# ORGANIC CHEMISTRY II: ALCOHOLS AND ALKANOIC ACIDS:

## 1. Alkanols
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- Preparation and properties of alcohols
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  - Hydration of alkenes
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## 2. Alkanoic acids
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## 3. Fats and oils

## 4. Soaps and soapless detergents
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➢ Condensation polymerization

## ALCOHOLS (ALKANOLS):

- They are derivatives of **alkanes** in which a **hydrogen** has been replaced by a **hydroxyl group** (OH); which is the functional group.
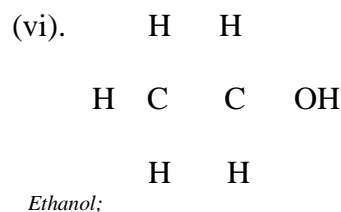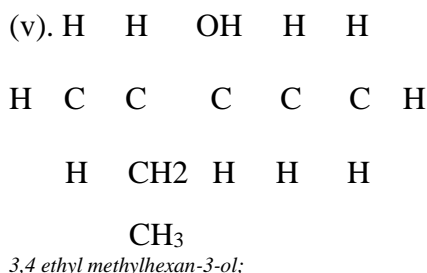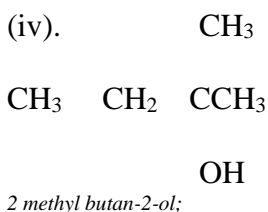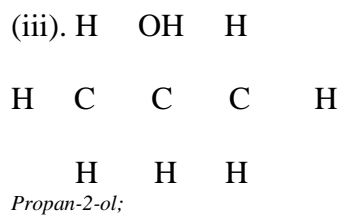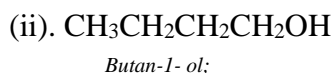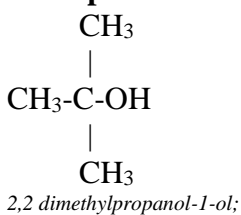- They form a homologous series of the general formula $C_nH_{2n+1}OH$, in which the OH can also be denoted as ROH, where R is an alkyl group.

**Note: alkanol** is the **IUPAC** name while **alcohol** is the common name;

### Nomenclature of alcohols

1. The 'e' of the corresponding alkane molecule is replaced with the suffix – ol;
2. The parent molecule is the longest chain containing the - OH group;
3. The numbering of carbon atoms is done such that the carbon atom with the hydroxyl group –OH- attains the lowest possible number
4. The constituent branch is named accordingly;

### Examples:

```
      CH₃                    (ii). CH₃CH₂CH₂CH₂OH              (iii). H    OH    H
       |                              Butan-1- ol;
    CH₃-C-OH                                                        H    C     C     C      H
       |
      CH₃                                                               H    H    H
2,2 dimethylpropanol-1-ol;                                      Propan-2-ol;


(iv).           CH₃        (v). H    H    OH    H    H     (vi).       H    H

 CH₃    CH₂   CCH₃              H    C    C     C    C    C    H        H    C    C    OH

              OH               H    CH2   H    H    H                       H    H
2 methyl butan-2-ol;                                                  Ethanol;
                                    CH₃
                               3,4 ethyl methylhexan-3-ol;
```
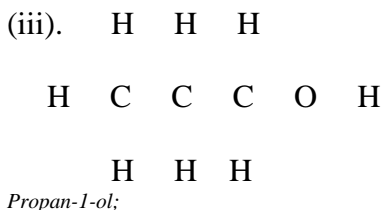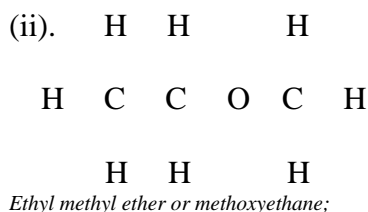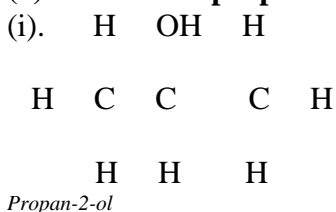
### Isomerism in alkanols.

- Alcohols exhibit **positional isomerism** due to the fact that the position of attachment of the functional group varies within the carbon chain;

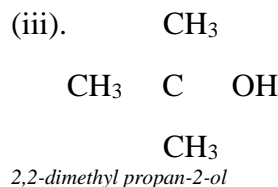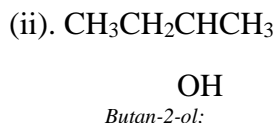### Examples of isomeric alcohols
### (a). Isomers of propanol

```
(i).   H    OH    H                     (ii).    H    H          H

  H    C    C     C    H                   H    C    C    O    C    H

     H    H    H                              H    H          H
Propan-2-ol                            Ethyl methyl ether or methoxyethane;


(iii).   H    H    H                    (iv).

   H    C    C    C    O    H

      H    H    H
Propan-1-ol;
```

**Note**: Ethyl methyl ether is not actually an alcohol as it lacks the –OH group;

- All have the molecular formula: $C_3H_7OH$

## (b). Isomers of butanol
(i). $CH_3CH_2CH_2OH$                    (ii). $CH_3CH_2CHCH_3$                    (iii).            $CH_3$

*Butan-1-ol;*

                                                    OH                    $CH_3$   C   OH

                                        *Butan-2-ol;*

                                                                                $CH_3$

                                                                        *2,2-dimethyl propan-2-ol*

**Note:** All have the molecular formula: $C_4H_9OH$

## (c). Draw the Isomers of pentanol, $C_5H_{11}OH$;
(i).   H  H  H      H  H                    (ii).                    (iii)                    (iv)

   H – C – C – C – O – C – C – H
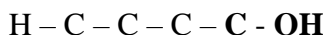
      H  H  H        H  H
            *Ethylpropylether*
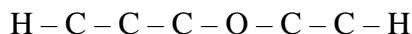
**Primary, secondary and tertiary alcohols.**
➤ **Primary alcohols:**
- Are alcohols in which the OH group is attached to a carbon atom to which **2 hydrogen atoms** are attached;
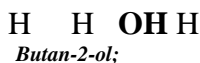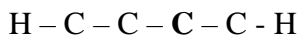- Thus they contain a **–CH₂OH** group;
**Examples**:
            H   H   H  **H**

      H – C – C – C – **C** - **OH**

      H    H  H  **H**
            *Butan-1-ol;*

➤ **Secondary alcohols:**
- Are alcohols in which the hydroxyl group is attached to the carbon atom to which **only one other hydrogen** atom is attached;
- The carbon atom with the OH group is thus bonded to two carbon atoms;
- They contain a **CHOH** group;
**Example**:
            H   H  **H**  H

      H – C – C – **C** – C - H

      H    H  **OH** H
            *Butan-2-ol;*

➤ **Tertiary alcohols:**
- The hydroxyl group is attached to a carbon atom with no hydrogen atoms attached
- The carbon atom with the OH group is bonded to **3 other carbon atoms**; hence sorrounded by the methyl groups;
- Tertiary alcohols thus a contain a **–COH** group;
**Examples**:
      H  **OH** H

   H – C – **C** – C - H

H    CH₃    H
*2-methyl propan-2-ol;*

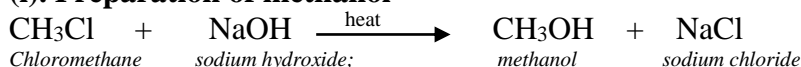## Preparation and properties of alkanols.

- Alkanols are prepared from three main methods.
➢ Hydrolysis of halogenoalkanes;
➢ Hydration of alkenes
➢ Fermentation of starches and sugars (mainly for ethanol)

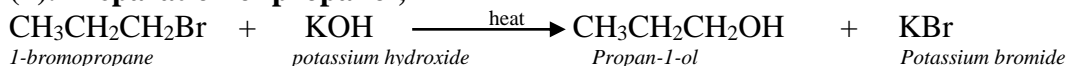### (a). **Hydrolysis of halogenoalkanes**;

- Halogenoalkanes are compounds in which one or more hydrogen atoms in an alkane are replaced by halogens;
- Addition of aqueous KOH or NaOH to a halogenoalkane and *heating* results to corresponding alcohol;
- Reaction involves replacement of the halogen atoms with the -OH from the alkali;

### Examples:
### (i). Preparation of methanol

$$CH_3Cl \quad + \quad NaOH \xrightarrow{\text{heat}} CH_3OH \quad + \quad NaCl$$
*Chloromethane*     *sodium hydroxide;*       *methanol*      *sodium chloride*

### (ii). Preparation of propanol;

$$CH_3CH_2CH_2Br \quad + \quad KOH \xrightarrow{\text{heat}} CH_3CH_2CH_2OH \quad + \quad KBr$$
*1-bromopropane*      *potassium hydroxide*      *Propan-1-ol*      *Potassium bromide*

**Note: -**the conversion of a halogenoalkane to an alcohol is known as **hydrolysis**;
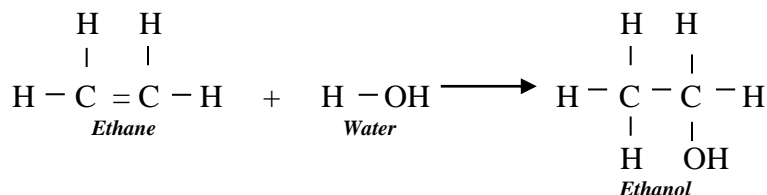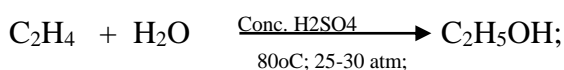- Reagent in this case is an alkali and condition for reaction is heat;
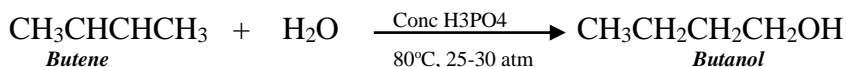
### (b). **Hydration of alkenes.**

- Conversion of an alkene to an alcohol is known as **hydration**;
- Main reagent for the reaction is water;
- Conditions for the reaction are:
➢ An acid catalyst, mainly conc. $H_2SO_4$ or phosphoric acid ($H_3PO_4$);
➢ High temperatures of about 80°C;
➢ High pressures of about 25-30 atmospheres;

### Examples:
### (i). **Preparation of ethanol from ethene.**

$$C_2H_4 \quad + \quad H_2O \xrightarrow[\text{80oC; 25-30 atm;}]{\text{Conc. H2SO4}} C_2H_5OH;$$

Ethane     Water     Ethanol

### (ii). **Preparation of butanol from butene.**

$$CH_3CHCHCH_3 \quad + \quad H_2O \xrightarrow[\text{80°C, 25-30 atm}]{\text{Conc H3PO4}} CH_3CH_2CH_2CH_2OH$$
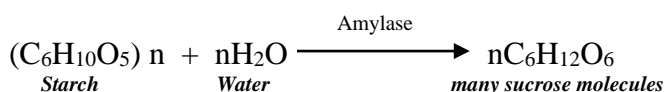*Butene*      *Butanol*

### (c). Preparation (of ethanol) by fermentation.

- It is prepared from the **fermentation** of starches or sugars in the presence of **yeast**;
- **Fermentation:** Is a chemical decomposition brought by bacteria or yeast (anaerobically) usually accompanied by evolution of carbon (IV) oxide and heat.
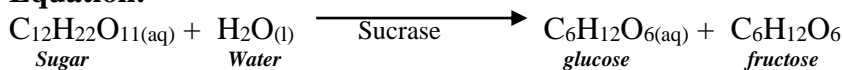
**The chemical process**
- Starch is broken into sugars by the action of the enzyme **amylase or diastase**;

Starch molecule + water $\xrightarrow{\text{Break up into}}$ sucrose molecules

$(C_6H_{10}O_5)\,n \;+\; nH_2O \xrightarrow{\text{Amylase}} nC_6H_{12}O_6$
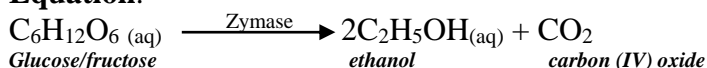*Starch*      *Water*      *many sucrose molecules*

- When yeast is added to dilute sucrose solution (ordinary sugar); the enzyme **sucrase** in yeast catalytically breaks down sugar (sucrose) into the simplest sugars, glucose and fructose i.e.

**Equation:**
$C_{12}H_{22}O_{11(aq)} + H_2O_{(l)} \xrightarrow{\text{Sucrase}} C_6H_{12}O_{6(aq)} + C_6H_{12}O_6$
*Sugar*      *Water*          *glucose*      *fructose*

- Finally the enzyme **zymase**, also produced by yeast converts glucose and fructose into ethanol and carbon (IV) oxide.

**Equation**:
$C_6H_{12}O_{6\,(aq)} \xrightarrow{\text{Zymase}} 2C_2H_5OH_{(aq)} + CO_2$
*Glucose/fructose*           *ethanol*      *carbon (IV) oxide*

**Optimum conditions for fermentation:**
➢ Temperatures of 25-30°C;
➢ Yeast catalyst;
➢ Absence of oxygen (airtight);

**Note:**
- When the reaction mixture contains about 12% by volume of ethanol, the activity of yeast ceases.
- This is because higher ethanol concentrations **kill** the yeast cells;
- Fermentation provides about 10% alcohol by volume;
- The concentration of resultant ethanol can be increased by **fractional distillation**.
- During the process, ethanol distills over fast due to its **lower** boiling point (78°C)
- The distillate at below 95°C is first collected (leaving water behind).
- The resultant fraction will have 95% alcohol by volume; and is called **rectified spirit**;
- Absolute ethanol; which is 99.5% by volume can be obtained by re-distillation of rectified ethanol between 78-82°C to remove all the water in the mixture;

- This can be done in **two** main ways:
➢ Addition of a small amount of **benzene** to the rectified spirit and then distilling; (benzene dissolves in the water in the alcohol)
➢ Distillation of rectified spirit over a suitable drying agent like **calcium oxide** and then over calcium; (calcium reacts with steam, calcium oxide takes in condensed water)

**Properties of alcohols (Ethanol)**
**(a) Physical properties**
(i). It is a **colourless, volatile** liquid **soluble in water** in all proportions forming a **neutral** solution;
(ii). Has a characteristic smell and boils at78.5°C

**Variation in physical properties of alkanols.**

| Name | Molecular formula | Molecular mass | Boiling point (ºC) | Melting point (ºC) | Solubility in 100g of water |
|---|---|---|---|---|---|
| Methanol | $CH_3OH$ | 32 | 64.5 | -94 | Soluble |
| Ethanol | $C_2H_5OH$ | 46 | 78.5 | -117 | Soluble |

| | | | | | |
|---|---|---|---|---|---|
| Propanol | $C_3H_7OH$ | 60 | 97 | -127 | Soluble |
| Butanol | $C_4H_9OH$ | 74 | 117 | -90 | Slightly soluble |
| Pentanol | $C_5H_{11}OH$ | 88 | 138 | -79 | Slightly soluble |
| Hexanol | $C_6H_{13}OH$ | 102 | 158 | -52 | Slightly soluble |
| Heptanol | $C_7H_{14}OH$ | 116 | 175 | -34.6 | Very slightly soluble |
| Octanol | $C_8H_{16}OH$ | 130 | 194 | -16 | Very slightly soluble; |

**Note:**
- Solubility of alkanols **decreases** with **increase** in **molecular mass**;
- Both melting and boiling points **increases** with **increase** in the relative molecular mass; due to progressive increase in number of van der waals forces;
- Alkanols have higher melting and boiling points than their corresponding alkanes with the same molecular formula;

**Reason:**
- Alkanols have **hydrogen bonding** between their molecules, caused by the presence of the OH group; alkanes have **van der waals** between its molecules; Hydrogen bonds are stronger than weak van der waals;

Diagram: Hydrogen bonding between four ethanol molecules.

**(b) Chemical properties /main reactions of ethanol.**
**Note;** the main reactions of ethanol are those of its functional group **–OH**;

**(iii). Combustion**
*Procedure*;
- A few drops of ethanol are placed in a watch glass and lit.
- A dry gas jar is held over the flame and the gas collected tested with limewater.

*Observation*:
- It burns with a **blue flame**, which is almost colourless.
- The resultant gas turns limewater into a **white precipitate**, indicating it is carbon (IV) oxide.

*Explanations:*
- Ethanol (alcohols) burns in air (oxygen) producing carbon (IV) oxide, water and heat energy;

- The lower members of the homologous series burn with a blue or non-luminous flame leaving no residue;
- As the hydrocarbon chain increases the flame becomes more luminous and smoky and a black residue remains;
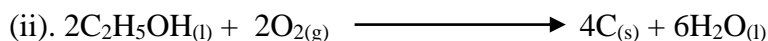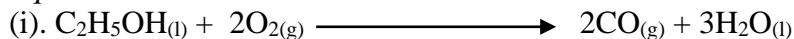
*Equation*

$$C_2H_5OH_{(l)} +\ 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$$
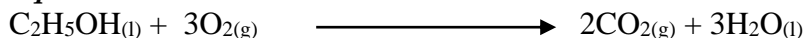
**Note:**
- If an alkanol is burnt in a limited supply of oxygen, then the combustion is incomplete and the products include carbon (II) oxide or carbon and water

*Equations*

(i). $C_2H_5OH_{(l)} +\ 2O_{2(g)} \longrightarrow 2CO_{(g)} + 3H_2O_{(l)}$

(ii). $2C_2H_5OH_{(l)} +\ 2O_{2(g)} \longrightarrow 4C_{(s)} + 6H_2O_{(l)}$

**(iv). Reaction with metals (sodium);**
*Procedure*:
- Tiny pieces of sodium one at a time; are added 1cm³ of pure ethanol in a boiling tube.

*Observation*;
- Sodium metal darts on the surface of the ethanol and then dissolves /disappears;
- The beaker becomes warmer indicating an **exothermic reaction**.
- **Effervescence** occurs and bubbles of a colourless gas are observed; gas burns with a **pop sound.**

*Explanation*:
- Sodium reacts with alcohol much as it does with water but the reaction is more **gentle**.
- Sodium reacts with ethanol to produce **hydrogen gas**, which on testing burns with a pop sound.
- The reaction is **exothermic** producing **heat** hence warmer beaker.
- A clear solution of **sodium ethoxide** is left formed in the boiling tube.
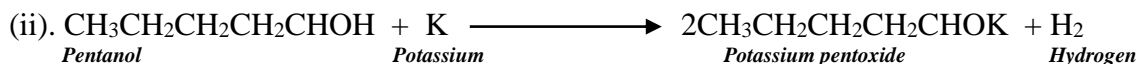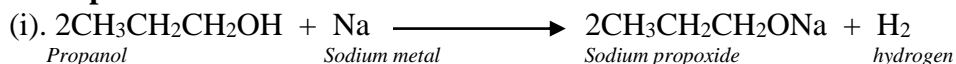
*Equation;*

$$2C_2H_5OH + Na_{(l)} \longrightarrow 2CH_3CH_2ONa_{(l)}\ + H_{2(g)}$$
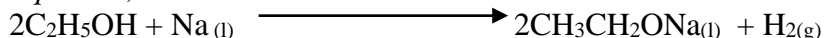
**Note:**
Alkanols react with electropositive metals such as sodium, potassium and aluminium to liberate hydrogen gas and form a solution of the metal salt, the **metal alkoxide**;

**Examples**

(i). $2CH_3CH_2CH_2OH\ + Na \longrightarrow 2CH_3CH_2CH_2ONa\ + H_2$
    *Propanol*            *Sodium metal*        *Sodium propoxide*       *hydrogen*

(ii). $CH_3CH_2CH_2CH_2CHOH\ +\ K \longrightarrow 2CH_3CH_2CH_2CH_2CHOK\ + H_2$
    *Pentanol*               *Potassium*           *Potassium pentoxide*       *Hydrogen*

**Note**: The reactivity of alkanols with metals decreases as the hydrocarbon chain increases;

**(v). Esterification;**
- It is the production of **esters** (alkyl alkanoates) from the reaction between alcohols and carboxylic acids;

*Procedure*

- 2-3 drops of concentrated sulphuric acid are added to a mixture of equal proportions of ethanol and pure ethanoic acid in an evaporating dish.
- The mixture is warmed gently in a water bath for sometime.
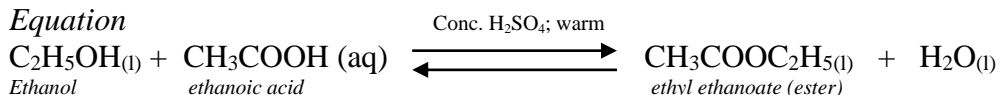- The mixture is poured into a beaker and smelt;

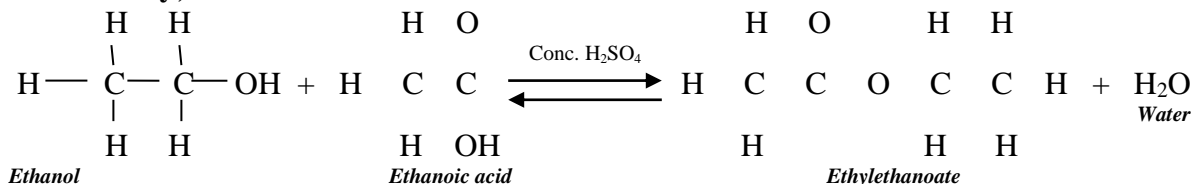*Observation*
A **fruity sweet smell** (of ethyl ethanoate);

*Explanation*
- Ethanol reacts with ethanoic acid in the presence of a few drops of concentrated sulphuric acid to form **ethyl ethanoate** and **water.**
- The reaction is very slow and so **catalyzed** by the **hydrogen ions** from the sulphuric acid.

*Equation*

$$C_2H_5OH_{(l)} + CH_3COOH \text{ (aq)} \underset{\longleftarrow}{\overset{\text{Conc. } H_2SO_4; \text{ warm}}{\longrightarrow}} CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

*Ethanol*      *ethanoic acid*                                       *ethyl ethanoate (ester)*

**Structurally;**



- The **alkyl** part of the ester is derived from the **alkanol**, while the **alkanoate** part is derived from the **alkanoic acid;**
- The alkanol attaches itself at the group in the carboxylic acid thereby displacing hydrogen atom;
- Under ordinary conditions the reaction takes place slowly; but in presence of **concentrated sulphuric acid which act as a catalyst** and warm (**heat**) conditions, the reaction is enhanced;

**Further examples:**
**Write balanced equations for each of the following esterification reactions:**
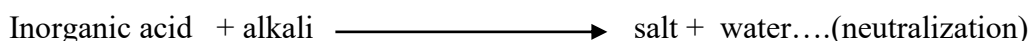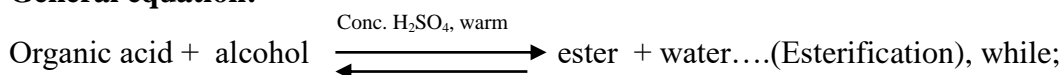**(i). Ethanol and propanoic acid;**

**(ii). Propanol and ethanoic acid;**

**(iii). Ethanol and methanoic acid;**

**Note:**
- Generally a reaction between alcohol and a carboxylic acid (-COOH-) produces an ester and water in a process called Esterification;

**General equation:**

Organic acid + alcohol $\underset{\longleftarrow}{\overset{\text{Conc. } H_2SO_4, \text{ warm}}{\longrightarrow}}$ ester + water….(Esterification), while;

Inorganic acid + alkali $\longrightarrow$ salt + water….(neutralization)

**Differences between neutralization and Esterification**

1. Esterification is slower than neutralization as the reaction is between molecules and not ions as in neutralization
2. Esterification is reversible; the forward reaction is **esterification** and the backward reaction is **hydrolysis.**
3. Esterification results to esters which are covalent compound; neutralization forms salts which are electrovalent.

