial use of radioactivity:

Over the years, radioisotope and radiation-based techniques like radiotracers, radiography, and nucleonic gauges have been widely used in industries for process monitoring, measurement, and material modification. These methods offer advantages such as high sensitivity, quick implementation, and cost-effectiveness over conventional approaches. Radioisotopes such as Ir^{192}, Tm^{176}, Cs^{137},Sr^{90}, Co^{60} ,Fe^{55} etc. have valuable use in the industry through **Beta(β)** and **Gamma(γ)** radiations. Some uses of radioisotopes in the industry are-

1. Non-Destructive Testing (NDT): A method of checking constructions and welds for internal defects without causing any harm. For example, X-ray radiography is used to inspect the welds in airplane parts and oil pipelines.

2. Thickness Gauging: It determines the thickness of materials during manufacture, such as metal, plastic, and paper. For example, in paper mills, beta radiation is utilized to regulate paper thickness.

3. Leak Detection: Underground pipeline leaks are found using radioactive tracers. For example, when a radioactive isotope is introduced to a pipeline's fluid, detectors locate the leak.

4. Sterilization: Some food items and medical equipment are sterilized with gamma rays. For example, cobalt-60 is used to disinfect surgical gloves and syringes.

5. Power Generation (RTGs): Employed in deep space missions and other locations where solar power is unreliable. For example, NASA's Voyager spacecraft and Mars rovers are powered by RTGs that use plutonium-238. ***(RTG: Radioisotope Thermoelectric Generator)***

6. Smoke detectors: Use a tiny quantity of radioactive material to detect smoke. The majority of smoke detectors in homes, for instance, use Americium-241 (Am^{241}).

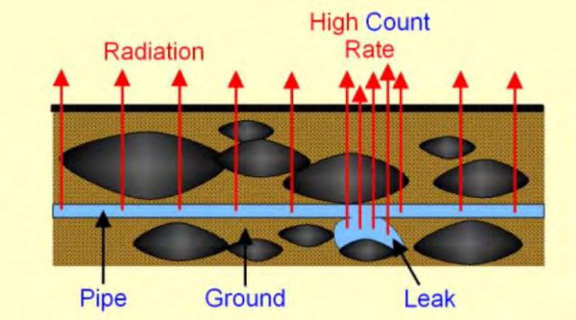


Fig: Use of radioisotope to detect leakage in pipeline

Fig: Sterilizing surgical instruments

21.7: Medical use of radioactivity:

In the medical field, radioisotopes are essential because they allow for accurate diagnosis and treatment of a wide range of illnesses. They are employed in imaging procedures such as **PET** and **CT** scans, which helps doctors to view internal organs and identify illnesses early on, including cancer or heart disease. Radioisotopes are used in radiotherapy to target and treat cancers while causing the least amount of harm to the surrounding healthy tissues. They also assist in keeping an eye on blood flow and organ function, which is crucial information for efficient treatment planning. In general, radioisotopes are crucial for enhancing patient outcomes and care. Some of the medical uses of radioisotopes are-

1. Diagnostic Imaging (Radiology):

In nuclear medicine, radioisotopes are utilized to aid in the visualization of internal organs and tissues using imaging methods like SPECT (Single Photon Emission Computed Tomography) and PET (Positron Emission Tomography), often combined with CT (Computed Tomography) scan to provide both functional and anatomical information. For example: Technetium-99m (Tc-99m) is commonly used in scintigraphy for imaging bones, heart, liver, and kidneys.

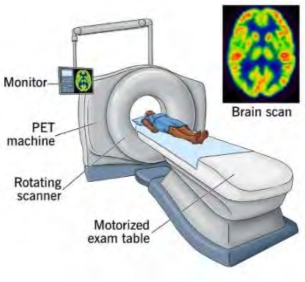


Fig: PET imaging

Do you know?

PET: PET scans use positron-emitting isotopes such as fluorine-18, oxygen-15, and nitrogen-13. When these isotopes are injected into the patient's body, the positron they release combines with nearby electrons to produce a simulated gamma ray emission that is picked up by a PET camera, providing an accurate image of the organ.