**Name and formulae of some common esters.**

| Alkanol | Alkanoic acid | Ester |
|---|---|---|
| Methanol $CH_3OH$ | Propanoic acid $$CH_3CH_2 \quad C \quad OH$$ with O above C | Methylpropanoate $$CH_3CH_2 \quad C \quad OCH_3$$ with O above C |
| Ethanol $C_2H_5OH$ | Methanoic acid $$H \quad C \quad OH$$ with O above C | Ethylmethanoate $$H \quad C \quad OCH_2CH_3$$ with O above C |
| Propan-1-ol | Ethanoic acid | |
| Butan-1-ol | Ethanoic acid | |

**(vi). Oxidation of primary alkanols;**
- On heating in presence of oxidising agents, primary alkanols are oxidised to alkanoic acids;
**Note:**
- During oxidation of alcohols, they first lose hydrogen to form compounds called *aldehydes (*compounds ending in –al)
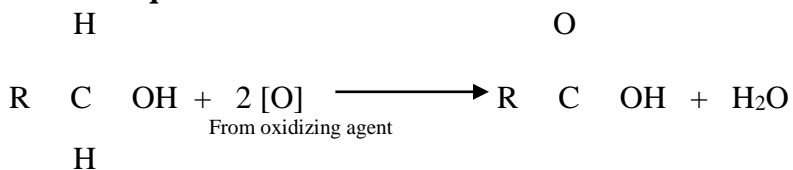- The resultant aldehydes (alkanal) then gain oxygen to form alkanoic acids.

**Equations:**
(i). Alkanol – hydrogen $\longrightarrow$ alkanal + water
Then;
(ii). Alkanal + oxygen $\longrightarrow$ alkanoic acid;

**General equation:**

$$
\begin{array}{c}
H \\
R \quad C \quad OH + 2\,[O] \longrightarrow R \quad C \quad OH + H_2O \\
H
\end{array}
$$

From oxidizing agent (under 2 [O])

(with H at top left and O at top right over the C on right side)

**Example: Oxidation of ethanol**
- Ethanol like all other alcohols is oxidized by strong oxidizing agents such as potassium dichromate (VI) and potassium manganate (VII) to form ethanoic acid.

**(a). Reaction with acidified potassium dichromate (VI):**

*Procedure*
- A little solution of acidified potassium dichromate (VI) is added to a little solution of ethanol in a test tube and then warmed gently;
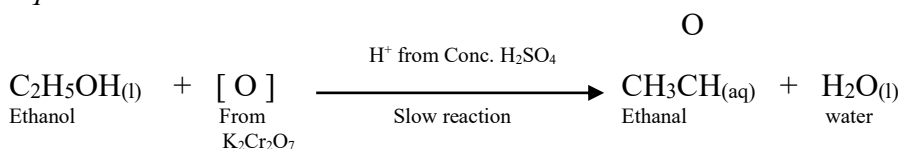
*Observation:*
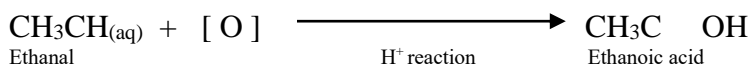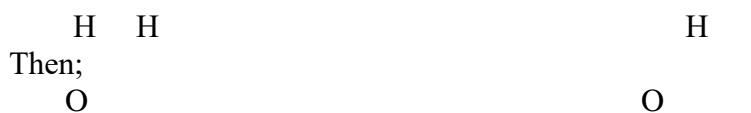- The solution (dichromate) changes from yellow to green;

*Explanation*
- The acidified potassium dichromate (VI) **oxidizes** the ethanol to ethanal then to ethanoic acid, while the dichromate undergoes **reduction** (chromate (VI) to $Cr^{3+}$ changing colour from **yellow** to **green**;

*Equations*

$$C_2H_5OH_{(l)} \; + \; [\,O\,] \xrightarrow[\substack{\text{Slow reaction}}]{H^+ \text{ from Conc. } H_2SO_4} CH_3CH_{(aq)} \; + \; H_2O_{(l)}$$

Ethanol    From $K_2Cr_2O_7$      Ethanal    water

**Structurally:**

$$
\begin{array}{cc}
\text{H} & \text{H} \\
| & | \\
\text{H} - \text{C} - \text{C} - \text{OH} + [\,O\,] \longrightarrow \\
| & | \\
\text{H} & \text{H}
\end{array}
\qquad
\begin{array}{cc}
\text{H} & \text{H} \\
| & | \\
\text{H} - \text{C} - \text{C} - \text{O} + H_2O \\
| & \\
\text{H} &
\end{array}
$$

Then;

$$CH_3CH_{(aq)} \; + \; [\,O\,] \xrightarrow{H^+ \text{ reaction}} CH_3C-OH$$

Ethanal                       Ethanoic acid

**General equation**

$$
\begin{array}{cc}
\text{H} & \text{H} \\
| & | \\
\text{H} - \text{C} - \text{C} - \text{OH}_{(l)} + 2[\,O\,] \\
| & | \\
\text{H} & \text{H}
\end{array}
\qquad
CH_3C-OH \; + \; H_2O
$$

**(b). Reaction with acidified potassium manganate (VII).**

*Procedure*
Acidified potassium permanganate solution is added to ethanol in a test tube end the mixture is warmed gently.
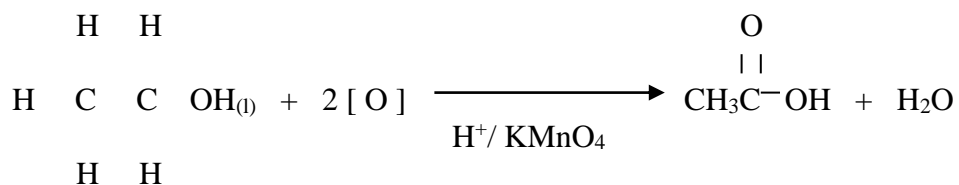
*Observation*
The permanganate solution turns from purple to colourless.
The characteristic smell of ethanoic acid is felt.

*Explanation*
The ethanol is oxidized to ethanal then to ethanoic acid. The reduced permanganate decolorizes (turns from purple to colourless);
-The $H^+/KMnO_4$ is decolourised due to reduction of manganate (VII) ions to $Mn^{2+}$

**General equation:**

$$\underset{\substack{|\;\;\;|\\ H\;\;\;H}}{\overset{\substack{H\;\;\;H\\ |\;\;\;|}}{H-C-C-OH_{(l)}}} + 2\,[\,O\,] \xrightarrow[\;H^+/\,KMnO_4\;]{} CH_3C\overset{O}{\overset{||}{-}}OH + H_2O$$

## (c). Catalytic oxidation of alkanols.

- Catalytic oxidation of alkanols results to a dehydrogenation (removal of hydrogen) resulting to the formation of an alkanal (aldehyde);
- These are compounds with the functional group COH;

**Example: Catalytic oxidation of ethanol with hot copper metal**

When ethanol is passed over heated copper at about 300 °C, it is dehydrogenated i.e. hydrogen is removed. This results into formation of an ethanal; and hydrogen gas is liberated.

**Equation**

$$CH_3CH_2OH(g) \xrightarrow[250^oC]{Cu(s)} CH_3CHO_{(l)} + H_{2(g)}$$

*Ethanol*                                *Ethanal*
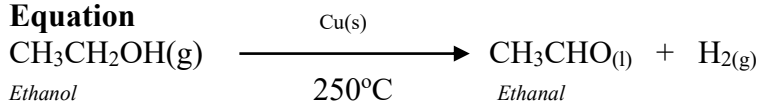
## (vii). Dehydration reactions of alcohols.

- Dehydration is the removal of water molecules from a compound;
- Excess concentrated sulphuric (VI) acid dehydrates alkanols and forms corresponding alkenes.

**Conditions required: -**

- High temperatures of 140-180°C.
- Catalysts such as conc. sulphuric acid, phosphoric acid and aluminium oxide;

**Example: Dehydration of ethanol**

*(i). Apparatus*

*(ii). Procedure*

- 15cm$^3$ of absolute ethanol are put in around bottomed flask and 5cm$^3$ of con $H_2SO_4$ added.
- The contents are mixed thoroughly by swirling the flask.

- The flask is then heated (warmed) gently with little shaking for about 1 minute.
- The gas collected is tested with acidified potassium manganate (VII) and bromine water.

*(iii). Observations*
- Evolution of a colourless gas that decolourises the purple acidified potassium manganate (VII)
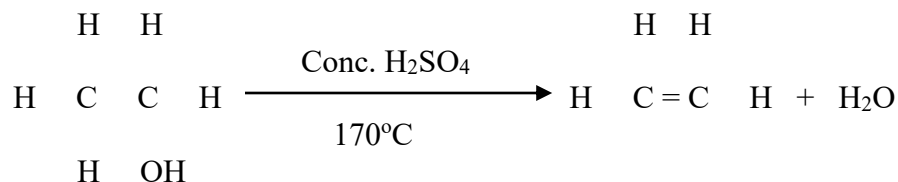- The resultant gas also decolourises the red brown bromine water.

*(iv). Explanations*
- On heating the alkanol (ethanol) undergoes an elimination reaction.
- It loses both a hydrogen (H) and a hydroxyl (OH) from two adjacent carbon atoms.
- The H and OH combine to form water; and the remnants form ethene.
- The sulphuric acid acts as a catalyst.

**Note:** Disadvantage of concentrated sulphuric acid over phosphoric acid.
- Being a strong oxidising agent the concentrated sulphuric acid oxidizes some of the alkanol formed to $CO_2$ and it is itself reduced to $SO_2$;
- This reduces the volume and purity of resultant alkanol; and is also a potential source of pollution;

**Equation**

$$\begin{array}{cccc} & \text{H} & \text{H} & \\ & | & | & \\ \text{H} & \text{C} & \text{C} & \text{H} \\ & | & | & \\ & \text{H} & \text{OH} & \end{array} \xrightarrow[170^oC]{\text{Conc. } H_2SO_4} \begin{array}{ccc} & \text{H} & \text{H} \\ & | & | \\ \text{H} & \text{C} = \text{C} & \text{H} \end{array} + H_2O$$

**Note:**
With cold concentrated sulphuric (VI) acid, alkanols react to form alkyl hydrogen sulphates.

**Example: Ethanol and cold conc. sulphuric acid.**

$$C_2H_5OH + H_2SO_{4(l)} \longrightarrow C_2H_5HSO_{4(l)} + H_2O_{(l)}$$
*Ethanol*                  *Ethyl hydrogen sulphate*
                             *(Ethoxyethane)*
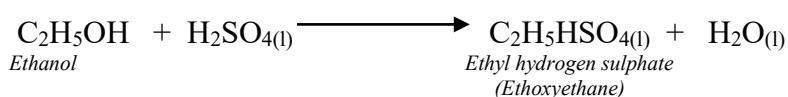
**Uses of ethanol**
1. Used as solvents; in the preparation of drugs, perfumes, liquors, vanish and paints.
2. Source of fuel e.g ethanol when blended with gasoline to form gasohol.
**Note:**
- Addition of ethanol to petrol improves the antiknock propertied of petrol, due to its low ignition point;
- The alkanol also absorbs any traces of moisture that may enter and damage the petrol system;
- Alkanols also ignite on their own to liberate heat;
**Example:**
$$CH_3CH_2OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} \quad \Delta H = -1368KjMol^-$$

3. Starting material for the manufacture of polyvinyl chloride (P.V.C)
4. Ethanol is used as a disinfectant (antiseptic) at special concentrations e.g for cleaning tissues and surgical equipments during operations and in dressing wounds;
5. Manufacture of alkanoic acids e.g ethanoic acid
6. Ethanol is used as thermometer liquid for measuring low temperatures;
7. Manufacture of alcoholic drinks
8. Large amounts of methanol are used in the manufacture of formaldehyde a chemical used in preservation of corpses;

9. They are used as antifreeze mixtures in car radiators e.g a mixture of ethanol and water freezes at lower temperatures that pure water;

10. Manufacture of esters to giver fruity flavourings for confectionery and drinks;

## Tests for primary alkanols.
### 1. Reaction with sodium metal
- Alkanols liberate hydrogen gas, a colourless gas that burns with a pop sound;

**Equation:**
$$2CH_3CH_2OH_{(l)} + 2Na_{(s)} \longrightarrow 2CH_3CH_2ONa + H_{2(g)}$$
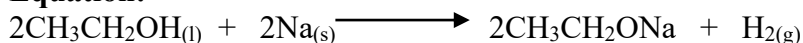
### 2. Reaction with phosphorus (V) chloride:
- Alkanols liberate misty fumes of hydrogen chloride gas;

**Equation:**
$$PCl_5(s) + CH_3CH_2OH \qquad\qquad 2CH_3CH_2OP + HCl_2$$

**Note:**
- Both alkenes and alkanols decolourise the purple acidified potassium manganate (VII);
- However, alkenes decolourise the red bromine water; while alkanols do not.

## Summary on preparation of alkanols (ethanol).
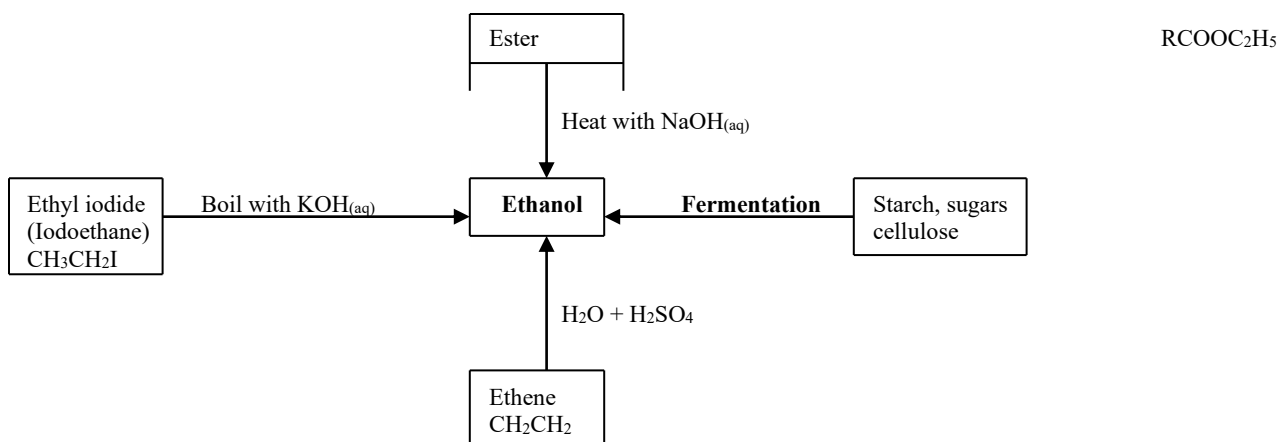


## Summary on reactions of alkanols.
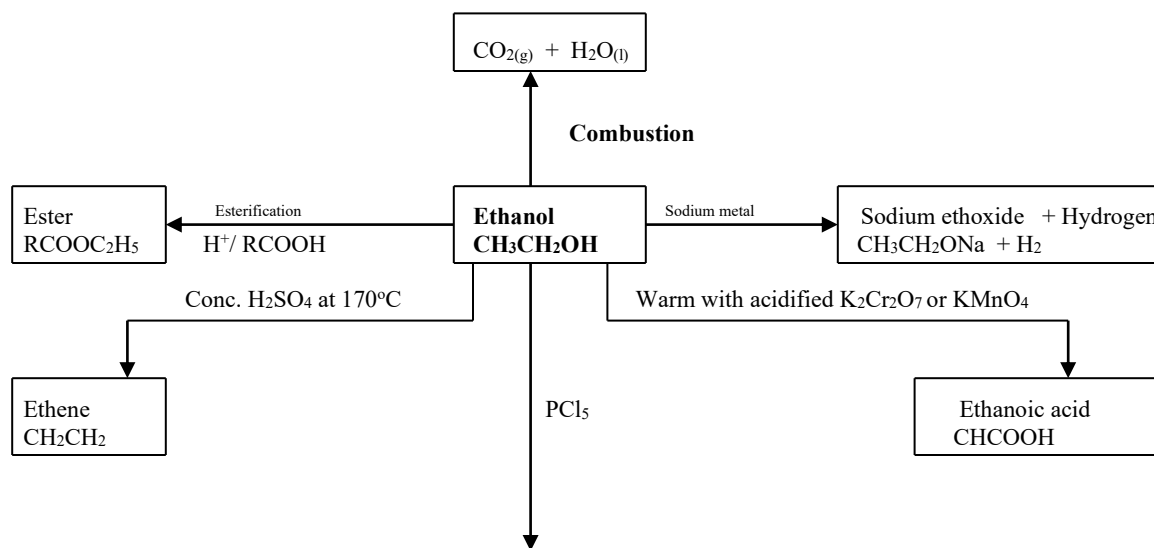
Chloroethane
$CH_3CH_2Cl$

# ALKANOIC ACIDS (CARRBOXYLIC ACIDS)
- Also called organic acids and form a homologous series with a general formula of $C_nH_{2n-1}OOH$
- The formula can also be written as $C_nH_{2n+1}COOH$; in which case n = (no. of carbon atoms - 1)
- Members differ from each other by an additional $CH_2$ group.
- Their functional group is the **carboxylic group** (-COOH) which is attached to the alkyl group.
- Graphical representation of carboxyl group; 
$$O$$
$$|$$
$$C-OH$$
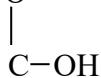
**Note:** All **carboxylic acids** have the –COOH as the functional group but **alkanoic acids** are strictly alkanoic acids derived from alkanes

## Nomenclature of alkanoic acids
- The ending of the corresponding alkane is replaced by ′oic acid'.

## Examples;
- Methane to methanoic acid.
- Ethane to ethanoic acid.

- They are named as if they are derived from alkanes through replacement of one of the hydrogen atoms by the -COOH group.

**Note: -**Unlike alkanols the functional group (COOH) in alkanoic acids can only be at the end of the carbon chain.
- The C in the COOH is always given the first position, while the substituents are given locants (numbers in reference to the first position).

## Examples:

| IUPAC name | Old (traditional ) name | Structural formula |
|---|---|---|
| Methanoic acid | Formic acid | OH<br>$\|$<br>H    C = O |
| Ethanoic acid | Acetic acid | OH<br>$\|$<br>$CH_3$ - C = O |
| Propanoic acid | Propionic acid | OH<br>$\|$<br>$CH_3CH_2$ – C = O |
| Ethanedioic acid | Oxalic acid | O      O<br>   C - C<br>HO      OH |
| Butanedioic acid | Succinic acid | O<br>$CH_2C$<br>$\|$    OH<br>     O<br>$CH_2C$<br>     OH |

**Branched alkanoic acids**

- The naming of branched alkanoic acids follow the same general rules like that of alkanes; as long as the carbon atom with the –COOH group is given the first position.
- The branch can either be an alkyl group or a halogen other than hydrogen.

**Examples:**

| Compound | IUPAC name |
|---|---|
| $$Cl - CH_2 - C \overset{\displaystyle O}{\underset{\displaystyle OH}{}}$$ | 2-chloroethanopic acid; |
| $$CH3 - \underset{\displaystyle CH_3}{CH} - C \overset{\displaystyle O}{\underset{\displaystyle OH}{}}$$ | 3-methylpropanoic acid; |
| $$CH_3 - \underset{\displaystyle OH}{CH} - C \overset{\displaystyle O}{\underset{\displaystyle OH}{}}$$ | 2-hydroxypropanoic acid; |
| $$CH_3 - \overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}} - C \overset{\displaystyle O}{\underset{\displaystyle OH}{}}$$ | 2-hydroxy, 2-methylpropanoic acid; |
| $$\underset{\displaystyle Br}{CH_2} - \underset{\displaystyle Cl}{CH} - CH_2 - C \overset{\displaystyle O}{\underset{\displaystyle OH}{}}$$ | 4-bromo, 3-chlorobutanoic acid; |

**Isomerism in alkanoic acids.**
- Due to the existence of branched alkanoic acids, it is possible to obtain various isomers for a given alkanoic acid;

**Example:**
*Draw all the isomers of pentanoic acid.*                                        *(3 marks)*

**Preparation of alkanoic acids**
**(a). Industrial manufacture**
- Is done by the oxidation of primary alkanols using air (oxygen) as the oxidising agent.

**Conditions:**
- Moderate temperatures
- 5 atm pressure
- Hot copper catalyst;

**Laboratory preparation.**
- Is done by the oxidation of primary alkanols using acidified potassium dichromate (VI).

**Example: Laboratory preparation of ethanoic acid.**
*(i). Apparatus*




*(ii). Procedure*
- Acidified potassium dichromate (VI) is heated in a water bath and ethanol added slowly from a water bath.
-The mixture is heated further and then distilled.
- The distillate is collected at about 105ºC.

*(iii). Observations and explanations.*
Colour of potassium dichromate (VI) changes from orange to green.
**Reason:**
The dichromate ions are reduced to chromium (III) ions.

**Equation:**
$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e^- \longrightarrow 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$$
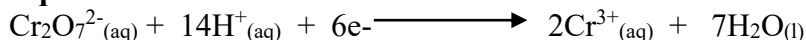
- The ethanol is oxidised to ethanal (acetaldehyde); which is further oxidised to alkanoic acid.
*Equations*

$$C_2H_5OH_{(l)} + [\,O\,] \xrightarrow[\text{Slow reaction}]{H^+ \text{ from Conc. } H_2SO_4} CH_3\overset{O}{C}H_{(aq)} + H_2O_{(l)}$$

Ethanol     From K$_2$Cr$_2$O$_7$     Ethanal     water

**Structurally:**

H   H                                         H   H

H   C   C   OH + [ O ] $\longrightarrow$ H   C   C   O + H$_2$O

H     H                                              H

Then;

   O                                              O

$CH_3CH_{(aq)}$  +  [ O ] $\longrightarrow$ $CH_3C$   OH
Ethanal                      $H^+$ reaction         Ethanoic acid

## General equation

H     H                                              O

H    C    C    $OH_{(l)}$  +  2 [ O ]                    $CH_3C$  OH  +  $H_2O$

    H     H
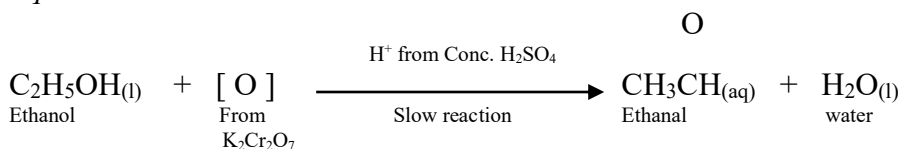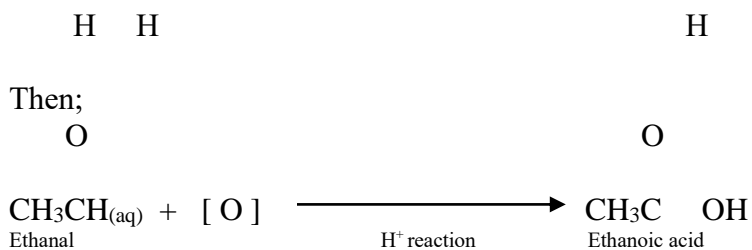
## Properties of alkanoic acids

## Gradation in physic al properties of alkanoic acids

| Name of acid | Formula (structural) | Molecular formula | M.P °C | B.P °C | Solubility |
|---|---|---|---|---|---|
| **Methanoic acid** | HC OOH | $CH_2O_2$ | 8.4 | 101 | Most Soluble |
| **Ethanoic acid** | $CH_3COOH$ | $C_2H_4O_3$ | 16.6 | 118 | |
| **Propanoic acid** | $CH_3CH_2COOH$ | $C_3H_6O_2$ | -20.8 | 141 | increasing solubility |
| **Butanoic acid** | $CH_3CH_2CH_2COOH$ | $C_4H_8O_2$ | -6.5 | 164 | |
| **Pentanoic acid** | $CH_3CH_2CH_2CH_2COOH$ | $C_5H_{10}O_2$ | -34.5 | 186 | |
| **Hexanoic acid** | $CH_3(CH_2)_4COOH$ | $C_6H_{12}O_2$ | -1.5 | 205 | Least soluble |

## Physical properties of ethanoic acid
- A colourless liquid with a sharp pungent smell.
- B.P is 118ºC and freezes at 17°c forming ice like crystals termed as glacial ethanoic acid.
- It is soluble in water and is weakly acidic with a P.H of approximately4.8.

## Note
- Concentrated ethanoic acid is only slightly ionized and is a poor conductor of electricity
- On dilution its conductance steadily improves as the extent of ionization increases

## Chemical properties (reactions) of alkanols.
## (i). Reaction with carbonates.
- Alkanoic acids react with metal carbonates to form a salt (metal alkanoate), carbon (IV) oxide and water.

## Examples:
*Ethanoic acid and sodium carbonate*
Ethanoic acid reacts with sodium carbonate to form sodium ethanoate and water with the liberation of carbon (IV) oxide gas.

*Equation*

$$Na_2CO_3 \ + \ 2CH_3COOH \longrightarrow 2CH_3COONa \ + \ CO_{2(g)} \ + \ H_2O_{(l)}$$
*Sodium carbonate*                          *Sodium ethanoate*
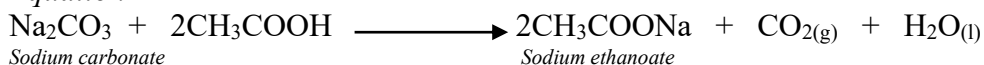
*Zinc carbonate and ethanoic acid.*

$$ZnCO_3 \ + \ 2CH_3COOH \longrightarrow (CH_3COO)_2Zn \ + \ CO_{2(g)} \ + \ H_2O_{(l)}$$
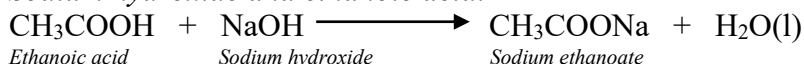*Zinc carbonate*                        *Zinc ethanoate*
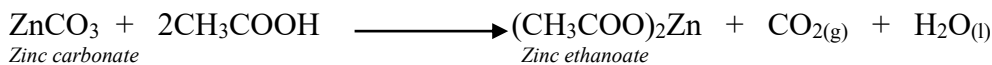
## (ii). Reaction with metal hydroxides (Neutralization)
Alkanols neutralize alkalis like sodium hydroxide forming a salt (metal alkanoate) and water only.

### Examples:
*Sodium hydroxide and ethanoic acid.*

$$CH_3COOH \ + \ NaOH \longrightarrow CH_3COONa \ + \ H_2O(l)$$
*Ethanoic acid*        *Sodium hydroxide*        *Sodium ethanoate*

*Potassium hydroxide and methanoic acid*

$$HCOOH \ + \ KOH \longrightarrow HCOOK \ + \ H_2O(l)$$
*Methanoic acid*      *Potassium hydroxide*      *Potassium methanoate*
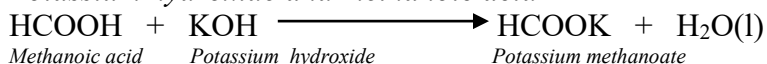
## (iii). Reaction with metal oxides (neutralization).
- Alkanoic acids react with metal oxides to produce salt (metal alkanoate and water only.

### Examples:
*Ethanoic acid and copper (II) oxide.*

$$2CH_3COOH \ + \ CuO \longrightarrow (CH_3COO)_2Cu \ + \ H_2O(l)$$
*Ethanoic acid*           *Copper (II) oxide*          *Copper ethanoate*
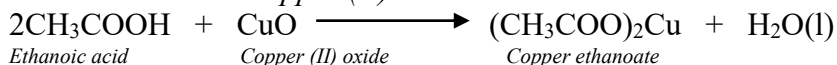
## (iv). Reaction with metals
Alkanoic acids react with reactive metals to form a salt (metal alkanoate) and hydrogen gas;

### Examples:
*Ethanoic acid and sodium metal*

$$2CH_3COOH \ + \ Na_{(s)} \longrightarrow 2CH_3COONa \ + \ H_{2(g)}$$
*Ethanoic acid*                        *Sodium ethanoate*
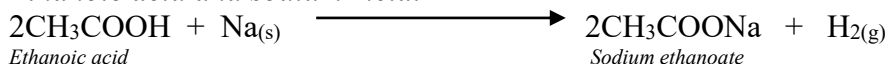
*Propanoic acid and magnesium metal*

$$2CH_3CH_2COOH \ + \ Mg \qquad\qquad (CH_3CH_2COO)_2Mg \ + \ H_{2(g)}$$
*Propanoic acid*                        *Magnesium propanoate*

## (v). Reaction with alkanols (Esterification)
- Alkanoic acids react with alkanols to form esters;
**Conditions:**
- Drops of concentrated sulphuric acid.
- Gentle warming.

## Reaction of ethanoic
- Ethanoic acid reacts with ethanol in the presence of a few drops of concentrated sulphuric acid forming a sweet fruity smelling compound called *ester.*
- The process is called esterification.

*Procedure*
- 2-3 drops of concentrated sulphuric acid are added to a mixture of equal proportions of ethanol and pure ethanoic acid in an evaporating dish.
- The mixture is warmed gently in a water bath for sometime.
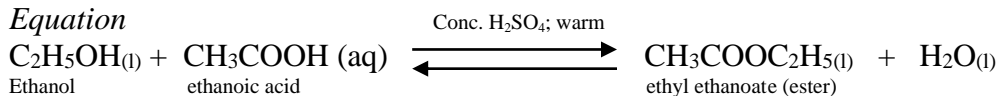- The mixture is poured into a beaker and smelt;
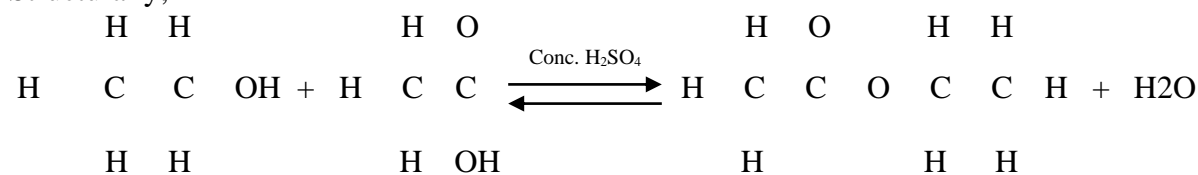
*Observation*
A fruity sweet smell (of ethyl ethanoate);

*Explanation*
- Ethanol reacts with ethanoic acid in the presence of a few drops of concentrated sulphuric acid to form ethyl ethanoate and water.
- The reaction is very slow and so catalyzed by the hydrogen ions from the sulphuric acid.

*Equation*

$$C_2H_5OH_{(l)} + CH_3COOH \text{ (aq)} \underset{}{\overset{\text{Conc. } H_2SO_4; \text{ warm}}{\rightleftharpoons}} CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

Ethanol      ethanoic acid      ethyl ethanoate (ester)

Structurally;



- The alkyl part of the ester is derived from the alkanol, while the alkanoate part is derived from the acid;
- The alkanol attaches itself at the group in the carboxylic acid thereby displacing hydrogen atom;
- Under ordinary conditions the reaction takes place slowly; but in presence of concentrated sulphuric catalyst and warm (heat) conditions, the reaction is enhanced;

If propanol were used in place of ethanol, the reaction would yield the ester *propyl ethanoate*, according to the following equation;

$$CH_3COOH_{(aq)} + CH_3CH_2CH_2OH_{(aq)} \rightleftharpoons CH_3COOCH_2CH_{3(aq)} + H_2O_{(l)}$$

*Ethanoic acid*      *propanol*      *Propylethanoate*
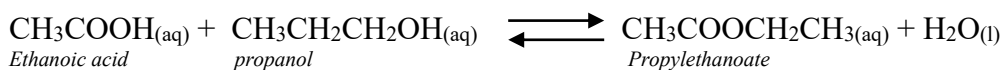
**Note: -**
Esters react with water to form the respective alkanoic acid and alkanol.
This reaction is termed hydrolysis and occurs in presence of concentrated sulphuric acid and heat as conditions.

**Example:**

$$CH_3COOCH_3 + H_2O \xrightarrow[\text{Heat}]{\text{Conc. } H_2SO_4} CH_3COOH + CH_3OH$$

*Methyl ethanoate*      *Ethanoic acid*      *Methanol*
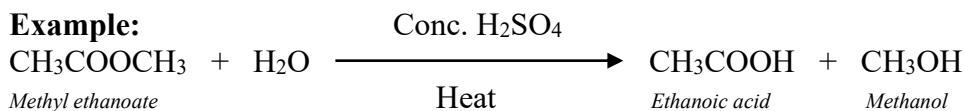
**(vi). Reaction with ammonia.**
Alkanoic acids react with ammonia to produce the ammonium salt of the acid.
General formula of the ammonium alkanoate salt is $RCOONH_4$

**Example:**
**Ethanoic acid and ammonia gas.**

$$CH_3COOH \ + \ NH_3 \longrightarrow CH_3COONH_4$$
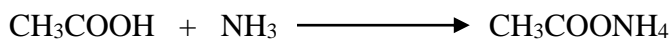
**Uses of alkanoic acids**
1.  In pharmaceuticals, for making medicines e.g ethanoic acid is used in the manufacture of aspirin.
2.  Manufacture of dyes and insecticides
3.  Seasoning food as vinegar
4.  Coagulation of rubber latex
5.  Preparation of polyethenyl ethanoate and cellulose ethanoate which are used are used to make artificial fibres such as rayon.
6.  Manufacture of soaps.
7.  Preparation of perfumes and artificial favours used in food manufacture.

**Tests for alkanoic acids.**
The following tests can be used to test for alkanoic acids.
Reaction with carbonates and hydrogen carbonates
Esterification

**Summary:** Draw a summary flow chart to show all the reactions of a named alkanoic acid.

**FATS AND OILS.**
- Are esters of long chain carboxylic acids and glycerol

**(a). Oils**
- Oils occur naturally in plants and animals.
**Examples:** Whale oil, groundnut oil, corn oil and castor oil.
- Oils are liquids at room temperature.
**Reason:**
- They have high proportion of esters derived from the unsaturated oleic acid in them.

**(b). Fats.**
- These occur naturally in animals only.
**Examples:** Tallow, butter from milk, lard from pigs etc.
- Fats are solids at room temperature
- Oils can be converted to fats /hardened into fats by **hydrogenation.**
- This is the conversion of oils into fats by use of hydrogen; and forms the basis of margarine manufacture.
- During hydrogenation:

➤ Hydrogen is bubbled into oils under *high pressure* and temperatures of about *400ºC* in the presence off a *nickel catalyst*

**Note**
- Fats and oils are important raw materials in the manufacture of soaps.

**Soaps and soapless detergents**
**Soaps**
**-** Are a variety of compounds produced when oils or fats are reacted with sodium hydroxide.
- They are similar in that they contain a long hydrocarbon chain ending in a **carboxylate anion** to which is attracted a sodium cation.
- A typical soap is sodium stearate; $C_{17}H_{35}COO^-Na^+$

**Structurally**

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C \overset{\displaystyle O}{\underset{\displaystyle O^-Na^+}{}}$$
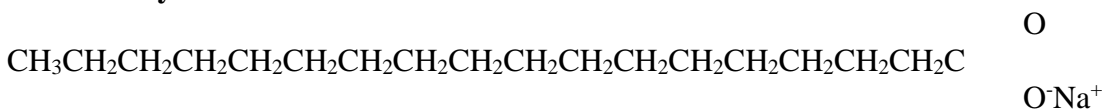
**Preparation of soaps**
- $2cm^3$ of castor oil and $10 \ cm^3$ of 4M sodium hydroxide are poured into a $100cm^3$ beaker.
- The mixture is then for about 10 minutes, stirring continuously and adding distilled water to make up for evaporation.

**Explanation:**
- On boiling an alkali with fat or oil, a hydrolysis reaction occurs.

**Equation:**

$$
\begin{array}{l}
CH_2 - COO - C_{17}H_{35} \\
| \\
CH - \ COO - C_{17}H_{35} \ + \ 3NaOH \\
| \\
CH_2 - COO - C_{17}H_{35} \\
\textit{Fat}
\end{array}
\quad \longrightarrow \quad
\begin{array}{l}
CH_2OH \\
| \\
3C_{17}H_{35}COO^- \ Na^+ \ + \ CHOH \\
\textit{Sodium stearate (soap)} \quad | \\
CH_2OH \\
\textit{Glycerol}
\end{array}
$$
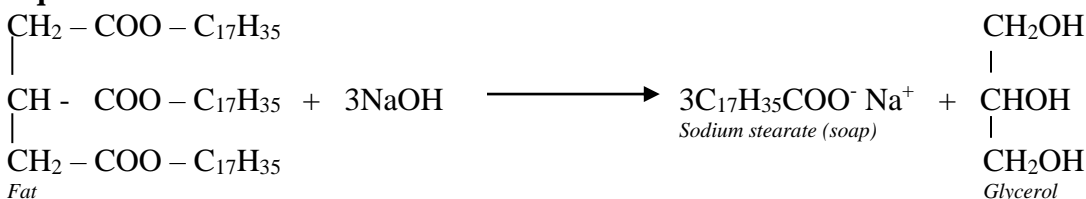
- When hydrolysis reaction occurs in the presence of an alkali (sodium hydroxide), the process is known as *saponification* (the chemical reaction between a fat and an alkali)
- In the fat hydrolysis NaOH neutralizes the acid formed (i.e. stearic acid) to form the sodium salt of the acid removing it from the aqueous mixture.
- Thus in excess alkali, all the fat is utilized.
- The sodium salt (sodium stearate) of the acid is termed soap if the number of carbon atoms per molecule is more than eight.

**Note:**
- KOH may be used in place of NaOH as the alkali.

2. To the boiled mixture 3 spatula measures of sodium chloride are added, stirred well and allowed to cool.
**Reason:**

- The NaCl helps in separating the soap from the glycerol.
- This step is called **salting** and it reduces the solubility of the soap in the aqueous layer.
- The lower layer consists of glycerol, salts and unused alkali solution.

**General formula of ordinary soap**

$C_nH_{2n+1}COO^-Na^+$ where n >8 (n is greater than eight)

3. The solid is filtered off and washed with cold distilled water, to remove impurities like NaCl

4. The solid sample is placed in a test tube with distilled water, then with tap water.

**Note:**
The resultant soap may not have lathered easily with tap water.
**Reason:**
Some tap water contains a high proportion of calcium or magnesium ions that make water hard.

**Summary on soap preparation**
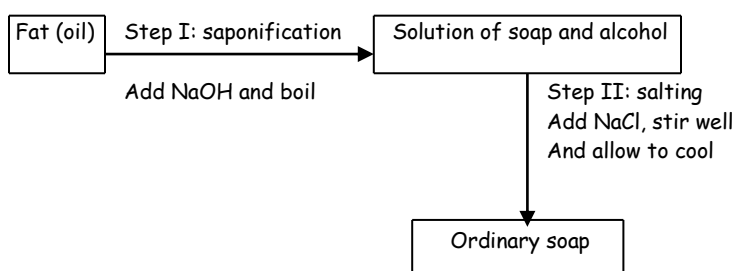


**The role of soap in cleaning**
**Note: functions of soap in water**
1.  It makes the water able to **wet** material more effectively by **lowering** the surface tension.
2.  **Emulsification** of oil and grease.
**-** Soap molecules have two dissimilar ends:
➢  A **hydrocarbon chain** which is **non-polar** and has no attraction for water- hence oil soluble
➢  A **Carboxylate end**, which is **polar** and is attracted to water; hence is water-soluble.
**Note**: the Carboxylate end is in fact negatively charged in water because after dissolution, the sodium ion and the carboxylate ion exist as separate entities.

**Illustration:**

$$\underset{\textit{Non polar}}{CH_3(CH_2)_{16}} - \underset{\textit{Carboxylate (Polar)}}{\overset{\overset{\displaystyle O}{\|}}{C} - O^-\, Na^+}$$
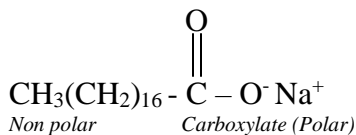
**Effects of soap on oil –water mixture (removal of oils and grease during washing)**
**Note**: schematic representation of a soap molecule

➢  On adding soap into oil water mixture the following build up occurs:

- A molecule of soap has a **polar** (hydrophilic) and **non-polar** (hydrophobic) parts;
- The non-polar end dissolves in oil and the polar end dissolves in water.
- When the mixture is agitated (thoroughly shaken) the hydrocarbon chain (tail) dissolves in grease while the carboxylate – sodium end of the soap molecule (the head) remains dissolved in water.

Diagrams: role of soap in cleaning.

- Each oil drop ends up with a large cloud of negative charge around it as the polar heads are negatively charged.
- Consequently the oil drops repel each other, hence preventing them from coalescing.
- The water –soluble sodium "heads" on the surface of the droplets keep the droplets emulsified (suspended) in the water.
- During rinsing the water carries away the oil droplets.

**Effect of hard water on soap**
- The Calcium and magnesium ions in hard water react with soap (sodium stearate) and remove it as an insoluble grey scum of *magnesium or calcium stearate*.

**Equations:**
(i). $2C_{17}H_{35}COO^-Na^+_{(aq)} + Ca^{2+}_{(aq)} \longrightarrow (C_{17}H_{35}COO^-)_2Ca^{2+}_{(s)} + 2Na^+_{(aq)}$
   *Sodium stearate (soap)*                                    *Magnesium stearate*

(ii). $2C_{17}H_{35}COO^-Na^+_{(aq)} + Mg^{2+}_{(aq)} \longrightarrow (C_{17}H_{35}COO^-)2Mg^{2+}_{(s)} + 2Na^+_{(aq)}$
   *Sodium stearate (soap)*                                    *Magnesium stearate*
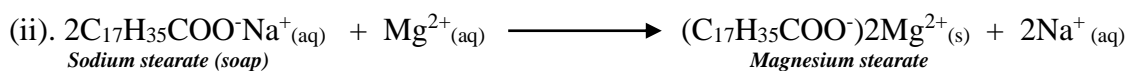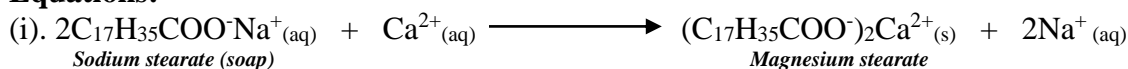
- Soap is wasted in this way until all the calcium (II) and magnesium (II) stearate has been removed.
- The resultant scum is deposited on fabrics, giving them an unsightly dull appearance.
- Thus in hard water districts it is obviously advantageous to remove hardness before washing.

**Removal of hardness:**
Depends on whether the hardness is temporary or permanent

**(a). Temporary hardness**
*Cause:*
- The presence of calcium hydrogen carbonate or magnesium hydrogen carbonate dissolved in water.

*Removal*
- By boiling the water
- During the process the soluble calcium or magnesium hydrogen carbonate is precipitated out as insoluble calcium or magnesium carbonate.

**Equation:**

$$Ca(HCO_3)_{2(aq)} \xrightarrow{\text{Heat}} CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)}$$
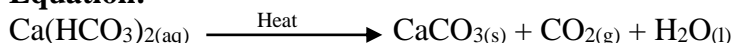
**(b). Permanent hardness**
*Cause:*
- Presence of calcium or magnesium chlorides and sulphates

*Removal*
Can be removed using the following methods:

**(i). Distillation**
- The water is distilled and the dissolved substances are left behind as water is evaporated and condensed

**(i). Addition of washing soda ($Na_2CO_3$)**
The washing soda reacts with the $Mg^{2+}$ and $Ca^{2+}{}_{(aq)}$ ions precipitating them as the insoluble carbonates
**Equations:**

$$2Na^+{}_{(aq)} + CO_3^{2-}{}_{(aq)} + 2Cl- + Ca^{2+}{}_{aq)} \longrightarrow CaCO_{3(s)} + 2Na^+{}_{(aq)} + 2Cl^-{}_{(aq)}$$

$$CO_3^{2-}{}_{(aq)} + Mg^{2+} \longrightarrow MgCO_{3(s)}$$
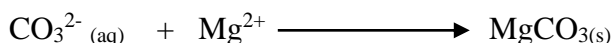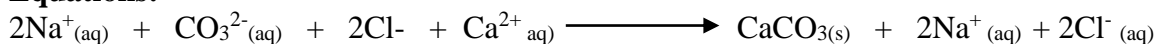
*Disadvantage of washing soda as a water softener*
- It is alkaline and can cause damage to wool and silk.
**(iii). Ion exchange process (e.g. in the permutit water softener)**
- It involves use of resins and compounds which will exchange their own $Na^+$ for $Ca^{2+}$or $Mg^{2+}$ dissolved in hard water
- Thus as the $Na^{2+}$ go into the water are left in the resin.

**Equation:**

$$2Na^+ (resin^-)_{(aq)} + Ca^{2+}{}_{(aq)} \longrightarrow Ca^{2+} (Resin)_{2\ (aq)} + Na^+{}_{(aq)}$$
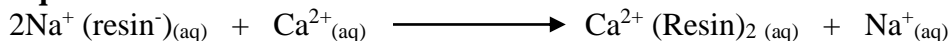
**Advantages and disadvantages of hard water**
**Advantages of hard water**
1. It is good for drinking purposes as calcium contained in it helps to form strong bones and teeth.
2. When soft water flows in lead pipes some lead is dissolved hence lead poisoning. However when lead dissolves in hard water insoluble $PbCO_3$ are formed, coating the inside of the lead pipes preventing any further reaction
3. It is good for brewing and the tanning industries;

**Disadvantages of hard water**
1. Soap forms insoluble salts with magnesium and calcium ions; **scum** (calcium or magnesium stearate) thereby wasting soap.
**Note:** For these reason soapless detergents are preferred to ordinary soaps because they do not form scum; but rather form soluble salts with $Mg^{2+}$ and $Ca^{2+}$
- Examples of soapless detergents: brand names such as omo, perfix, persil, and fab e.t.c.