2. Cancer Treatment (Radiotherapy):

By providing precise radiation to cancer cells, radioisotopes help cure cancer by either killing or shrinking tumors. For iodine, Iodine-131 (I-131) targets thyroid cells specifically in order to treat thyroid cancer. Similarly, Cobalt-60 (Co-60) and Bismuth-213 (Bi-213) etc are also used in radiotherapy to control cancer growth.

3. Barchytherapy:

It involves placing radioactive isotope directly inside or very close to the tumor for localized treatment. It is used for prostate, breast, cervical and skin cancer. For example, Irridium-192 (Ir-192), Radium-223 (Ra-223) etc are used to treat prostate cancer.

4. **Iron-59 (Fe-59)** is the isotope commonly used to study **iron metabolism**, including in the **spleen**, **liver**, and **bone marrow**.

5. **Sodium-24 (Na-24)** is used to determine the amount of blood flow in the patient of anemia.

6. **Sulfur-35 (S-35)** and **Phosphorus-32 (P-32)** are commonly used in biological research to label proteins and nucleic acids, allowing scientists to track metabolic processes and study cellular functions.

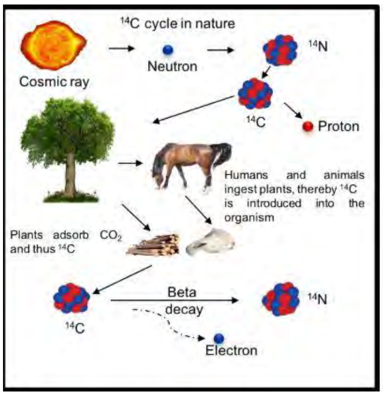
Test yourself:

Q. Write the medical use of Cesium-137.

21.8: Radiocarbon dating:

Willard Frank Libby (17th December, 1908 – 8th September, 1980), American physical chemist, is renowned for his contribution to the 1949 invention of **radiocarbon dating**, which transformed paleontology and archaeology. In 1960, Libby received the **Nobel Prize in Chemistry** for his work on the group that created this method.

Carbon-14, produced by the bombardment of nitrogen atoms by neutrons from cosmic rays, is oxidized to CO_2 and eventually absorbed by plants and animals. When the plant or animal dies, the intake of carbon-14 stops, and the existing carbon-14 in the dead tissue begins to decrease due to radioactive decay. This process of determining the age of once-living materials by measuring the remaining carbon-14 is called **radiocarbon dating**.



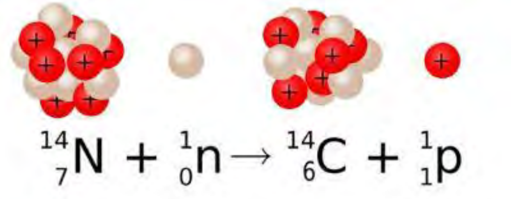


Fig: Formation of C-14

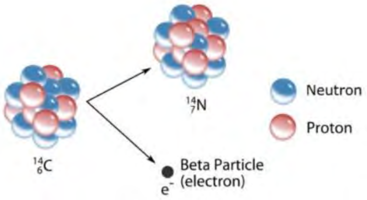


Fig: Decay of C-14

Fig: Carbon-14

The half life period of C-14 is 5,730 years. By measuring the remaining amount of C-14 (or the number of Beta particles emitted) in a dead sample, scientists can estimate how long ago the organism died. Following formula is used to determine the age,

$$t = \frac{t1/2}{\log 2}\, log \frac{N0}{N}$$

Where, **N_0** = the **original amount** of carbon-14 (C-14) in the sample when the organism was alive
N = the **remaining amount** of carbon-14 in the sample at the time of measurement
$t_{1/2}$ = Half life of carbon-14 (5730 years)

Do you know?

Carbon-14 decay follows first-order kinetics, meaning it decays at a rate proportional to the amount remaining.

21.9: Harmful Effects of Nuclear Radiations:

There are numerous applications of radiations in industry, research, and health, including energy generation, cancer treatment, and medical imaging. However, exposure of nuclear radiation can cause severe health issues. Some of the harmful effects of nuclear radiations are-

1. Causes cell and DNA damage.
2. Increases the risk of cancer.
3. Leads to radiation burns and sickness.
4. May cause infertility or birth defects.
5. Weakens the immune system.
6. Contaminates the environment.