2. Deposition of insoluble magnesium and calcium carbonates and sulphates formed from hard water result into blockage of water pips due to the formation of boiler scales

3. Formation of kettle fur which make electrical appliances inefficient and increases running costs.

**Soap and pollution effects.**

1. The wash water with soap and the dirt (grease) ends up in rivers and lakes thus affecting aquatic life; since plants do not grow well in soapy water.

**Note:** soaps are however **biodegradable** and so do not persist long in the environment.

**Soapless detergents (synthetic detergents)**
- Are cleansing agents lacking the carboxylate ions; but also act like soap in the cleaning process
- Instead they have sulphates ($-OSO_3^-Na^+$) or sulphonate groups ($-SO_3^-Na^+$) groups.
Are thus of two main types:
➤ Sodium alkyl sulphates
➤ Sodium alkylbenzene sulphonate.

**(i). Sodium alkyl sulphates.**
- Are detergents with the formula $R – OSO_3Na$

**Illustration.**
- Consider the structure of sulphuric acid

$$\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{HO-S-OH}}$$
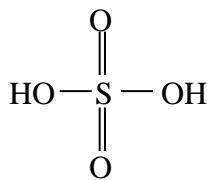
- Replacing one of the hydrogen atoms with an alkyl group, **R** results into the compound
**R – OSO₃H**;
- This is known as **alkyl hydrogen sulphate**;
- If the alkyl group (R) is a long chain such as dodecyl; **CH₃(CH₂)₁₀CH₂ -** ; then the formula of the compound becomes **CH₃(CH₂)₁₀ – OSO₃H** (alkylhydrogen sulphate)
- Reacting the alkylhydrogen sulphate with an alkali (NaOH) results into a compound with the formula
**CH₃(CH₂)₁₀ – OSO₃Na**.
- This is the soapless detergent, and is known as **sodium dodecyl sulphate.**

**(ii). Sodium alkyl benzene sulphonates.**
- Are formed when one of the $OH^-$ groups in sulphuric acid is replaced with an **alkyl benzene group**.

- Have the general formula **R -⟨⬡⟩- SO₃Na**

**Illustration.**
- If the alkyl benzene is of formula $CH_3(CH_2)_{10}CH_2$ - ; then the resultant compound is of formula
$CH_3(CH_2)_{10}CH_2$ ⬡ - **SO₃H** (hydrogen dodecyl benzene sulphonate)

- The sodium alkylbenzene sulphonate is neutralized using sodium hydroxide to obtain the detergent,
$CH_3(CH_2)_{10}CH_2$ - ⬡ $SO_3Na$

The compound $CH_3(CH_2)_{10}CH_2$ - ⬡ $SO_3Na$ is called **sodium dodecyllbenzene sulphonate.**

**Conclusion:**
The two main types of soapless detergents are:
➢ Sodium alkyl sulphates; **$CH_3(CH_2)_{10} – OSO_3Na$**
➢ Sodium alkylbenzene sulphonate; **$CH_3(CH_2)_{10}CH_2$ -** ⬡ **- $SO_3Na$**

**Note:**
- Due to lack of carboxylate ions, soapless detergents do not form scum with hard water. Advantage over soap
- They are not affected by hard water, as they do not form scum in hard water as follows:
**Preparation of soapless detergents**
- Most are made from residues from crude oil distillation
- The hydrocarbons are treated with concentrated sulphuric acid  (instead of alkalis in cases of soap)

**Procedure**
- About 10cm³of olive oil in a small beaker, which is then stood in a larger one with ice-cold water.
- While stirring with a glass rod, concentrated sulphuric acid is carefully added to the olive oil using a dropping pipette.
- The acid is added until the yellow oil turns uniformly brown.
- 20cm³of 6M NaOH is then added; to neutralize the acid solution, resulting into a slightly basic product.
The soap is then tested with tap water and distilled water.

**Explanation**
- Some compounds like olive oil contain double bonds which can react concentrated sulphuric acid to form compounds of alkylhydrogen sulphate

**Example:**

$R – CH = CH – CH – CH_2 – Est  +  H_2SO_{4\ (l)}$ $\longrightarrow$ $R – CH – CH – CH - CH_2 – Est$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ |      |
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ H    $OSO_3H$
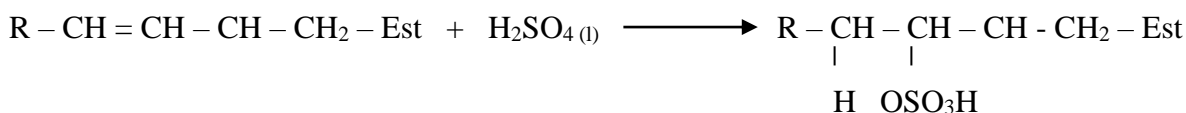
- In this case; R=alkyl group, either branched or straight; while Est = ester group.
- On adding NaOH, the alkyl hydrogen sulphate is neutralized where the hydrogen of the hydrogen sulphate is replaced by a sodium atom.
- The resultant compound is sodium alkylsulphate; R-CH  - CH-CH₂-Est;
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ |      |
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ H     $OSO_3Na$

**Equation:**

$R – CH – CH – CH - CH_2 – Est  +  NaOH_{(aq)}$ $\longrightarrow$ $R – CH - CH – CH – CH_2 – Est  +  H_2O_{(l)}$
    |       | $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ |      |
   H   $OSO_3H$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ H     $OSO_3Na$
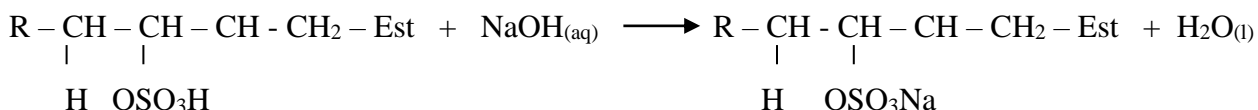
- The R - CH  - CH – CH - CH₂ - Est is the detergent and lathers easily with both tap and distilled water.

|       |
H     $OSO_3Na$

**Note:**

- Alkylhydrogen sulphates can also be from alcohols.

**Example:**

$R - CH - CH_3$  +  $H_2O_{(l)}$  $\longrightarrow$  $R - CH - CH_3$  +  $H_2O_{(l)}$
|                                                |
OH                                               $OSO_3H$
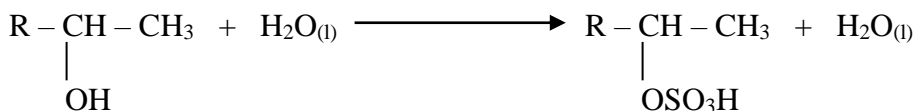
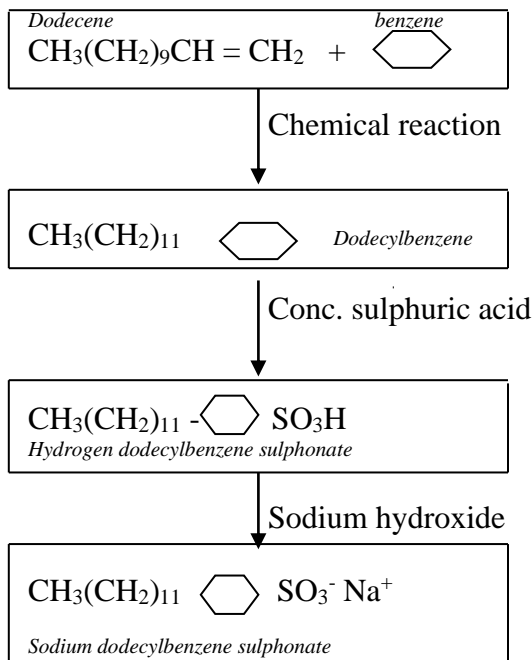- Most soapless detergents are **sodium alkyl sulphates** with a general formula **$ROSO_3Na$**

- Sodium alkylbenzene soapless detergents are industrially manufactured from alkylbenzene;
- In this process alkylbenzene (a petroleum product) reacts with $SO_3$ to form sulphuric acid
- Upon neutralization with NaOH, sulphuric acid forms **sodium alkylbenzene sulphonate**,

$R - \langle \ \rangle - SO_3Na$, a detergent.

**Summary: manufacture of soapless detergents**

*Dodecene*                    *benzene*
$CH_3(CH_2)_9CH = CH_2$  +  $\langle \ \rangle$

↓ Chemical reaction

$CH_3(CH_2)_{11} \langle \ \rangle$   *Dodecylbenzene*

↓ Conc. sulphuric acid

$CH_3(CH_2)_{11} - \langle \ \rangle SO_3H$
*Hydrogen dodecylbenzene sulphonate*

↓ Sodium hydroxide

$CH_3(CH_2)_{11} \langle \ \rangle SO_3^- Na^+$
*Sodium dodecylbenzene sulphonate*

**Mode of action of soapless detergent.**

Soapless detergents have two ends; a long hydrocarbon part, the tail and a short ionic part the head.

Simple representation of a detergent molecule.

$$SO_3^- \ Na^+$$
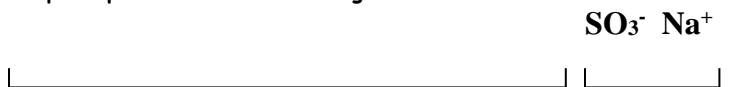
*Non-polar tail (water hating)*          *Polar head (water loving)*

**Examples:**
**(i). Sodium lauryl sulphate**

$CH_3(CH_2)_{10}CH_2 - O - SO_3^-Na^+$

```
Tail                    head
```

## (ii). Sodium alkylbenzene sulphonate

$$CH_3(CH_2)_{10}CH_2 - \langle \hexagon \rangle SO_3^-Na^+$$

```
Tail                    head
```
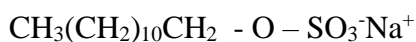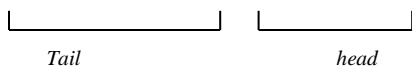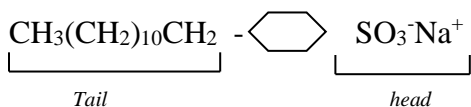
- The tail is non-polar and dissolves in oil or grease (waterphobic) while the head is polar and dissolves in water (waterphilic).
- Each oil or grease gets sorrounded by the detergent molecules and hence a cloud of charged heads hence repel each other and do not coalesce.
- The dirt (grease loses its direct contact with the fabric being washed.
- Any agitation at this point then removes the dirt from the object.

### Advantages of soapless detergents over soap;
1. They lather easily with hard water since the corresponding calcium and magnesium salts are soluble in water due to lack of the carboxylate ions.
2. Are mainly prepared from non-food raw materials.
3. They do not react with acidic water.

### Note:
- Soapless detergents with branched chain alkyl groups are not easily broken down by bacteria and are therefore the cause of frothing in sewerage plants, rivers etc.
- Consequently modern industry is overcoming this disadvantage by making the detergents from alkylbenzene with straight chain alkyl groups.

### Pollution effects of soapless detergents.
1. The active ingredients such as alkylbenzene sulphonates are non-biodegradable, hence accumulate in water sources and end up in human bodies.
2. Some of the additives such as phosphates cause eutrophication hence excessive build up of algae (algal blooms) which change the water taste and odour, and also reduce oxygen supply hence poor growth of aquatic organisms.
3. Because of their high lathering tendency, they cause excessive frothing and foaming in water sources especially after heavy rains.

### Comparisons between soaps and soapless detergents.

| Detergents | Soaps |
|---|---|
| Have strong cleansing action | Have weaker cleansing action |
| Are highly soluble in water; hence can be used in acidic or hard water. | Are not very soluble in water, and tend to be wasted when used in hard water; They cannot be used in acidic water. |
| Are made from byproducts of petroleum industry; which helps to conserve edible fats and oils | Are made from edible fats and oils; |
| They cuse water pollution; | Are biodegradable and have minimum pollution effects. |
| They are expensive. | Are cheaper than detergents. |

**POLYMERS**
- A polymer is a macromolecule formed when two or more molecules link together to form a larger unit.
- Polymers have different properties different from those of the monomers.
- The process of polymer formation is called **polymerization.**
- Two types of polymers exist; natural and synthetic /artificial polymers.

**(a). Natural polymers and fabrics**
- Natural polymers occur naturally in living systems.

**Examples:**
- Rubber (latex), starch, cellulose, wool and proteins.

**Natural rubber.**
- Rubber trees give out a liquid called latex, which is collected from cuts in the trunks of rubber trees.
- Natural rubber is made out of latex from rubber trees.
- Latex is a hydrocarbon $C_5H_8$, called isoprene (2,methylbut 1,3 diene).
**Formula of isoprene.**

$CH_2 = C – CH = CH_2$

$\qquad CH_3$
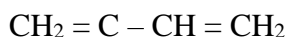
- Coagulation of latex leads to formation of a hydrocarbon polymer consisting of *isoprene*
(2, methylbut-1, 3-diene) units.
- This polymer is called polyisoprene with the formula; [ $CH_2 - C = CH - CH_2$ ]

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3$
**Characteristics of natural rubber.**
- Soft and sticky;
- Low resistance and low tensile strength; thus breaks easily upon stretching;
- Loses its rubber like properties at temperatures above 60oC;

**Note:**
- These are not good qualities and for industrial purposes this quality must be improved.
- This is done through vulcanisation of rubber.

**Vulcanization of rubber.**
- Is a chemical reaction in which raw rubber is heated with sulphur and is done purposely to improve the wear quality of rubber.

**Process of vulcanization;**
- Rubber is heated with sulphur

- The sulphur atoms form links between chains of rubber molecules.
- This reduces the number of double bonds in the polymer; making the material tougher, less flexible and less softer.
- During the process the sulphur atoms attach themselves to the rubber molecule in such a way that the molecules become locked in place and are prevented from slipping.

**Note: -**
- Soft rubber has about 2% sulphur, while toughened rubber about 10 % sulphur.

- Rubber can also be made artificially in industries and this gives a form of synthetic rubber.
- Other than undergoing vulcanisation it has chemicals that give it desired properties.
- It is made from byproducts of petroleum industry.
- Examples of synthetic rubber include **neoprene** and **thiokol.**

**Note:** Neoprene is made by polymerization of chloroprene (2, chlorobut 1, 3 diene), $C_4H_5Cl$

**Equation:**

$CH_2 = C - CH = CH_2 \longrightarrow CH_2 - C = CH - CH_2$

$\qquad\;\; |\qquad\qquad\qquad\qquad\qquad\qquad\quad\; |$

$\qquad\;\; Cl \qquad\qquad\qquad\qquad\qquad\qquad\quad Cl$

*Chloroprene*           *Neoprene or polychloroprene*


**Properties of synthetic rubber.**
1. Are unreactive, hence they don't react with industrial chemicals like oils, grease, petrol etc.
2. Are non-inflammable, as they don't catch fire easily.
3. Capable of withstanding wide range of temperatures without changing shape.
4. Have high mechanical strength.

**Uses of synthetic rubber.**
1. Manufacture of insulating materials for electrical connections.
2. Making conveyor and seat belts.
3. Manufacture of car tyres and tubes.
4. Making gaskets, flexible pipes.

**Advantages and disadvantages of natural polymers.**
➢ **Advantages.**
- Are **biodegradable** hence not a likely cause of environmental pollution.
- Are made from renewable resources such as wool and trees; hence not easily exhaustible.
- Most are not easily flammable hence good materials for items like clothing.

➢ **Disadvantages**
- Are often very expensive compared to synthetic polymers.
- Some do not last for very long.
- Are easily affected by acids, alkalis, air etc.

**(b). Synthetic polymers**
- They are man-made e.g. polythene, Perspex
- They are of two main types; thermoplastic and thermosetting polymers.

➤ **Thermoplastic;**
- Softens on heating and becomes rigid on cooling.
*Examples:* nylon, polythene, polystyrene, etc.

➤ **Thermosetting:**
- Are those that become hard on heating and cannot be softened by heating.

**Advantages of synthetic polymers and fibres over natural polymers**
1. They can be made into different shapes easily.
2. They are cheaper.
3. Are often unaffected by ac ids, alkalis, water and air.
4. Are usually less denser and yet stronger

**Disadvantages**
1. Plastics are non-biodegradable hence causes a lot if problems in disposal
2. Plastics burn more readily than natural material
3. Some synthetic polymers give off poisonous gases when they burn. E. g. polyurethane gives off cyanide and carbon monoxide

**Methods of polymerization:**
**1. Addition polymerization;**
- Occurs when unsaturated molecules (monomers) join to form a long chain molecule (polymer) without the formation of any other product.
- Usually the monomers must have at least a double or triple bond.
- One of the bonds in the double or triple bonds in the monomer opens up, and the unbonded electrons form bonds with neighbouring molecules.

**Conditions for polymerization.**
- High pressures.

**Examples.**
**Polymerization of ethene to Polythene**

$$CH_2 = CH_2 \ + \ CH_2 = CH_2 \longrightarrow [-CH_2 – CH_2 – CH_2 – CH_2 -]$$
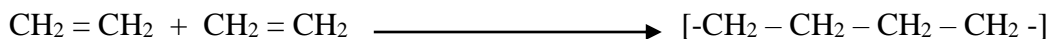
**Calculations involving polymers.**
*1. A polyisoprene molecule is represented as:* -[ $CH_2 – C = CH – CH$ -]n
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | $
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3$
*- Given that the relative formula mass of polyisoprene is 748 000, calculate the number of isoprene units in the polymer.*

**Summary on common addition polymers.**

| Monomer | Polymer | properties | Uses |
|---|---|---|---|
| H⠀⠀⠀⠀⠀H<br>⠀⠀C = C<br>H⠀⠀⠀⠀⠀H<br>*Ethene* | H⠀⠀H<br><br>⠀C - C<br><br>⠀H⠀⠀H<br>*Polythene* | Light, tough, and durable | - Polythene bags, bowls packaging, electrical insulation; plastic pipes etc |
| ⠀⠀H⠀⠀H⠀⠀H<br><br>H⠀⠀C⠀⠀C = C – H<br><br>⠀⠀⠀H<br>*Propene* | H⠀⠀⠀⠀H<br><br>⠀C⠀⠀⠀⠀C<br><br>⠀$CH_3$⠀H<br>*Polypropylene* | Light, tough and durable | - Making crates, boxes; and plastic ropes |
| H⠀⠀⠀⠀⠀H<br>⠀⠀C = C<br>H⠀⠀⠀⠀⠀Cl<br>*Chloroethene* | H⠀⠀H<br><br>⠀C - C<br><br>⠀H⠀⠀Cl<br>*Polychloroethene(polyvinyl chloride)* | Strong and hard (not as flexible as polythene) | - Making plastic pipes,<br>-electrical insulators, floor tiles, credit cards, |
| ⬡ CH = $CH_2$<br><br>*Phenyl ethene (styrene)* | ⠀H⠀⠀H<br><br>⠀C - C<br><br>⠀⬡⠀Cl<br><br>*Polyphenylethene (polystyrene)* | Light, poor heat conductor, brittle; | -Insulation,<br>-packaging materials and food containers; |
| F⠀⠀⠀⠀⠀F<br>⠀⠀C = C<br>F⠀⠀⠀⠀⠀F<br><br>*Tetrafluoroethene* | ⠀F⠀⠀⠀F<br><br>⠀C -⠀C<br><br>⠀F⠀⠀F<br>*Polytetrafluoroethene (Teflon)* | Non-stick surface; Withstands high temperatures | - Non-stick coatings on pans; Insulation; |
| ⠀⠀⠀⠀O<br><br>$CH_2$ = C – C – O – $CH_3$<br><br>⠀⠀⠀$CH_3$<br>*Methylmethacrylate* | ⠀H⠀⠀$CH_3$<br><br>⠀C -⠀C<br><br>⠀H⠀⠀C – O – $CH_3$<br><br>⠀⠀⠀O<br>*Polymethylmethacrylate (Perspex)* | | -Optical components<br>- transparent doors and windows;<br>- Display signs;<br>- dental fillings; |

## 2. Condensation polymerization

- Occurs when monomers (similar or different) combine to form a long chain molecule; with the loss of small molecules like ammonia or water.
- The monomers should have at least two functional groups.

**Reason:**

- For molecules to join at both ends permitting chain formation;

**Illustration**

- Consider two molecules A and B; each with 2 functional groups:
➢ Molecule A; HO – A – OH, with two OH functional groups;
➢ Molecule B; HOOC – B – COOH, with two -COOH functional groups

**On condensation**

HO – A – O H + H O O C – B – COOH + HO – A – OH +…………..

        *Lost to form water*

Hence;

HO – A – OH + HOOC – B – COOH $\longrightarrow$ [HO-A-OOC-B-CO]$_n$ + 2H$_2$O$_{(l)}$
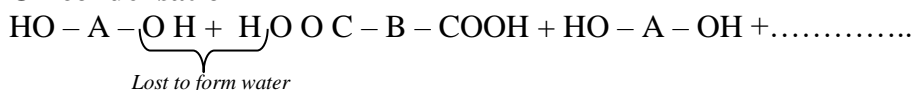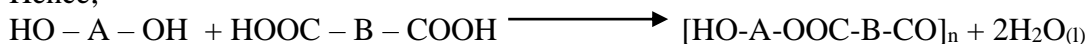
**Types of condensation polymers.**

- Are of two types:
➢ **Polyesters**
- Are polymerized formed by an ester linkage; usually with the liberation of a water molecule.

**Examples**



*A dioic acid*     *A diol*     *Polyester*
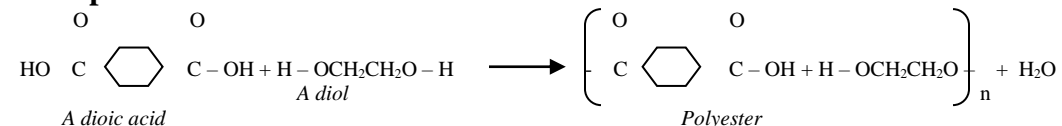
➢ **Polyamides.**

- Are condensation polymer involving monomers that have at least an **amine group** (in at least one of them); and thus usually result to the evolution of ammonia gas or water.

**Example:**
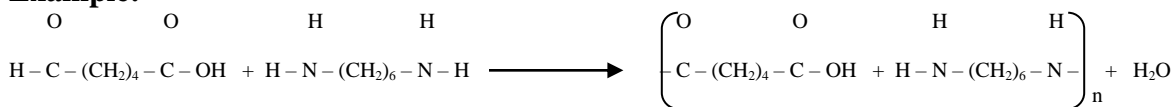


**Examples of condensation polymers and their uses.**

| Polymer | Monomer | Uses |
|---------|---------|------|
| Polyvinyl chloride | Vinyl chloride | Making rain coats, plastic discs, plastic water pipes, and electric insulation; |
| Starch | Glucose | Laundry |
| Cellulose. | Glucose | Paper and clothing manufacture |
| Silk and wool | Proteins (amino acids) | Making clothes |
| Polyester (terylene) | Terephthalic acid and Ethan 1,2 diol | Clothes and seat belts |
| Bakelite | Urea and methanol | Electrical fittings |
| Perspex | Methylmethacrylate | Safety belts, windscreen, and plastic lenses; |
| Nylon | Hexane-1,6-dioyl dichloride; and hexane- 1,6- diamine; | Used in making safety glass; reflectors; contact lenses; false teeth |

**Further examples of polymerization reactions.**

**Formation of nylon.**

H                                      H     O                          O                                          H              H   O                O
    NCH₂CH₂CH₂CH₂CH₂CH₂N      +      CCH₂CH₂CH₂CH₂C          ⟶          - N – (CH2)6 – N – C – (CH2)4 – C -
H                                      H     Cl                         Cl                                                                                       n

*Hexane – 1,6 – diamine*                    *hexane – 1,6 – dioyl dichloride*                                        *Nylon*
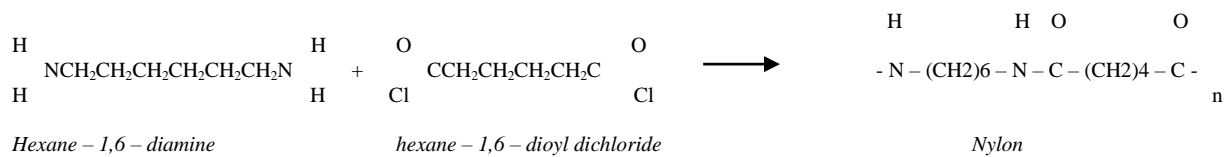
## Formation of Terylene

# UNIT 2: ACIDS, BASES AND SALTS

## Unit Checklist:

**1. Acids;**
➢ Meaning
➢ Strong and weak acids
➢ Concentrated and weak acids
➢ Comparing strength of acids
  ▪ Using evolution of hydrogen and carbon (IV) oxides
  ▪ Using electrical conductivity
  ▪ Using PH
➢ Role of solvents in acidic properties of solvents
  ▪ Hydrogen chloride in water
  ▪ Hydrogen chloride in methylbenzene

**2. Bases:**
➢ Meaning
➢ Strong and weak bases (alkalis)
➢ Measuring strength of alkalis
  ▪ Using electrical conductivity
  ▪ Using PH values
➢ Effect of solvent type on properties of ammonia solution
  ▪ Ammonia n water
  ▪ Ammonia in methylbenzene

**3. Uses of acids and bases**

**4. Oxides and hydroxides**
➢ Basic oxides
➢ Acidic oxides
➢ Neutral oxides
➢ Amphoteric oxides
  ▪ Meaning of amphoteric oxides
  ▪ To verify amphoteric oxides
  ▪ Reactions of amphoteric oxides

**5. Salts**
➢ Meaning
➢ Preparation methods (summary)
➢ Solubility of salts
➢ Qualitative tests for cations using NaOH and $NH_4OH$;
➢ Effect of heat on metal oxides and hydroxides.
➢ Effect of sodium carbonate on salt solutions
➢ Properties of cations with sodium chloride, sodium sulphate and sodium sulphite

**6. Solubility and solubility curves**
➢ Definition of solubility
➢ Factors affecting solubility
➢ Solubility curves and related calculations.
➢ Fractional crystallization

**7. Water**
➢ Hardness of water
➢ Temporary hardness (Meaning; causes; and removal)
➢ Permanent hardness (meaning; cause; and removal)


# 1. Acids

- Are substances whose molecules yield hydrogen ions in water; or

- Are substances, which contain replaceable hydrogen, which can be wholly or partially replaced by a metal.

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
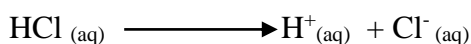
**OR:** - Acids are **proton donors** i.e. a substance which provides protons or hydrogen ions.

## Strength of Acids
- Acids can be categorized as either strong or weak acids;

### (a) Strong acids
- Are those which dissociate or ionize completely to a large extent in water, to yield many hydrogen ions.
- They yield to the solution as many protons as they possibly can.

➢ **Examples**

Hydrochloric acid; $HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Sulphuric acid; $H_2SO_{4(aq)} \longrightarrow 2H^+_{(aq)} + SO_4{}^{2-}_{(aq)}$

Nitric acid; $HNO_{3(aq)} \longrightarrow H+_{(aq)} \quad NO_3^-{}_{aq)}$
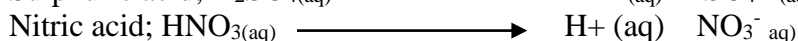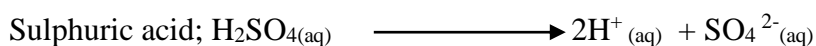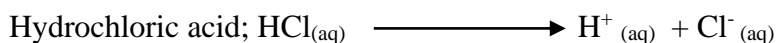
### (b) Weak acids.
- Are acids, which undergo partial dissociation to yield fewer hydrogen ions.
- They do not ionize in water completely or to a large extent i.e. some of their molecules remained unionized in solution.

## Examples:

*Carbonic acid:*
$$H_2CO_{3(aq)} \xrightarrow{\text{water}} H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

*Ethanoic acid*
$$CH_3COOH_{(aq)} \xrightarrow{\text{water}} H^+_{(aq)} + CH3COO_{(aq)}$$
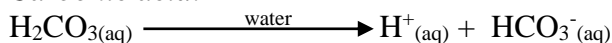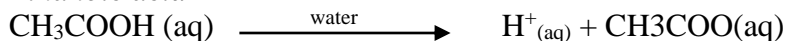
**Note: - concentrated acids and dilute acids**
**Concentrated acids**
- Is an acid with a high number of acid molecules per given volume.

**Dilute acids:**
Are acids with a low number of acid molecules per given volume.

- Thus there are concentrated strong acids or dilute strong acids; as well as concentrated weak acids and dilute weak acids.

**Comparing the strength of acids**
**(i). Using rate of evolution of hydrogen**
*Apparatus:*
- Boiling tubes; 1M HCl/ $H_2SO_4$/ $HNO_3$; Methanoic acid/ tartaric acid; magnesium ribbon.

*Procedure:*

- One boiling tube is half filled with 1M HCl; while another is half filled with 1M Ethanoic acid.
- 2 pieces of magnesium ribbons are cleaned to remove a layer of oxide on the surface.
- One of the two pieces is put in each tube of the acid.

*Observations:*
- Hydrochloric acid evolves hydrogen much more quickly than Ethanoic acid yet they were of equal concentration.

*Conclusion*
- Hydrochloric acid is a strong acid;
- Ethanoic acid is a weak acid.

**Note:** -
- The same experiment can be repeated with marble chips ($CaCO_3$) in acids of same concentration.
-The marble chips dissolve more quickly in HCl, which is a strong acid.

## (ii). Using electrical conductivity
*Procedure:*
- 50cm$^3$ of 2M-hydrochloric acid solution is placed into a beaker and set up apparatus as shown below.
- The switch is closed and the brightness of the bulb noted.

**Diagram: Electrolytic circuit**
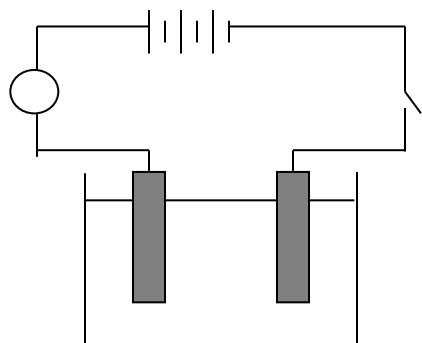


*Observations*
- Strong acids like HCl, $HNO_3$ and sulphuric acid gave a brighter bulb light than weak acids like ethanoic, carbonic acids e.t.c

*Explanations*
- Strong acids are completely dissociated and have more $H^+$ in solution and hence have got a higher electrical conductivity; than solutions of weak acids which are only partially ionized thus have fewer hydrogen ions in solution

## (iii). Using PH

*Procedure*

- 2cm$^3$ solutions of different acids of equal concentrations are paired into different test tubes.
- To each test tube 2 drops of universal indicator are added.
- Acids tested: HCl, $H_2SO_4$, $HNO_3$; ethanoic acid, carbonic acid, and tartaric acid.
- All acids are of 2M solutions
- The indicator colour and hence the PH number of each is noted; by comparing against the indicator chart.

*Observations*

| Substance (1M) | Colour of universal indicator | PH |
|---|---|---|
| Sulphuric acid | Red | 3 |
| Hydrochloric acid | Red | 3 |
| Nitric acid | Red | 3 |
| Ethanoic | Orange | 5 |
| Carbonic acid | Yellow | 6 |
| Tartaric acid | orange | 5 |

*Explanations*
- Solutions of strong acids contain a higher concentration of hydrogen ions than those of weak acids
- Strong acids have low PH usually less than 3.
- Weak acids have higher PH values usually between 5 - 6.

**Role of solvents on acidic properties of a solute.**

**Experiment: - to find out if solutions of HCl in different solvents display acidic properties**

*Apparatus and reagents*
- Hydrogen chloride gas, water and methylbenzene
- Beakers and a funnel
- Blue and red litmus papers.

*Procedure*
- Solutions of hydrogen chloride gas are made by bubbling the dry gas from a generator into water and into methylbenzene contained in separate beakers.
- The hydrochloric gas is passed into the solution using an **inverted funnel** to prevent **sucking back**.

*Apparatus*

The resultant solutions are each separately subjected to various tests as shown below and observations recorded

*Tests and observations*

| Test. | Aqueous HCl solution | Solution of HCl in methylbenzene |
|---|---|---|
| 1. A piece of dry blue litmus paper is dropped into solution | Blue litmus turns red | No effect on litmus |
| 2. Dry universal indicator paper | - Turns red (strong acid) | - Turns green (neutral) |
| 3. Add magnesium ribbon | - Evolution of hydrogen | - No reaction |
| 4. Add small marble chips | - $CO_2$ evolved | - No reaction |

| 5. Electrical conductivity | - Good conductor | - Does not conduct |
|---|---|---|

*Explanation*
- The results show that the aqueous solution of hydrogen chloride behaves as an acid; but the solution in methylbenzene lacks acidic properties
- When HCl gas dissolves in water it changes from molecules to ions;

**Equation:**

$$HCl_{(aq)} \xrightarrow{\text{water}} H^+_{(aq)} + Cl^-_{(aq)}$$
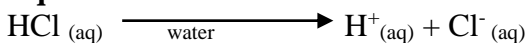
- It is the hydrogen ions which give the acidic properties and these can only be formed in the presence of water
- HCl in water conducts electric current due to presence of free ions in solution
- HCl gas in methylbenzene does not conduct electric current because the HCl exists as molecules hence lack free ions

**Note:** - hydrogen chloride gas dissolves in water because both HCl and water polar molecules;
- This causes mutual attraction of both ends of HCl molecule by different water molecules causing the dissociation of HCl molecules into ions.

*Illustration:*

Hence:

$$HCl_{(g)} + water \longrightarrow HCl_{(aq)}$$

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
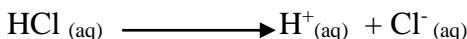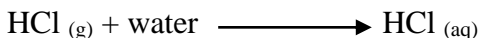
- The presence of hydrogen ions in aqueous solution of hydrogen chloride explains the electrical conductivity and acidic properties of hydrogen chloride
  ➢ **Acidic properties: -**
  - turns blue litmus paper red;
  - evolves hydrogen gas when reacted with magnesium;
  - evolves carbon dioxide on reaction with $CaCO_3$;

$$2H^+_{(aq)} + CaCO_{3(s)} \longrightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

$$2H^+_{(aq)} + Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + H_{2(g)}$$
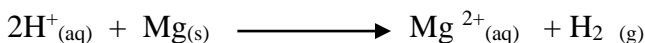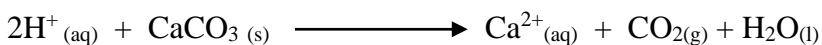
- Methylbenzene has a weak attraction for hydrogen chloride and hence hydrogen chloride remains as molecules in methylbenzene

**2. Bases**
- Are substances which accept the protons donated by acids and are hence proton acceptors

$$NH_{3(aq)} + H^+_{(aq)} \longrightarrow NH_4^+_{(aq)}$$

$$CuO_{(s)} + 2H^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + H_2O_{(l)}$$
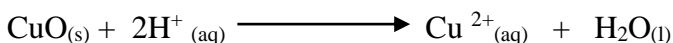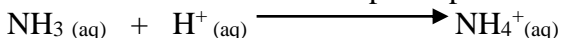
**Alkalis**
- An alkali is a soluble base i.e. a base that is soluble in water.
- They are compounds, which produce hydroxyl ions in aqueous solutions.

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$
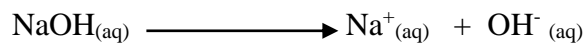
**Note: -**
When an acid proton reacts with a base (hydroxyl ions) in aqueous solution, a neutralization reaction occurs.

**Strength of an Alkali**
- Alkalis can be grouped as either strong or weak alkalis.

**(a). Strong alkalis**
- Are alkalis that undergo complete dissociation in aqueous solution; yielding a large number of hydroxyl (OH-) ions

*Examples:*
- Sodium hydroxide.
- Potassium hydroxide.

**(b). Weak alkalis**
- Are alkalis that undergo only partial dissociation in aqueous solution (water) yielding fewer numbers of hydroxyl ions.

*Examples*
- Calcium hydroxide
- Ammonium hydroxide

**Measuring the strength of alkalis**
**(i). Using electrical conductivity**

*Procedure*

50 cm$^3$ of 2 M sodium hydroxide solution is put into a beaker and the apparatus set as shown below
*Apparatus*

*Procedure*
- The same procedure is repeated using other alkalis like $NH_4OH$; Ca $(OH)_2$ e.t.c.

*Observation*
- The bulb lights brightly with KOH and NaOH as electrolyte than with $NH_4OH$ and Ca $(OH)_2$

*Explanation*
- NaOH and KOH are strong alkalis and are completely dissociated and have more ions in solution and hence have got a higher electrical conductivity than the weak alkalis of $NH_4OH$ and $Ca(OH)_{2(aq)}$

**(ii). Using PH values**

*Procedure*

- 2 cm$^3$ of NaOH and 2 cm$^3$ of $NH_4OH$ are each poured into 2 different test tubes separately
- Into each test tube 2 drops of universal indicator are added.
- The colour change is noted and the corresponding PH scale recorded

*Observations*

| Alkali | Colour of universal indicator | PH |
|---|---|---|
| - Ammonium hydroxide (1M) | Blue. | 11 |
| - Calcium hydroxide (1M) | Blue. | 10 |
| - Sodium hydroxide (0.1M) | Purple. | 13 |
| - Sodium hydroxide (1M) | Purple. | 14 |
| - Potassium hydroxide | Purple. | 14 |

**Note: the PH scale**
- Is a scale which gives a measure of the acidity of alkalinity of a substance.

Illustration: a PH scale.

1  2  3  4  5  6  7  8  9  10  11  12  13  14

*Strong acid*      *Weak acids*    *Neutral*   *Weak alkali*        *Strong alkali*

*Increasing acidity*
*(High H⁺ ion concentration)*

*Increasing alkalinity*
*(Low H⁺ ion concentration)*
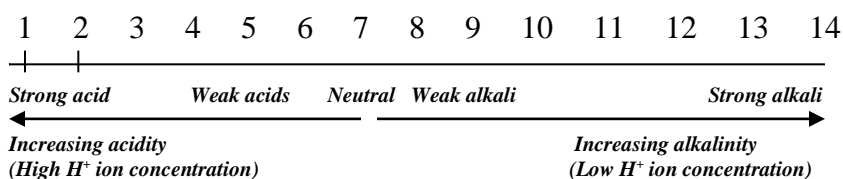
## Indicator colours:

| PH | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Colour | Red | | | Orange/ red | Yellow/ Green | | Green | Green/ Blue | | Blue/ Purple | | | Purple | |

## Effects of type of solvent on the properties of ammonium solution
## Procedure
- Ammonium solution is prepared by bubbling the gas from a generator into methylbenzene (toluene) and into water contained in separate beakers
- The solutions are each divided into 3 portions and tested with litmus paper; universal indicator and for electrical conductivity

## Apparatus

## Observations

| Test | Solution of NH₃ in water | Solution of NH₃ in methylbenzene (toluene) |
|---|---|---|
| Dry litmus paper | Red litmus paper turns blue; | No effect |
| Dry universal indicator paper | Colour turns purple (alkaline PH) | Turns green (Neutral PH) |
| Electrical conductivity | Poor conductor | Non-conductor |

## Explanations
- When $NH_{3(g)}$ dissolves in water it changes from molecules to ions.
## Equation:
$$NH_{3(g)} + H_2O_{(l)} \longrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$
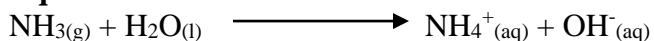
- It is the hydroxide ions that cause alkaline properties.
- Since ammonium hydroxide is a weak alkali, it dissociates partially releasing fewer hydroxide ions hence the poor electric conductivity.
- Ammonium gas in methylbenzene or trichloromethane exists as molecules without free ions hence no alkaline properties and the electrical conductivity.
## Uses of acids and bases
## 1. Acids
- Refer to the various acids for uses of sulphuric, nitric and hydrochloric acids.

## 2. Bases/ alkalis

- Some weak bases e.g milk of magnesia, are used to relieve stomach disorders.

## Amphoteric oxides and hydroxides.
  - ➢ **Oxides**
- An oxide is a binary compound of oxygen and another element.
- Are of four categories:
  - ▪ Basic oxides
  - ▪ Acidic oxides
  - ▪ Neutral oxides
  - ▪ Amphoteric oxides

### (i). Basic oxides
- Are usually oxides of metals (electronegative elements)
- They react with acids to form salt and water only.
**Examples**
CaO, MgO, CuO etc.

### (ii). Acidic oxides
- Are usually oxides of non metals (electronegative elements).
- Many of them react with water to form (give) acids and are known as acid anhydrides
**Examples**
$CO_2$; $SO_2$; $SO_3$; $P_2O_5$ and $NO_2$

### (iii). Amphoteric oxides
- Are oxides, which behave as both bases and acids.
- Are mainly oxides of certain metals in the middle group of the periodic table.
**Examples**
Oxides of Zn, Al, Pb

## Experiment: - To verify amphoteric oxides
**Procedure**
- A small sample of aluminium oxide is placed in a test tube and 5 cm$^3$ of 2M nitric acid added to it and the mixture shaken.
- The procedure is repeated in different test tubes with ZnO, PbO, CuO and CaO.
- The experiments are repeated using excess 2M sodium hydroxide in place of nitric acid

## Observations

| Name of solid | Observations when | |
| --- | --- | --- |
| | acid is added | hydroxide is added |
| Aluminium oxide | Oxide dissolves | Oxide dissolves |
| Zinc oxide | Oxide dissolves | '' |
| Lead II oxide | '' | '' |
| Zinc hydroxide | Hydroxide dissolves | Hydroxide dissolves |
| Lead hydroxide | '' | '' |
| Aluminium hydroxide | " | " |

**Explanations**
- These oxides are soluble in acids as well as in the alkalis (NaOH)
  - ➢ **Reaction with acids**
- Oxides react with acids to form a salt and water only in a reaction called neutralization reaction.

## Equations
  - ➢ **Oxides**
(i).$PbO_{(s)} + 2H^+_{(aq)} \longrightarrow Pb^{2+}_{(aq)} + H_2O_{(l)}$

(ii). $Al_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$

(iii). $ZnO_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_2O_{(l)}$

> **Hydroxides:**

(i). $Pb(OH)_{2(s)} + 2HCl_{(aq)} \longrightarrow PbCl_{2(aq)} + 2H_2O_{(l)}$

(ii). $Zn(OH)_{2(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + 2H_2O_{(l)}$

(iii). $Al(OH)_{3(s)} + 3HCl_{(aq)} \longrightarrow AlCl_{3(aq)} + H_2O_{(l)}$
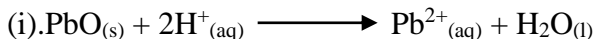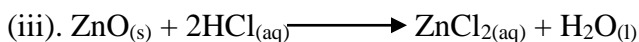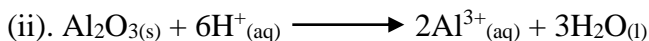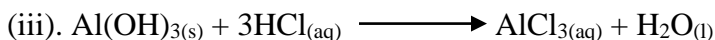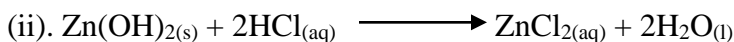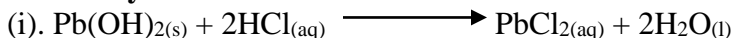
**Note:** in these reactions the metal oxides are reacting as bases

> **Reaction with alkalis**

- These oxides and hydroxides also react with alkalis e.g sodium hydroxide in which case they are reacting as acids.
- Their reactions with alkalis involve the formation of complex ions; $M(OH)^{2-}_4$

**Equations**

> **Oxides**

(i). $PbO_{(s)} + 2NaOH_{(aq)} + H_2O_{(l)} \longrightarrow Na_2Pb(OH)_{4(aq)}$

**Ionically:** $PbO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow [Pb(OH)_4]^{2-}_{(aq)}$

(ii). $Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2[Al(OH)_4]^-_{(aq)} + 3H_2O_{(l)}$

**Ionically:** $Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2[Al(OH)_4]^-_{(aq)}$

(iii). $ZnO_{(s)} + 2NaOH_{(aq)} + H_2O_{(l)} \longrightarrow Na_2Zn(OH)_{4(aq)}$

**Ionically:** $ZnO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow [Zn(OH)_4]^{2-}_{(aq)}$

> **Hydroxides:**

(i). $Al(OH)_{3(s)} + NaOH_{(aq)} \longrightarrow NaAl(OH)_{4(aq)}$

**Ionically:** $Al(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow [Al(OH)_4]^-_{(aq)}$

(ii). $Zn(OH)_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2Zn(OH)_{4(aq)}$

**Ionically**: $Zn(OH)_{2(s)} + 2OH^-_{(aq)} \longrightarrow [Zn(OH)_4]^{2-}_{(aq)}$

(iii). $Pb(OH)_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2Pb(OH)_{4(aq)}$

**Ionically:** $Pb(OH)_{2(s)} + 2OH^-_{(aq)} \longrightarrow [Pb(OH)_4]^{2-}_{(aq)}$

**Salts**

- Is a compound formed when cations derived from a base combine with anions derived from an acid.
- Salts are usually formed when an acid reacts with a base i.e. when the hydrogen ions in an acid re wholly or partially by a metal ion or ammonium ($NH_4^+$) radical.