Exercise

A. Multiple choice questions

1. Which of the following is used in radiocarbon dating?
   a. Uranium-238 b. Carbon-14 c. Cobalt-60 d. Iodine-131

2. Which type of radiations have least penetrating power?
   a. X-ray b. γ c. β d. α

3. What type of nuclear reaction powers nuclear reactors?
   a) Fusion b) Combustion c) Fission d) Ionization

4. Which of the following is correct symbol of alpha particles?
   a. ${}_2He^4$ b. ${}_0n^1$ c. ${}_{-1}e^0$ d. ${}_1H^3$

5. Which is true for nuclear fusion?
   a. A heavy nucleus combines with neutron to produce complex nucleus
   b. Two lighter nuclei combine to give a single heavy nucleus
   c. A heavy nucleus breaks in to two or more lighter nuclei
   d. A single lighter nucleus fuses with neutron to give heavy nucleus.

6. Which process releases more energy?
   a. Chemical reaction b. Nuclear fission c.Nuclear fusion d. Beta decay

7. What is the SI unit of radioactivity?
   a.Curie b. Rutherford c. Siemen d. Bacquerel

8. Which of the following is used as a fuel in nuclear fission reactor?
   a. Cobalt-60 b. Plutonium-239 c. Helium-3 d. Deuterium

9. Which radioisotope is artificially produced?
   a. Uranium-235 b. Thorium-232 c. Radium-226 d. Cobalt-60

10. Which of the following is not a product of natural radioactive decay?
    a. Neutron beam b. Gamma rays c. Beta particles d.Alpha particles

B. Short answers questions:

11. Give reason,
    a. Carbon-14 is used in the dating of ancient biological substances.
    b. Alpha particles have low penetrating power.

12. Nuclear fusion is not yet used widely for energy production, why?

13. What is radioactivity? Write its unit.

14. What are radioactive substances? Give example.

15. Differentiate between-
    a. Nuclear reaction and chemical reaction
    b. Natural and artificial radioactivity

16. Compare nuclear fusion and nuclear fission.

17. Plutonium-239 absorbs a neutron and splits into xenon-140 and strontium-94, releasing neutrons and energy. Present schematic diagram for nuclear fission of plutonium.
18. Two carbon-12 nuclei fuse to form neon-20 and helium. Write the balanced nuclear equation for this fusion reaction.

19. Write the nuclear reaction for the formation of carbon-14 in the upper atmosphere.

20. What is natural radioactivity? Give one example. Also mention any one application of it.

21. Define artificial radioactivity with example. Write one important application of it.

22. What is nuclear power? Write advantages and disadvantages of nuclear power.

23. What do you mean by nuclear weapons? Give some examples.

24. Write an example of fission and fusion based nuclear weapons.

25. What are radioisotopes? List some medical uses of radioisotopes.

26. What are controlled and uncontrolled nuclear fission?

27. Write down the medical use of radioisotopes.

28. Write the uses of following radioisotopes-
    Co-60, I-131, Na-24, F-18

29. What are the harmful effects of nuclear radiations?

30. Write a note on- Radiocarbon dating.

31. Compare the properties of alpha, beta and gamma rays.

C. Long answer question:

32. Radioisotopes are widely used in both medicine and industry, but they also pose risks. Evaluate the benefits and potential dangers of using radioisotopes in modern society. How can their use be made safer?

34. What is radiocarbon dating? Explain the principle of radiocarbon dating.

PROJECT WORK

1. Visit a hospital or diagnostic center and choose any one imaging device (CT scan, PET scan, ultrasound (USG), and X-rays etc). Make a poster that describing how radioactivity is used in medical diagnosis including health hazard.
2. Design a poster or digital presentation that compares nuclear fusion and nuclear fission. Use diagrams, labeled parts, and bullet points to highlight differences in their reactions, energy output, safety concerns, and real-world applications (e.g., power plants, weapons).
3. Research and create a chart showing different radioisotopes used in fields like medicine, industry and research etc.

Radioisotope	Type of radiations	Field	Main use
Iodine-131	Beta, Gamma	Medicine	Treatment of thyroid cancer and hyperthyroidism.
Cobalt-60			
Phosphorous-32			
Ceasum-137			
Americum-241			
Carbon-14			
Sodium-24			
Iridium-192			
Uranium-238			

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