**Laboratory preparations of salts**

- Salts are prepared in the laboratory using various depending on property of the salt especially solubility
**Examples**
**(a). Preparations by direct synthesis**

**Equation:**

$$Fe_{(s)} + Cl_{2(g)} \longrightarrow 2FeCl_{3(s)}$$
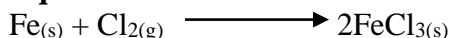
## (b). Reactions of acids with metals, metal oxides, metal hydroxides and metal carbonate

**Equations:**

$$Zn_{(s)} + H_2SO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + H_{2(g)}$$

$$CuO_{(s)} + H_2SO_{4(aq)} \longrightarrow CuSO_{4(aq)} + H_2O_{(l)}$$

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

$$PbCO_{3(s)} + 2NHO_{3(aq)} \longrightarrow Pb(NO_3)_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$
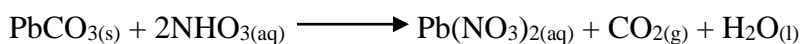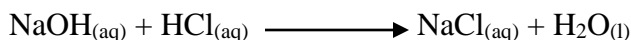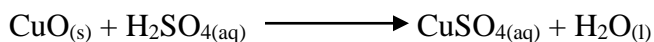
**Note:**

- Acid + metal method will not be suitable if:
  ➢ The metal is too reactive e.g. sodium or potassium.
  ➢ The salt formed is insoluble; as it will form an insoluble layer on the metal surface preventing further reaction.
  ➢ The metal is below hydrogen in the reactivity series.

## (c). Double decomposition/ precipitation

- Mainly for preparations of insoluble salts
- Involves formation (precipitation) of insoluble salts by the reaction between two solutions of soluble salts.

**Equations:**

$$Pb(NO_3)_{2(aq)} + 2NaCl_{(aq)} \longrightarrow PbCl_{2(s)} + 2NaNO_{3(aq)}$$

$$AgNO_{3(aq)} + HCl_{(aq)} \longrightarrow AgCl_{(s)} + HNO_{3(aq)}$$
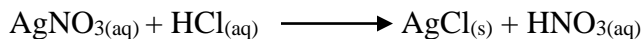
**Types of salts:**

- Are categorized into three main categories:
  ➢ Normal salts
  ➢ Acid salts
  ➢ Double salts

**Solubility of salts: - a summary**

- All common salts of sodium, potassium and ammonium are soluble.
- All common nitrates are soluble.
- All chlorides are soluble except silver, mercury and lead chlorides.
- All sulphates are soluble except calcium, barium, lead and stomium sulphates.
- All carbonates are insoluble except sodium, potassium and ammonium carbonates.
- All hydroxides are insoluble except sodium, potassium ammonium and calcium hydroxides is     sparingly soluble.

**Note:**

- Lead(II) chloride is soluble in hot water.
- Calcium hydroxide is sparingly soluble in water.

## Reactions of some cations with NaOH$_{(aq)}$ and NH$_4$OH$_{(aq)}$ and solubilities of some salts in water

| Cation | Soluble compounds in water | Insoluble compounds in water | Reaction with NaOH$_{(aq)}$ | Reaction with NH$_4$OH solution |
|---|---|---|---|---|
| K$^+$ | all | None | No reaction | No reaction |
| Na$^+$ | all | None | No reaction | No reaction |
| Ca$^{2+}$ | Cl$^-$; NO$_3^-$ | CO$_3^{2-}$; O$^{2-}$; SO$_4^{2-}$; OH$^-$; | White precipitate insoluble in excess | No precipitate |
| Al$^{3+}$ | Cl$^-$; NO$_3^-$; SO$_4^{2-}$; | CO$_3^{2-}$; O$^{2-}$; OH$^-$; | White precipitate soluble in excess | White precipitate insoluble in excess |
| Pb$^{2+}$ | NO$_3^-$; ethanoate; | All others | White precipitate soluble in excess | White precipitate insoluble in excess |
| Zn$^{2+}$ | Cl$^-$; SO$_4^{2-}$; NO$_3^-$; | CO$_3^{2-}$; OH$^-$; | White precipitate soluble in excess | White precipitate soluble in excess |
| Mg$^{2+}$ | Cl$^-$; SO$_4^{2-}$; NO$_3^-$; | CO$_3^{2-}$; OH$^-$; | White precipitate insoluble in excess | No precipitate |
| Fe$^{2+}$ | Cl$^-$; SO$_4^{2-}$; NO$_3^-$; | CO$_3^{2-}$; O$^{2-}$; OH$^-$; | (dark) green precipitate insoluble in excess | Green precipitate insoluble in water |
| Fe$^{3+}$ | Cl$^-$; SO$_4^{2-}$; NO$_3^-$; | CO$_3^{2-}$; O$^{2-}$; OH$^-$; | (red) brown precipitate insoluble in excess | Brown precipitate insoluble in excess |
| Cu$^{2+}$ | Cl$^-$; SO$_4^{2-}$; NO$_3^-$; | CO$_3^{2-}$; O$^{2-}$; OH$^-$; | Pale blue precipitate insoluble in excess | Pale blue precipitate soluble in excess forming a deep blue solution |
| NH$_4^+$ | all | none | Ammonium gas on warming | Not applicable |

**Explanations**

- In these experiments NaOH forms insoluble hydroxides with ions of Zn$^{2+}$, Al$^{3+}$, Cu$^{2+}$, Fe$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Fe$^{3+}$, and Pb$^{2+}$.

- These hydroxides have a characteristic appearance, which form the basis of their identification

**Examples**

**Equations:**

$$Zn^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \longrightarrow Zn(OH)_{2(s)}$$
*(White ppt).*

$$Cu^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \longrightarrow Cu(OH)_{2(s)}$$
*(Pale blue ppt).*

$$Fe^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \longrightarrow Fe(OH)_{2(s)}$$
*(Dirty green ppt).*

$$Fe^{3+}{}_{(aq)} + 2OH^-{}_{(aq)} \longrightarrow Fe(OH)_{3(s)}$$
*(Red-brown ppt).*

$Pb^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Pb(OH)_{2(s)}$
*(White ppt).*
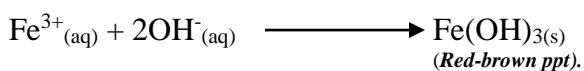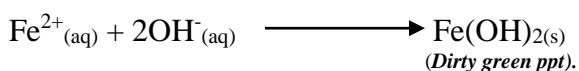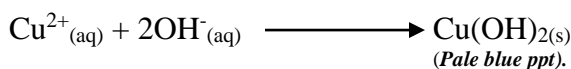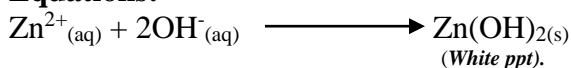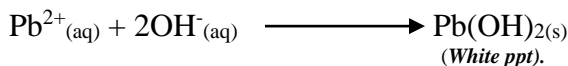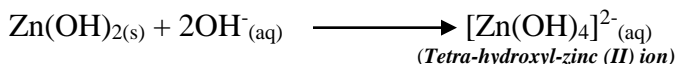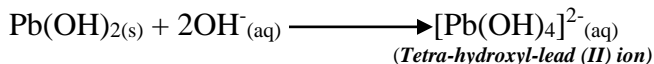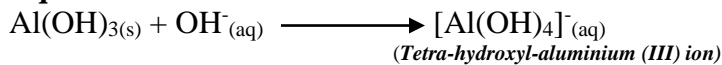
- The hydroxides of aluminum, zinc and lead dissolves in excess sodium hydroxide solution because of complexes are formed

**Equations:**

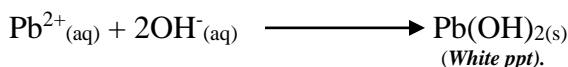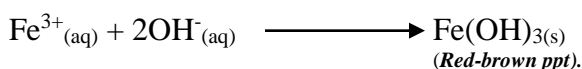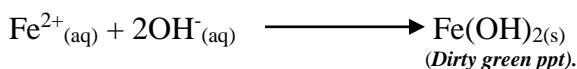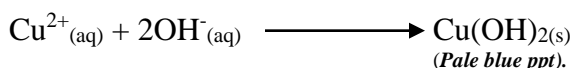$Al(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow [Al(OH)_4]^-_{(aq)}$
*(Tetra-hydroxyl-aluminium (III) ion)*

$Pb(OH)_{2(s)} + 2OH^-_{(aq)} \longrightarrow [Pb(OH)_4]^{2-}_{(aq)}$
*(Tetra-hydroxyl-lead (II) ion)*

$Zn(OH)_{2(s)} + 2OH^-_{(aq)} \longrightarrow [Zn(OH)_4]^{2-}_{(aq)}$
*(Tetra-hydroxyl-zinc (II) ion)*

**Note:** - in these reactions $KOH_{(aq)}$ may be used instead of sodium hydroxide

**With ammonia solution**

- Insoluble metals hydroxides are similarly formed.

$Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Zn(OH)_{2(s)}$
*(White ppt).*

$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Cu(OH)_{2(s)}$
*(Pale blue ppt).*

$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Fe(OH)_{2(s)}$
*(Dirty green ppt).*

$Fe^{3+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Fe(OH)_{3(s)}$
*(Red-brown ppt).*

$Pb^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Pb(OH)_{2(s)}$
*(White ppt).*
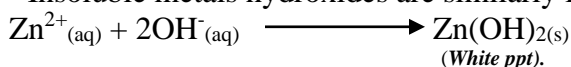
- However hydroxides of copper and zinc dissolve in excess ammonia solution due to formation of complex ions/ salts

**Equations:**

$Zn(OH)_{2(s)} + 4NH_{3(aq)} \longrightarrow [Zn(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)}$
*(White ppt)*      *(Tetra-amine zinc (II) ion; colourless solution)*

$Cu(OH)_{2(s)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)}$
*(Pale blue ppt)*      *(Tetra-amine copper (II) ion; deep blue solution)*
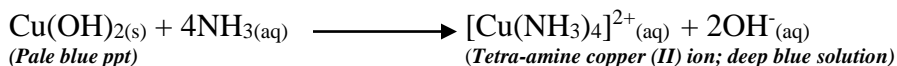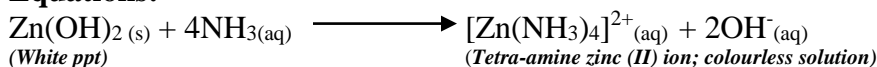
**Effects of heat on metal hydroxides**

**Procedure**

- Hydroxides of Zn, Ca, Pb, Cu e.t.c are strongly heated in a test tube each separately

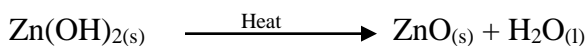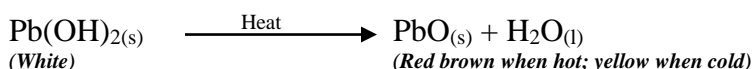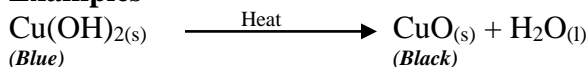**Observation**

- Most metal hydroxides are decomposed by heat to form metal oxides and water
- Sodium and potassium hydroxides only decompose at very high temperatures.
- Hydroxides of metals lower in the reactivity series are readily decomposed by heat than those metals higher in the series.
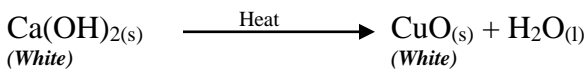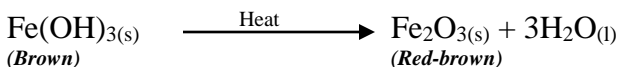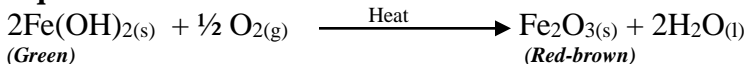
**Examples**

$Cu(OH)_{2(s)} \xrightarrow{\text{Heat}} CuO_{(s)} + H_2O_{(l)}$
*(Blue)*      *(Black)*

$Pb(OH)_{2(s)} \xrightarrow{\text{Heat}} PbO_{(s)} + H_2O_{(l)}$
*(White)*      *(Red brown when hot; yellow when cold)*

$Zn(OH)_{2(s)} \xrightarrow{\text{Heat}} ZnO_{(s)} + H_2O_{(l)}$

*(White)*                                    *(Yellow when hot; white when cold)*

$$Ca(OH)_{2(s)} \xrightarrow{\text{Heat}} CuO_{(s)} + H_2O_{(l)}$$
*(White)*                    *(White)*

## Note:
- Both iron (II) and iron (III) hydroxides give iron (III) oxide when heated.
## Equations:
$$2Fe(OH)_{2(s)} + ½ O_{2(g)} \xrightarrow{\text{Heat}} Fe_2O_{3(s)} + 2H_2O_{(l)}$$
*(Green)*                                    *(Red-brown)*

$$Fe(OH)_{3(s)} \xrightarrow{\text{Heat}} Fe_2O_{3(s)} + 3H_2O_{(l)}$$
*(Brown)*                    *(Red-brown)*

These oxides do not decompose on further heating

## Effects of sodium carbonate on various salt solutions
## Procedure
- 3 drops of $NaOH_{(aq)}$ are added to $2cm^3$ of 1M solution containing magnesium ions in a test tube
the procedure is repeated with salt solutions containing

| Solution containing | Observations after adding sodium carbonate |
|---|---|
| $Mg^{2+}$ | A white precipitate is formed |
| $Ca^{2+}$ | A white precipitate |
| $Zn^{2+}$ | A white precipitate |
| $Cu^{2+}$ | A green precipitate |
| $Pb^{2+}$ | A white precipitate |
| $Fe^{2+}$ | A green precipitate |
| $Fe^{3+}$ | A brown precipitate and a colourless gas that forms a white ppt. in lime water; |
| $Al^{3+}$ | A white precipitate and a colourless gas that forms a white ppt. in lime water; |

## Explanations:
- Sodium carbonate, potassium and ammonium carbonate are soluble in water; all other metal carbonates are insoluble
- Hence their solutions may be used to precipitate the insoluble metal carbonates.
## Ionic equations:
$$Ca^{2+}(aq) + CO_3{}^{2-}{}_{(aq)} \longrightarrow CaCO_{3(s)}$$
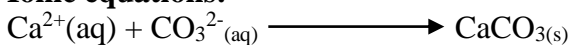
## Note:
Iron (III) and Aluminium salts hydrolyse in water giving acidic solutions which react with carbonates to liberate carbon dioxide gas; hence **effervescence.**

## Reaction of metal ions in salt solutions with sodium chloride, sodium sulphate and sodium sulphate
## (i). Procedure
- $2cm^3$ of a 0.1M solution containing lead ions is placed in a test tube.
- 2-3 drops of 2M sodium chloride solution are added and the mixture warmed;
- The procedure is repeated using salt solutions containing $Ba^{2+}$; $Mg^{2+}$; $Ca^{2+}$; $Zn^{2+}$; $Cu^{2+}$; $Fe^{2+}$ and $Fe^{3+}$
- Each experiment (for each salt) is repeated using $Na_2SO_4$ and $Na_2SO_3$ respectively, in place of sodium chloride.
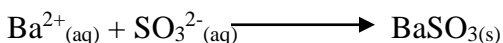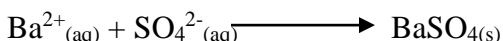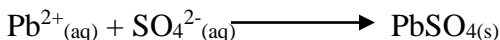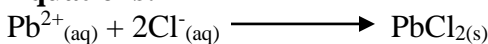
## (ii). Observations

| Solution containing | Sodium sulphate | Sodium chloride | Sodium sulphate |
|---|---|---|---|
| $Zn^{2+}$ | - Colourless solution | - Colourless solution | Colourless solution |
| $Mg^{2+}$ | - Colourless solution | - Colourless solution | Colourless solution |
| $Cu^{2+}$ | - Blue solution | - Blue solution | Blue solution |

| | | | |
|---|---|---|---|
| $Fe^{2+}$ | - Greenish solution | - Green solution | - |
| $Fe^{3+}$ | - Yellow solution | - Yellow/ dark brown solution | - |
| $Pb^{2+}$ | - White precipitate | - White precipitate which dissolve on warming | White precipitate |
| $Ba^{2+}$ | - White precipitate | - White precipitate | White precipitate |

## Explanations

- All the listed cations soluble salts except $Ba^{2+}$ and $Pb^{2+}$
- Lead sulphate and barium sulphate are insoluble in water;
- Lead chloride and barium sulphite are insoluble; however $PbCl_{2(s)}$ **dissolves on warming**

## Equations:

$$Pb^{2+}_{(aq)} + 2Cl^-_{(aq)} \longrightarrow PbCl_{2(s)}$$

$$Pb^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \longrightarrow PbSO_{4(s)}$$

$$Ba^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \longrightarrow BaSO_{4(s)}$$

$$Ba^{2+}_{(aq)} + SO_3^{2-}_{(aq)} \longrightarrow BaSO_{3(s)}$$

## Note:

- To distinguish the precipitate of barium sulphate from barium sulphite; dilute $HNO_{3\ (aq)}$ or $HCl_{(aq)}$ is added to both;
- $BaSO_{3(s)}$ will dissolve in the dilute acid but barium sulphate will not.

## Uses (importance) of precipitation reactions.

- Precipitation of metal carbonate from aqueous solutions is useful in softening hard water; usually by removing calcium and magnesium ions from water as insoluble carbonate

## Useful information on salts (qualitative analysis)
## Colours of substances in solids and solutions in water.

| COLOUR | | |
|---|---|---|
| **SOLID** | **AQUESOUS SOLUTION (IF SOLUBLE)** | |
| 1. White | Colourless | Compound of $K^+$; $Na^+$, $Ca^{2+}$; $Mg^{2+}$; $Al^{3+}$; $Zn^{2+}$; $Pb^{2+}$; $NH_4^+$ |
| 2. Yellow | Insoluble | Zinc oxide, ZnO (turns white on cooling); Lead oxide, PbO (remains yellow on cooling, red when hot) |
| | Yellow | Potassium or sodium chromate; |
| 3. Blue | Blue | Copper (II) compound, $Cu^{2+}$ |
| 4. Pale green | Pale green (almost colourless) Green | Iron (II) compounds, $Fe^{2+}$ |
| Green | | Nickel (II) compound, $Ni^{2+}$; Chromium (II) compounds, $Cr^{3+}$; (Sometimes copper (II) compound, $Cu^{2+}$) |
| 5. Brown | Brown (sometimes yellow) | Iron (III) compounds, $Fe^{3+}$; |
| | Insoluble | Lead (IV) oxide, $PbO_2$ |
| 6. Pink | Pink (almost colourless) Insoluble | Manganese (II) compounds, $Mn^{2+}$; Copper metal as element (sometimes brown but will turn black on heating in air) |
| 7. Orange | Insoluble | Red lead, $Pb_3O_4$ (could also be mercury (II) oxide, HgO) |
| 8. Black | Purple Brown Insoluble | Manganate (VII) ions ($MnO^-$) as in $KMnO_4$; Iodine (element)-purple vapour Manganese (IV) oxide, $MnO_2$ Copper (II) oxide, CuO |

| | | Carbon powder (element) |
|---|---|---|
| | | Various metal powders (elements) |

## Reactions of cations with common laboratory reagents and solubilities of some salts in water

| CATION | SOLUBLE COMPOUNDS (IN WATER) | INSUOLUBLE COMPOUNDS (IN WATER) | REACTION WITH AQUEOUS SODIUM HYDROXIDE | REACTION WITH AQUEOUS AMMONIA SOLUTION |
|---|---|---|---|---|
| $Na^+$ | All | None | No reaction | No reaction |
| $K^+$ | All | None | No reaction | No reaction |
| $Ca^{2+}$ | $Cl^-$; $NO_3^-$; | $CO_3^{2-}$; $O^{2-}$; $SO_4^{2-}$; $OH^-$; | White precipitate insoluble in excess | White precipitate insoluble in excess, on standing; |
| $Al^{3+}$ | $Cl^-$; $NO_3^-$; $SO_4^{2-}$ | $O^{2-}$; $OH^-$; | White precipitate soluble in excess | White precipitate insoluble in excess |
| $Pb^{2+}$ | $NO_3^-$; ethanoate; | All others; | White precipitate soluble in excess | White precipitate insoluble in excess |
| $Zn^{2+}$ | $Cl^-$; $NO_3^-$; $SO_4^{2-}$ | $CO_3^{2-}$; $O^{2-}$; $SO_4^{2-}$; $OH^-$; | White precipitate soluble in excess | White precipitate soluble in excess |
| $Fe^{2+}$ | $Cl^-$; $NO_3^-$; $SO_4^{2-}$ | $CO_3^{2-}$; $O^{2-}$; $OH^-$; | (Dark) pale green precipitate insoluble in excess | (Dark) pale green precipitate insoluble in excess |
| $Fe^{3+}$ | $Cl^-$; $NO_3^-$; $SO_4^{2-}$ | $CO_3^{2-}$; $O^{2-}$; $OH^-$; | (Red) brown precipitate insoluble in excess | (Red) brown precipitate insoluble in excess |
| $Cu^{2+}$ | $Cl^-$; $NO_3^-$; $SO_4^{2-}$ | $CO_3^{2-}$; $O^{2-}$; $OH^-$; | Pale blue precipitate insoluble in excess | Pale blue precipitate soluble in excess forming a deep blue solution |
| $NH_4^+$ | All | None; | Ammonias gas on warming | Not applicable. |

## Qualitative analysis for common anions.

| | $SO_4^{2-}$(aq) | $Cl^-$(aq) | $NO_3^-$(aq) | $CO_3^{2-}$(aq) |
|---|---|---|---|---|
| TEST | Add $Ba^{2+}$(aq) ions from $Ba(NO_3)_2$(aq); acidify with dilute $HNO_3$(aq) | Add $Ag^+$(aq) from $AgNO_3$(aq). Acidify with dilute $HNO_3$ Alternatively; Add $Pb^{2+}$ from $Pb(NO_3)_2$ and warm | Add $FeSO_4$(aq); Tilt the tube and carefully add 1-2 cm$^3$ of concentrated $H_2SO_4$(aq) | Add dilute $HNO_3$(aq); bubble gas through lime water; |
| OBSERVATION | The formation of a white precipitate shows presence of $SO_4^{2-}$ ion; | The formation of a white precipitate shows presence of $Cl^-$ ion; Formation of a white precipitate that dissolves on warming shown presence of $Cl^-$(aq) ions | The formation of a brown ring shows the presence of $NO_3^-$ ions | Evolution of a colourless gas that forma a white precipitate with lime water, turns moist blue litmus paper red; and extinguishes a glowing splint shows presence of $CO_3^{2-}$ ions |
| EXPLANATION | Only $BaSO_4$ and $BaCO_3$ can be formed as white precipitates. $BaCO_3$ is soluble in dilute acids and so $BaSO_4$ will remain on adding dilute nitric acid | Only AgCl and $AgCO_3$ can be formed as white precipitates. $AgCO_3$ is soluble in dilute acids but AgCl is not; - $PbCl_2$ is the only white precipitate that dissolves on warming | Concentrated $H_2SO_4$ forms nitrogen (II) oxide with $NO_3^-$(aq) and this forms brown ring complex ($FeSO_4.NO$) with $FeSO_4$; | All $CO_3^{2-}$ or $HCO_3^-$ will liberate carbon (IV) oxide with dilute acids |

**Checklist:**
1. Why is it not possible to use dilute sulphuric acid in the test for $SO_4^{2-}$ ions;
2. Why is it not possible to use dilute hydrochloric acid in the test for chloride ions?
3. Why is it best to use dilute nitric acid instead of the other two mineral acids in the test for $CO_3^{2-}$ ions?
4. How would you distinguish two white solids, $Na_2CO_3$ and $NaHCO_3$?

**What to look for when a substance is heated.**

| 1. Sublimation | White solids on cool, parts of a test tube indicates $NH_4^+$ compounds;<br>Purple vapour condensing to black solid indicates iodine crystals; |
|---|---|
| 2. Water vapour (condensed) | Colourless droplets on cool parts of the test tube indicate water of crystallization or $HCO_3^-$ (see below) |
| 3. Carbon (IV) oxide | $CO_3^{2-}$ of $Zn^{2+}$; $Pb^{2+}$; $Fe^{2+}$; $Fe^{3+}$; $Cu^{2+}$; |
| 4. Carbon (IV) oxide and water vapour (condensed) | $HCO_3^-$ |
| 5. Nitrogen (IV) oxide | $NO_3^-$ of $Cu^{2+}$; $Al^{3+}$; $Zn^{2+}$; $Pb^{2+}$; $Fe^{2+}$; $Fe^{3+}$ |
| 6. Oxygen | $NO_3^-$ or $BaO_2$; $MnO_2$; $PbO_2$; |

**Reduction-oxidation (Redox reactions)**
**(a). Displacement reactions.**
(i) More reactive halogens metals will displace less reactive metals from solutions of their salts in the series:
**Zn**            **Fe  Pb  Cu**
*More reactive*   ⟶   *Less reactive*

**Example:**
- Zinc powder placed in a solution of copper (II) sulphate, which contains $Cu^{2+}_{(aq)}$ ions, will become $Zn^{2+}_{(aq)}$ ions and brown copper solid (metal) will be deposited.
- The $Cu^{2+}_{(aq)}$ is reduced to copper by addition of electrons and the zinc is oxidized to $Zn^{2+}_{(aq)}$ by removal of electrons.

(ii). More reactive halogens will displace less reactive halogens from solutions of their salts in series:
**Cl₂**            **Br₂  I₂**
*More reactive*   ⟶   *Less reactive.*

**Example:**
- Chlorine bubbled into a solution of potassium iodide (colourless), which contains $I^-_{(aq)}$ ions will turn grey (black) as iodine is liberated.
- The chlorine is reduced to $Cl^-_{(aq)}$ ions by addition of electrons and the $I^-_{(aq)}$ ions are oxidized to iodine by removal of electrons.

**(b). Decolourisation of purple potassium manganate (VII) ions.**
When a few drops of purple $KMnO_4$ solution are added to a compound and the purple colour disappears, then this shows that the $MnO_4^-_{(aq)}$ ions have been reduced to almost colourless $Mn^{2+}_{(aq)}$ ions
The substance in the solution has been oxidized.

**Example:**

- $KMnO_4$ will oxidize $Fe^{2+}_{(aq)}$ ions to $Fe^{3+}_{(aq)}$ ions; pale green solution turns red-brown.
- $KMnO_4$ will oxidize $Cl^-_{(aq)}$ ions to $Cl_{2(g)}$; colourless solution results to a green gas with a bleaching action;

**(c). Orange potassium chromate (VI) turning to a green solution.**
- Orange solution of dichromate ions, $Cr_2O_7^{2-}{}_{(aq)}$, changes to green $Cr^{3+}_{(aq)}$ ions when the dichromate is reduced.
- The substance causing this change is oxidized.

**Example:**
- $K_2Cr_2O_7$ will oxidize $Fe^{2+}_{(aq)}$ to $Fe^{3+}_{(aq)}$
- $K_2Cr_2O_7$ will oxidize $SO_{2(g)}$ to $SO_4^{2-}{}_{(aq)}$
- Formation of sulphate ions in solution from sulphur (IV) oxide gas is often used in the test for sulphur (IV) oxide gas.

**(d). Oxidation of $Fe^{2+}_{(aq)}$ to $Fe^{3+}_{(aq)}$ ions by concentrated nitric acid.**

**Solubility and solubility curves**
  ➢ **Solubility**
- Is the maximum number of grams of a solid which will dissolve in 100g of solvent (usually water) at a particular temperature
- A solution is made up of two parts: - a **solute** and a **solvent.**

**Solute**
- The solid part of a solution usually dispersed in the solvent e.g. a salt.

**Solvent**
- The liquid part of the solution into which the solute is dissolved.

**Experiment: to determine the solubility of potassium nitrate at 20ºC.**
**(i). Materials**
- Beakers, evaporating dish, measuring cylinder, burner, scales, thermometer, distilled water and potassium nitrate

**(ii). Apparatus**

**(iii). Procedure**
- About 50cm$^3$ of distilled water is placed in a beaker
- Potassium nitrate is added to it a little at a time stirring continuously.

- The nitrate is added until no more will dissolve and there is an excess undissolved salt present. This is the **saturated solution** of $KNO_3$ at the temperature.

**Note:**
> ➤ **Saturated solution:** solution that cannot dissolve any more of the solid/ solute at a particular temperature

- The solution is allowed to settle and it is temperature recorded.
- About 25 $cm^3$ of clear solution is poured in a previously weight evaporating dish.
- The mass of the dish and solution is recorded.
- The dish is then heated in a water bath (to avoid **spurting**) till the solution is concentrated.
- The concentrated solution is allowed to cool and the dish weighted with its contents.

**Results and calculations**

| Temperature | 20.0°C |
|---|---|
| Mass of evaporating dish + solution | 100.7g |
| Mass of evaporating dish | 65.3g |
| Mass of solution | 35.4g |
| Mass of evaporating dish + dry salt | 73.8g |

**Calculating:**

Mass of salt dissolved = (73.8 – 65.3)g = 8.5g;

Mass of water (solvent) = (35.4 – 8.5)g = 26.9g

**Thus:**

If 26.9g of water dissolves 8.5g of KNO3 at 20oC;

Then 100g of water will have ? = $\underline{100 \times 8.5}$ = 31.6g of salt;
$\phantom{Then 100g of water will have ? = 100 x 8.5}$ 26.9

Therefore the solubility of $KNO_3$ at 20°C = 31.6g per 100g of water

**Factors affecting solubility.**

**(i). Temperature**

- For most salts solubility increases with rise/ increase in temperature.

**Reason**

- Increased temperature increases the kinetic energy, and hence the momentum and velocity of the solvent molecules so that they can disintergrate the solute molecules more effectively.
- However solubilities of certain salts remain almost constant with temperature change
- Solubility of gases however decreases with increase in temperature;

**Reason:**

Increase in temperature causes the gas molecules to expand and hence escape from the solvent.

Experiment: To investigate the effect the effect of temperature on solubility.

Requirements: potassium nitrate, distilled water, test tube, thermometer, stirrer, bunsen burner, 250 $cm^3$ glass beaker, 4.5g of potassium nitrate.

(ii). Procedure.

Using a 10ml measuring cylinder, measure 5 $cm^3$ of distilled water and add it to the boiling tube containing solid **potassium nitrate**. Insert a thermometer into the boiling tube and heat the mixture gently in a water bath or while shaking to avoid spillage. Continue heating until all the solid has dissolved. Stop heating and allow the solution to cool while gently stirring with a thermometer. Record the temperature at which the crystals of **potassium nitrate** first appear. Note this in the table below.

Retain the boiling tube and its contents for further experiments.

Measure 2 $cm^3$ of distilled water and add to the mixture in the boiling tube. Heat until the crystals dissolve, then cool while stirring with a thermometer. Record the temperature at which the crystals again first stat to reappear.

Repeat this procedure, each time adding more 2 cm³ of distilled water, heating, cooling and recording the crystallization temperature until the table is completely filled.

**Table 2:**

| Experiment number | I | II | III | IV | V |
|---|---|---|---|---|---|
| Volume of water added | 5 | 7 | 9 | 11 | 13 |
| Temperature at which crystals appear (°C) | | | | | |
| Solubility of K in g/100g of water | | | | | |

**Questions:**
(a). Complete the table and calculate the solubility of solid X in g/100g of water at different temperatures.

(2 marks)

(b). Using the table above, plot a graph of solubility of solid X in g/100g of water against temperature.

(5 marks)

(c). From the graph:
(i). calculate the mass of K that would be obtained if the saturated solution is cooled from 60°C to 40°C.

(2 marks)

(ii). determine the solubility at 70°C.                                                                                    (1mark)

(iii). at what temperature would solubility of K be 100g/100g of water?                         (1mark)

**(ii). Stirring**
- Stirring increases the solubility of a solid
**Reason**
- Stirring causes the molecules of solvent and solute to move faster causing the solute particles to disintergrate more effectively

**Solubility curves**
- Are curves showing the variation of solubility with temperature.

**Uses / importance of solubility curves**
- Can be used to determine the mass of crystals that would be obtained by cooling a volume of hot saturated solution from one known temperature to another.
- Solubility differences can be used to separate substances i.e. **recrystallization** or **fractional crystallization** *(refer to separation of mixtures)*
- Separation of salts from a mixture of salts with differing solubilities e.g. extraction of sodium carbonate from Trona (refer *to carbon and its compounds*)
- Manufacture of certain salts e.g. sodium carbonate by the **Solvay process** *(refer to carbon and its compounds)*

**Worked examples**
1. An experiment was carried out to determine the solubility of potassium nitrate and the following results were obtained.

| Temperature | 10 | 15 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|---|

| Mass of KNO$_3$ per 100g of water | 20 | 25 | 45 | 63 | 85 | 106 |
|---|---|---|---|---|---|---|

(a). What is meant by solubility? (1 mark)

(b). Plot a graph of mass of potassium nitrate against temperature. (3 marks)

(c). From the graph work out the mass of KNO$_3$ that would crystallize if a solution containing 70g of KNO$_3$ per 100g of water was cooled from 45ºC to 25ºC. (2 marks)

(d). Explain what would happen if 100g of KNO$_3$ was put in cold water and heated to 50ºC. (2 marks)

6. The table below shows the solubility of sulphur (IV) oxide at various temperatures.

| Temperature (ºC) | 0 | 5 | 10 | 15 | 20 | 25 | 35 | 40 | 45 | 50 | 55 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mass of SO$_2$ per 100g of water | 22 | 18.4 | 15.4 | 13.0 | 10.8 | 9.05 | 7.80 | 6.80 | 5.57 | 4.80 | 4.20 | 3.60 |

(a). On the grid provided plot a graph of solubility against temperature. (3 marks)

(b). From the graph determine:
(i). The lowest temperature at which 100cm$^3$ of water would contain 11.6g of sulphur dioxide.(1 mark)

(ii). The maximum mass of sulphur (IV) oxide that would dissolve in 2 litres of solution at 10ºC. (Assume that the density of the solution is 1gcm$^{-3}$) (3 marks)

(c) (i). Sulphur (IV) oxide reacts with sodium hydroxide solution to form sodium sulphite and water. (1 mark)
(ii). Write the equation for this reaction. (1 mark)

(iii). Using the information from the graph, determine the volume of the saturated sulphur (IV) oxide solution that can neutralize 153 cm$^3$ of 2M sodium hydroxide solution at 25ºC. (3 marks)

**Water**
- Can be pure or impure
**Pure water**
- Is a pure substance which is a compound of hydrogen and oxygen; that boils at 100ºC; melts at 0ºC and has a density of 1gcm$^{-3}$ at sea level.

**Impure water**
- Are the natural waters constituted of dissolved solutes in pure water.

**Hardness of water**
- Water without dissolved substances (salts) hence lathers easily with soap is referred to as soft **water** while water with dissolved substances that does not lather easily with soap is termed as **hard water**

**Experiment: effect of water containing dissolved salts on soap solution**
**Procedure**
- 2 cm$^3$ of distilled water is put in a conical flask.
- Soap solution from a burette is added into the water and shaken until formation of lather is noted.
- If the soap fails to lather more soap solution is added from the burette till it lathers and the volume of the soap required for lathering recorded.

- The procedure is repeated with each of the following: tap water, rain water, dilute solutions of $MgCl_2$, $NaCl$, $CaCl_2$, $a(NO_3)_2$, $CaSO_4$, $MgSO_4$, $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, $ZnSO_4$ , $NaHCO_3$, and $KNO_3$.
- The procedure is repeated with each of the solutions when boiled.
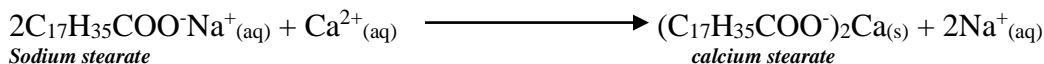
**Observations**

**Explanations**
- Distilled water requires very little soap to produce lather because it lacks dissolved salts and hence termed soft water.
- Solutions containing $NaCl$, $ZnSO_4$, $KNO_3$ and $NaHCO_3$ do not require a lot of soap to form lather
Water containing $Ca^{2+}$ and $Mg^{2+}$ ions do not lather easily (readily) with soap
**Reason:**
- These ions react with soap (**sodium stearate**) to form an insoluble salt (metal stearate) called (Mg and Ca stearate respectively); which is generally termed scum.

**Equations:**
**With $Ca^{2+}$**
$2C_{17}H_{35}COO^-Na^+_{(aq)} + Ca^{2+}_{(aq)}$ $\longrightarrow$ $(C_{17}H_{35}COO^-)_2Ca_{(s)} + 2Na^+_{(aq)}$
*Sodium stearate*                                                  *calcium stearate*

**With $Mg^{2+}$**
$2C_{17}H_{35}COO^-Na^+_{(aq)} + Mg^{2+}_{(aq)}$ $\longrightarrow$ $(C_{17}H_{35}COO^-)_2Mg_{(s)} + 2Na^+_{(aq)}$
*Sodium stearate*                                                  *Magnesium stearate*
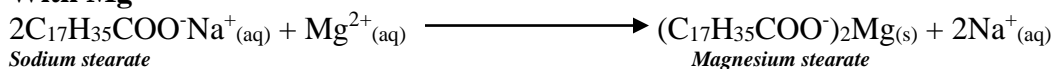
- Thus water with Mg and Ca is termed hard water and can only be made soft by removing these ions upon which the water will lather easily with water
- When $Ca(HCO_3)_{2(aq)}$ and $Mg(HCO_3)_{2(aq)}$ are boiled the amount of soap required for lathering decreases than before boiling

**Reason**
- Boiled decomposes the 2 salts into their respective carbonate s which precipitates from the solution leaving soft water which leathers easily with water

- The amount of soap solution used with solutions containing sulphates and chlorides of calcium and magnesium did not change significantly even after boiling

**Reason**

- The soluble sulphates and chlorides of Mg and Ca do not decompose upon boiling hence can not be precipitated out.

**Types of water hard ness**

**Temporary hardness**

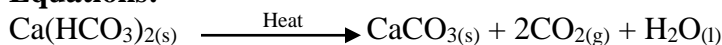- Is hardness due to the presence of $CaHCO_3$ or $Mg(HCO_3)_2$ in water; and can usually be removed by **boiling.**

**Removal of temporary hardness in water:**

**(i). Boiling:**

- Boiling decomposes and an insoluble chalk of $CaCO_3$ and $MgCO_3$ respectively is deposited in the sides of the vessel.
- This forms an encrustation commonly known as **furr** the process being **furring.**

**Equations:**

$$Ca(HCO_3)_{2(s)} \xrightarrow{\text{Heat}} CaCO_{3(s)} + 2CO_{2(g)} + H_2O_{(l)}$$

$$Mg(HCO_3)_{2(s)} \xrightarrow{\text{Heat}} MgCO_{3(s)} + 2CO_{2(g)} + H_2O_{(l)}$$

**(ii). Distillation:**

- Water containing dissolved salts is heated in a distillation apparatus;
- Pure water distils over first leaving dissolved salts in the distillation flask (refer to separation of mixtures)
- Is of less economic value as it is too expensive hence disadvantageous.

**(iii). Addition of calcium hydroxide:**

- Involves adding correct amount of lime water where $CaCO_3$ is precipitated out.
- This method is cheap and can be used on large scale at water treatment plants.
- However if excess lime ($Ca^{2+}$) ions is added this will make water hard again.

**Equation:**

$$Ca(HCO_3)_{2(aq)} + Ca(OH)_{2(aq)} \longrightarrow 2CaCO_{3(s)} + 2H_2O_{(l)}.$$
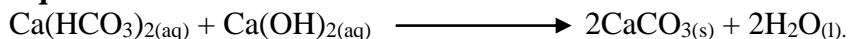
**(iv). Addition of ammonia solution:**

- Addition of aqueous ammonia to water containing calcium and magnesium hydrogen carbonates (temporary hard) precipitates calcium and magnesium ions as corresponding carbonates.

**Equations:**

$$Ca(HCO_3)_{2(aq)} + 2NH_4OH_{(aq)} \longrightarrow CaCO3_{(s)} + 2H_2O_{(l)} + (NH_4)_2CO_{3(aq)}$$
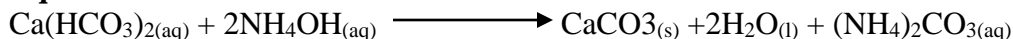
**(ii). By permutit softener (ion exchange).**

- Uses a complex sodium salt (NaX), such as **sodium aluminium silicate** commonly known as **sodium permutit.**
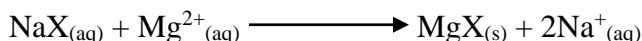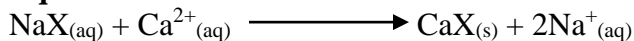- Permutit is a manufactured **ion exchange resin.**

  ➢ **Iron exchange resin:** materials that will take ions of one element out of it's compounds and replace it with ions another element

## Working principle
- The permutit is contained in a metal cylinder
- The hard water is passed through the column of permutit in the cylinder and it emerges softened at the other end
- As hard water passes through the column ion exchange takes place.
- The $Ca^{2+}$ and $Mg^{2+}$ remain in the column while sodium ions from the permutit pass into water thus softening it.

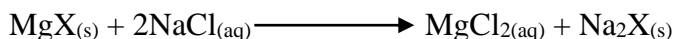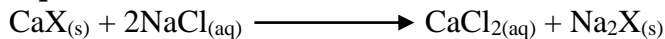**Diagram: permutit water softener.**

## Equations:
$$NaX_{(aq)} + Ca^{2+}_{(aq)} \longrightarrow CaX_{(s)} + 2Na^{+}_{(aq)}$$

$$NaX_{(aq)} + Mg^{2+}_{(aq)} \longrightarrow MgX_{(s)} + 2Na^{+}_{(aq)}$$

- When all the $Na^{+}$ ions in the permutit have been replaced by $Ca^{2+}$ and $Mg^{2+}$ ions the permutit can not go on softening water.
- It is then regenerated by washing the column with **brine** (a strong NaCl solution); during which calcium and magnesium chlorides are washed away.

## Equation:
$$CaX_{(s)} + 2NaCl_{(aq)} \longrightarrow CaCl_{2(aq)} + Na_2X_{(s)}$$

$$MgX_{(s)} + 2NaCl_{(aq)} \longrightarrow MgCl_{2(aq)} + Na_2X_{(s)}$$

## Permanent hardness
- Is that due to soluble **sulphates** and or **chlorides** of **calcium** and or **magnesium** and cannot be removed by boiling

## Removal of permanent hardness
### (i). By the addition of washing soda (sodium carbonate)
- Washing soda softens hard water by causing the formation of insoluble $CaCO_3$ or $MgCO_3$
- The soluble sodium salts left in water do not react with soap.

## Equations:
$$Na_2CO_{3(aq)} + CaCl_{2(aq)} \longrightarrow 2NaCl_{(s)} + CaCO_{3(S)}$$

## Ionically:
$$Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow CaCO_{3(s)}$$

$$Na_2CO_{3(aq)} + MgSO_{4(aq)} \longrightarrow Na_2SO_{4(s)} + CaCO_{3(S)}$$

**Ionically:**

$$Mg^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow MgCO_{3(s)}$$
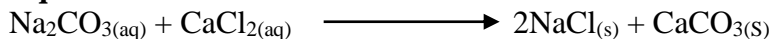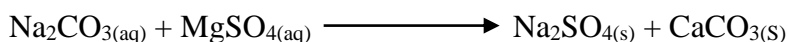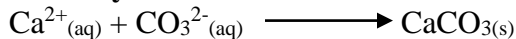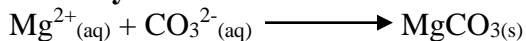
- This method is very convenient and economical on large scale. It softens both temporary and permanent hardness

(ii). By permutit softener (ion exchange); explanations as before
(iii). Distillation.

## Advantages of hard water

(i). It is good for drinking purposes as calcium ions contained in it helps to form strong bones and teeth.

(ii). When soft water flows in lead pipes some lead is dissolved hence lead poisoning. However when lead dissolves in hard water insoluble $PbCO_3$ are formed, coating the inside of the lead pipes preventing any further reaction; this reduces any chances of lad poisoning.

(iii). It is good for brewing and the tanning industries; it improves wine or beer flavour in brewing industries.

## Disadvantages of hard water

(i). Soap forms insoluble salts with magnesium and calcium ions; scum (calcium or magnesium stearate) thereby wasting soap.
- For these reason soapless detergents are preferred to ordinary soaps because they do not form scum; but rather form soluble salts with $Mg^{2+}$ and $Ca^{2+}$
  ➢ Examples of **soapless detergents**: omo, perfix, persil, fab e.t.c.

(ii). Deposition of insoluble magnesium and calcium carbonates and sulphates formed from hard water result into blockage of water pips due to the formation of boiler scales

(iii). Formation of kettle fur which makes electrical appliances inefficient hence increasing running costs.

(iv). Formation of scum on clothing reduces their durability and aesthetic appearance

## UNIT 3: ENERGY CHNAGES IN CHEMICAL AND PHYSICAL PROCESSES (THERMOCHEMISTRY)

**Unit Checklist.**
1. Introduction
2. Specific heat capacity and enthalpy of a system
3. Endothermic and exothermic reactions.
4. Activation energy
5. Determination of heat changes
   - Heat of combustion
     - Meaning
     - Determination
     - Calculations
   - Fuels
     - Meaning
     - Heating value of a fuel
     - Fuel pollution
     - Choice of a fuel
   - Heat of neutralization
     - Meaning
     - Determination
     - Calculations
   - Enthalpy of solution
     - Meaning
     - Determination
     - Calculations
   - Enthalpy of displacement
     - Meaning
     - Determination
     - Calculations
   - Enthalpy of precipitation.
     - Meaning
     - Determination
     - Calculations
6. Energy level diagrams
7. Thermochemical cycles
8. Hess's law
9. Enthalpy of formation.
10. Heat of formation and bond energies.
11. Latent heat
    - Latent heat of fusion
    - Latent heat of vapourisation
    - Relationship between vapourisation, fusion and structure.

## Introduction:
- Most chemical and physical process are accompanied by energy changes which occur in the form of heat measured in joules (J) and kilojoules (KJ).
- The heat results from the motion of atoms and molecules.

## Specific heat capacity
- Specific heat capacity of a substance is the number of joules required to raise the temperature of **one gram** of the substance by **one degree Kelvin** e.g. – SHC for water is $4.18Jg^{-1}K^{-1}$

## The heat content (Enthalpy) of a system.
- Heat content is denoted by H; while heat change is denoted as $\Delta H1$;
- And; $\Delta H = H_{Products} - H_{Reactants}$
$$= H_2 - H_1$$
- Heat changes in chemical reactions can either be **exothermic** and **endothermic**.

## Endothermic and exothermic reactions.
### (a). Endothermic reactions
- Is a reaction accompanied by a **fall in temperature** and energy is absorbed from the surroundings.
- The enthalpy change is normally **positive** since heat of products ($H_{Products}$) is higher than heat of reactants ($H_{reactants}$).
- Thus $H_2 - H_1$ is a positive value; since $H_I$ is less than $H_2$.

**Graphically this can be denoted as follows;-**
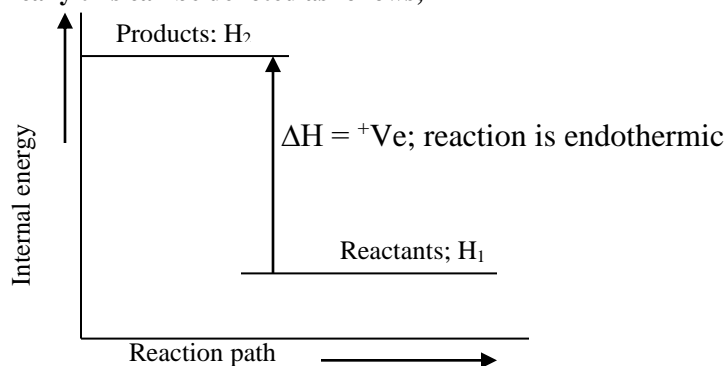


**Examples:**
(i). When $NH_4NO_3$ dissolves in water, the temperature of the solution drops.

## Procedure
- A spatula end-full of ammonium nitrate is dropped into a test tube of water.
- The bottom of the test tube is felt with the hand.

## Observations:
- The hand feels cold.
## Reason:
- Energy is absorbed by the products, cooling the test tube.

Thus $H_1$ is less than $H_2$ giving a positive $\Delta$ H1 showing an endothermic reaction.

(ii) $N_{2(g)} + O_{2\,(g)} \longrightarrow 2NO_{(g)}$; $\Delta H = +91KJMol^{-1}$
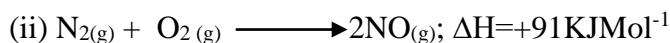
**(b). Exothermic reactions.**
- Are reactions accompanied by a **rise in temperature** and energy is liberated to the surroundings.
- The **enthalpy change** is normally **negative**, since heat of reactants ($H_1$) is normally higher than heat of products ($H_2$).
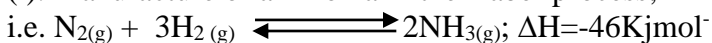- Thus, $H_2$-$H_1$ gives a negative value since $H_1$ is higher than $H_2$.

Exothermic reactions can be represented graphically as follows;-
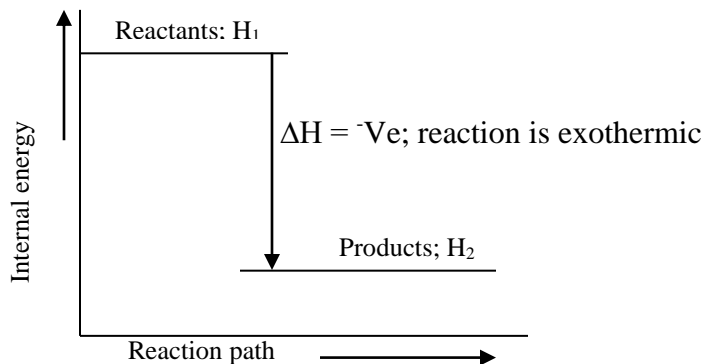


- In exothermic reactions $H_2$ is lower than $H_1$.

**Examples:**
(i). Manufacture of ammonia in the Haber process;
i.e. $N_{2(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3(g)}$; $\Delta H = -46 Kjmol^-$

(ii) Dissolving sodium hydroxide pellets in water,
-The temperature of the resulting $NaOH_{(aq)}$ is higher than the temperature of water at room temperature.
-This implies the internal temperature of products is lower than the reactants' original temperature.
-Thus (H products – H reactants) = -ve value, an exothermic reaction.

**Activation energy.**
- Is the energy required to **activate** the reactants before a reaction can take place.
- Thus activation energy is the energy required to initiate a reaction.
- The size of activation energy will differ from one reaction to another and so will be the gap between the energy of reactants and the energy is products.

**Examples:**
**(i). Exothermic reactions**
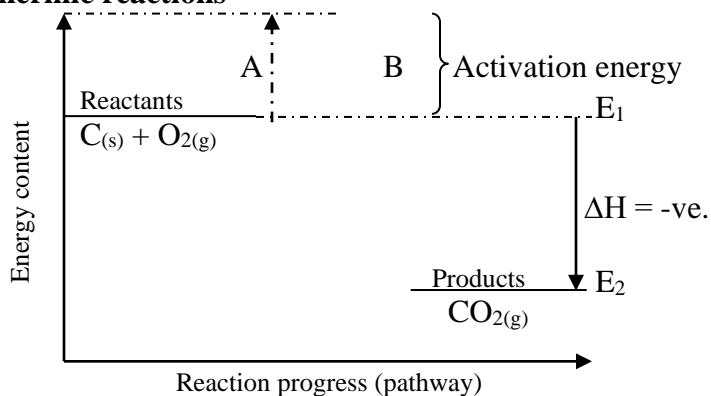


- At A; bonds are being broken and the energy is absorbed.
- At B; bonds are now being formed, and so energy is evolved.

**Endothermic reactions**
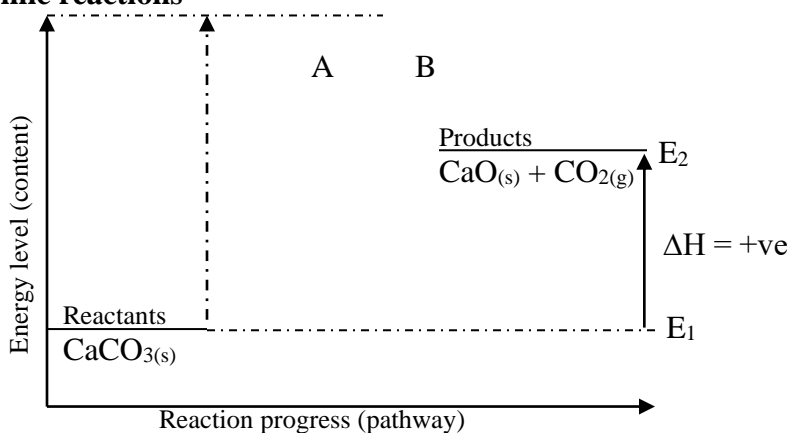


- At A; bonds are broken and energy is absorbed.
- At B; bonds are formed and energy is evolved.

**Determination\ measurement of Enthalpy (heat) changes.**
Calorimeters are sued and have to be insulated to reduce heat loss to the surrounding.

**Source of errors:**
- Heat loss to the surrounding.
- Absorption of heat by the calorimeter (vessels).

**Main heat changes under consideration:**
- ➤ Enthalpy of combustion ($\Delta H_c$)
- ➤ Enthalpy of neutralization ($\Delta H_{neut}$)
- ➤ Enthalpy of solution ($\Delta H_{soln}$)
- ➤ Enthalpy of precipitation ($\Delta H_{precip}$)
- ➤ Enthalpy of displacement ($\Delta H_{Disp}$)
- ➤ Enthalpy of formation ($\Delta H_f$)

## 1. Heat of combustion $\Delta H_c$

- Is the heat changes when the mole of a substance is completely burned in oxygen, at one atmospheric pressure.
- Since heat is usually evolved and hence $\Delta H$ is usually negative.

**Example;**

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \; ; \; \Delta H = -394 \; Kjmol^{-1}$$
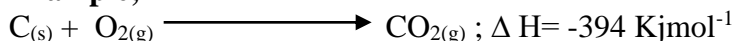
**Apparatus for finding $\Delta H_c$ of a fuel.**

| Heat evolved = Specific heat capacity of water x Mass of water x Temperature rise |
|---|

$= \mathbf{CM\Delta T;}$ joules, where; C = specific heat capacity.

M = mass of water.

$\Delta T$= temperature change.

## Examples

*1. Assume*

| | |
|---|---|
| *Volume of water in calorimeter* | *= 100cm³* |
| *Initial temperature of water* | *= 225ºC* |
| *Final temperature of water* | *= 50.5ºC* |
| *Change in temperature of water* | *= 28.0ºC* |
| *Mass of water* | *= 100g* |
| *Mass of lamp before burning* | *= 30.46g* |
| *Mass of lamp after burning* | *= 30.06g* |
| *Mass of ethanol burnt* | *= 30.46 -30.06* |

*= 0.40g*

*(a). Determine the heat evolved;*

$$= \Delta H = CM\Delta T$$
$$= 4.2 \times 100 \times 28$$
$$= 11760 \text{ Joules}$$
$$= 11.760 \text{ KJ}$$

*(b). Hence calculate the molar heat of combustion of ethanol;*

Moles of ethanol burnt = $\dfrac{\text{Mass of ethanol burnt}}{\text{RFM of ethanol}}$; $\dfrac{0.4}{46}$ = 0.008695 moles.

Thus if 0.008695 moles = 11.76 kilojoules,
　　　Then 1mole = ?

$$1 \text{ mole} = \frac{11.76 \times 1}{0.008695} = -1352.50 \text{ KJMol}^-$$

$$= -1352.5 \text{ KJMol}^{-1} \text{ (negative value as the reaction is exothermic since heat is evolved).}$$

*2. When ethanol was burnt in the apparatus shown (in example 1), the results were: mass of fuel burnt, $M_1=1.50g$; mass of water, $M_2=500g$; $\Delta T= 13.0^oC$. (C=12; H=1; O=16; SHC of water=4.18KJKg$^-$K$^-$). Find the molar enthalpy of combustion of ethanol.*
*Compare the experimental value with the listed value of –1368 KJMol$^-$ and explain any difference.*

**Solution:**
Heat evolved = CMΔT
$$= 4.18 \times \frac{500}{1000} \times 13$$
$$= 27.17 \text{KJ}$$
Molar mass of ethanol, $C_2H_5OH = [(12 \times 2) + (1 \times 6) + (1 \times 16)] = 46$
Thus if 1.5g = 27.17KJ
Then 46 g = ?
$$= \frac{46 \times 27.17}{1.5}$$
$$= 833.213 \text{KJMol}^-$$

*3. In an experiment to determine the heat of combustion of methanol, $CH_3OH$ a student used a set up like the one shown in the diagram below. Study the set up and the data and answer the questions that follow.*

*Data:*
*Volume of water      =500 cm³*
*Final temperature of water =27.0ᵒC*
*Initial temperature of water =20.0ᵒC*
*Final mass of lamp + menthol = 22.11g*
*Initial mass of lamp + methanol =22.98g*
*Density of water- 1gcm⁻³*
*(Heat change = mass x temperature change x 4.2Jg⁻¹ᵒC⁻1*

*Questions:*
*(a). Write an equation for the combustion of methanol.*                    *{1mark}*

*(b). calculate:*
*(i). The number of moles of methanol used in the experiment*                *{2marks}*

*(ii). The heat change for this experiment.*                              *{1mark}*

*(iii). The heat of combustion per mole of methanol.*                      *{2marks}*

*(c) Explain why the molar heat of combustion for methanol obtained in this experiment is different from the theoretical value.*                                        *{2marks}*

*4. When 0.6g of element J were completely burned in oxygen, all the heat evolved was used to heat 500 cm³ of water, the temperature of the water rose from 23.0ᵒC to 32.0ᵒC. Calculate the relative atomic mass of element J given that the specific heat capacity of water = 4.2jg⁻¹k⁻¹, density of water=1.0gcm⁻³ and molar heat of combustion of J is 380JMol⁻*                     *{3marks}*

*5. Hydrogen peroxide contained in 100cm³ of solution with water was completely decomposed. The heat evolved was 1380J. Determine the rise in temperature due to the reaction.*
*(SHC of water = 4.2Jg⁻¹k⁻¹; density of water = 1gcm⁻³; O =16; H = 1)*          *{3 marks}*

**Fuels:**
- Are compounds which produce a high heat of combustion.
- Fuels can be:-
  - **Solids;** such as charcoal, wood, coal.
  - **Liquids;** such as ethanol, gasoline
  - **Gaseous;** such as methane, water, gas etc.

**Basic concepts:**
  - ➢ **Calorific value**
- Is the energy content of a fuel;
- Is the heat evolved when a given mass of fuel is completely burnt in oxygen;

**Note:**
- Sometimes fuels may undergo **incomplete combustion**.
- Incomplete combustion of fuel is disadvantageous in that:-
  - It reduces the energy content.
  - It leads to pollution.

> **Heating value:**
- Is the amount of heat energy given out when a **unit mass or unit volume** of a fuel is completely burnt in oxygen.

**Fuel pollution.**
- Is commonly caused by internal combustion engine.
- Fuel in engine (e.g. petrol) burns completely to water and carbon (IV) oxide, only under ideal conditions.

**Causes of fuel pollution:**
(i). Incomplete combustion which causes production of (produces) CO and unburnt carbon (soot).

(ii). Some fuels contain sulphur and nitrogen and on combustion release $SO_2$ and $NO_2$. These gases are acidic, resulting to acidic rain which corrodes buildings and affects trees and animals in various ways.

(iii). Fuel additives; e.g. tetraethyl lead, $Pb (C_2H_5)_4$ added to petrol to enhance burning efficiency produces volatile lead compounds in the exhaust fumes.
- Lead is very poisonous and affects the nervous system and the brain in children.

**Factors to consider when choosing a fuel.**
(i) Heating value,
(ii) Ease and rate of combustion.
(iii) Availability
(iv) Ease of transportation
(v) Ease of storage
(vi) Environment effects.

**2. Heat of neutralization;**
**-** Is the heat evolved when acid and a base react to form and mole of water.
- Alternatively;
- It is the heat evolved when one mole of **hydrogen ions** from an acid reacts with one mole of **hydroxide ions** from an alkali to form\ give one mole of water.

**Equation:**
$$OH^-_{(aq)} + H^+_{(aq)} \longrightarrow H_2O_{(l)}$$
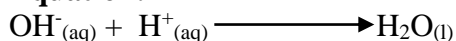
- Neutralization reactions are **exothermic**.
- Are determined by:
        - measuring the temperature rise produced when a known volume of acid is neutralized by a known volume of alkali.
**Examples.**
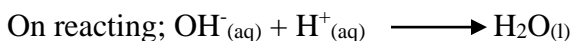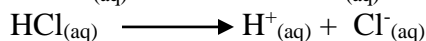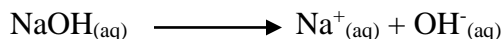**(a). Strong acids reacting with strong alkalis.**
The $\Delta H$ is always about $-57KJMol^-$ and higher than that for weak acids – weak alkalis.
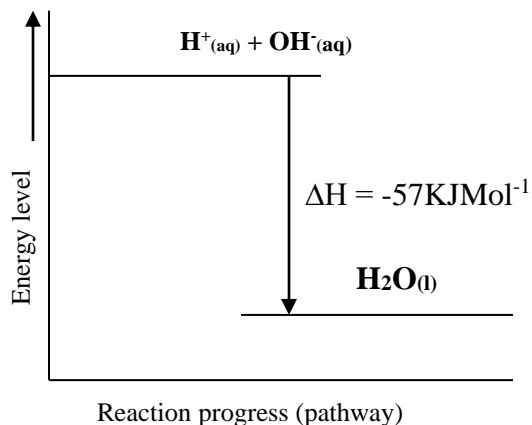**Reason:-**
- Strong acids and alkalis are already **fully ionized** in aqueous solution and no heat is lost in ionizing the acid or the alkali.

**Consider:**
- Reaction between sodium hydroxide and hydrochloric acid

$NaOH_{(aq)}$ ⟶ $Na^+_{(aq)} + OH^-_{(aq)}$
$HCl_{(aq)}$ ⟶ $H^+_{(aq)} + Cl^-_{(aq)}$

On reacting; $OH^-_{(aq)} + H^+_{(aq)}$ ⟶ $H_2O_{(l)}$

**Diagrammatically (energy level diagram)**



Reaction progress (pathway)

## (b). Neutralization reactions involving weak acids or weak alkalis.
- The ΔH is lower than expected, e.g. only –52Kjmol-; and hence lower than that for strong acids-strong alkalis.

**Reason:**
- Weak acids and weak alkalis are **NOT fully ionized** in aqueous solutions and some heat is used in ionizing them.
Consider; reaction between ethanoic acid and ammonia solution.



Reaction pathway ⟶
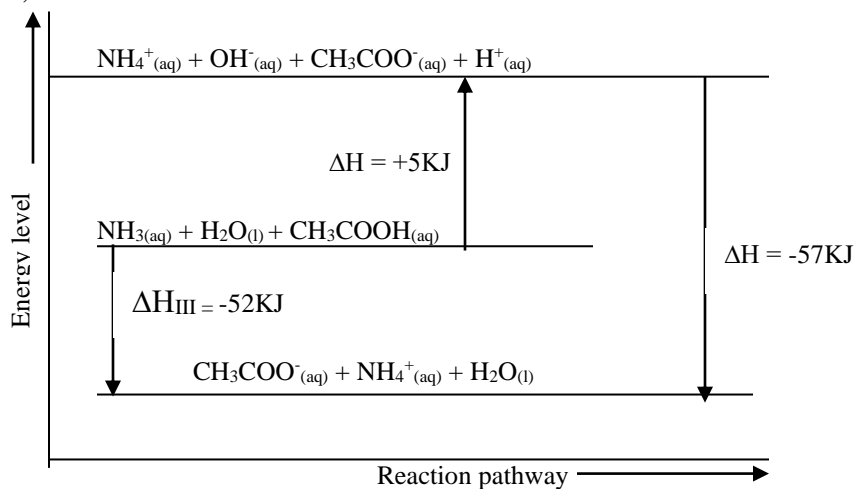
Therefore;
      ΔH is given by;
      $ΔH = ΔH_I + ΔH_{II}$
         = 5 + (-57)
         = -52KJMol$^{-1}$

**Note:** -

- Dibasic acids e.g. $H_2SO_4$ contains two replaceable hydrogen atoms hence on incomplete neutralization, they form two moles of water.

- Therefore, H neutralization = $\boxed{\text{½ x ΔH reaction.}}$

**Experiment: - To determine the heat of neutralization of hydrochloric acid by sodium hydroxide.**
**(i) Procedure:-**
- A clean dry 250 $cm^3$ glass or plastic beaker is wrapped with a newspaper leaf.
- Exactly 50 $cm^3$ of 2.0M hydrochloric acid solution is transferred into the beaker.
- The temperature $T_1$ of the acid solution is noted.
- Using another clean dry measuring cylinder, exactly 50 $cm^3$ of 2.0M NaOH solution is measured and its steady temperature $T_2$ is noted.
- The contents of the beaker (acid), are carefully stirred with a thermometer while adding NaOH.
- The highest temperature $T_4$ attained by the resulting mixture is noted.

**(ii) Apparatus**




**(iii). Results:**
- Temperature of the acid, $T_1$ = $^o$C;
- Temperature of the hydroxide, T2 = $^o$C;
- Average temperature of the two solutions; $\dfrac{T_1 + T_2}{2}$ = $T_3$ = $^o$C

-The highest temperature of the mixture; $T_4$ = $^o$C;
-The temperature change, ΔT= ($T_4$ –$T_3$) = $^o$C;

**Sample calculations:**
Given: Temperature of hydrochloric acid solution $T_1$= 22.75$^o$C;
      Temperature of sodium hydroxide solution $T_2$ = 22.80$^o$C;
      Average temperature of acid and alkali $\dfrac{T_1 + T_2}{2}$ = $T_3$ = 22.78$^o$C;

      Highest temperature of alkali and acid mixture, $T_4$ = 36.40$^o$C;
      Temperature change, ΔT= $T_4$ – $T_3$ = (36.40 – 22.78)$^o$C;
                =13.62$^o$C;

➢ **Assumption:** the specific heat capacity of the solution= 4.2KJKg$^{-1}$K$^{-1}$.

- In the experiment, 50 $cm^3$ of 2M HCl are neutralized by 50 $cm^3$ of NaOH, thus; volume of the mixture= (50 + 50) $cm^3$ = 100 $cm^3$.
- Taking density of the resultant solution to be 1gcm-3, then;-
      Mass of solution M;
                =density x volume
                =1g/$cm^3$ x 100$cm^3$= 100g.

$$=0.1 \text{ kg i.e. } (100/1000)$$

Thus heat evolved,

         Mass of solution x specific heat capacity x temperature change
         = MCΔT,
         = 0.1Kg x 4.2kj/kg k x 13.62°C
         =- 5.7 KJ.

- But 50 cm$^3$ of 2M HCl contains $\underline{2 \times 50}$ moles, = 0.1 moles of H$^+$ ions.
                                        1000

- Similarity 50 cm$^3$ of 2M NaOH contains $\underline{2 \times 50}$ = 0.1 moles of OH$^-$ ions.
                                            1000

- This implies that the two solutions neutralize each other completely.
Therefore;

         Molar heat of neutralization (heat liberated when one mole of each reagent is used;-
                 0.1 Mole = 5.72KJ
                     1mole = $\underline{1 \times 5.72}$ = -57.2 KJMol$^{-1}$
                              0.1

- Since heat is evolved, the reaction is exothermic, the molar heat of neutralization= -57.2 KJMol$^{-1}$.
Thus, enthalpy change;

                H$^+_{(aq)}$ + OH$^-_{(aq)}$   ⟶   H$_2$O$_{(l)}$; ΔH$_{(neut)}$ = -57.2 KJMol$^-$. (Thermochemical equation)
                *1mole*         *1mole*               *1mole*
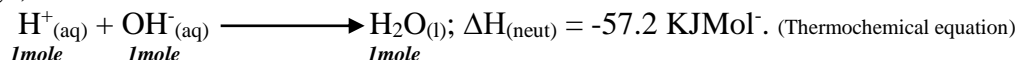
**Note:**
**Thermochemical equation**: refers to a chemical equation which shows the enthalpy change.

**Worked examples:**
*1. Given, $T_1$= 21.0$^o$C; T2=22.0$^o$C; $T_4$ = 34.5$^o$C; volume of hydrochloric acid= 100 cm$^3$, volume of NaOH$_{(aq)}$ =100 cm$^3$, molarity of the solutions are each 2M. Calculate the heat of neutralization for the two reagents. (Assumptions, density of the mixture=1gcm$^{-3}$ and SHC=4.2KJKg$^{-1}$K$^{-1}$)*

*2 (a). When 100g of water at 94.0$^o$C were added to a calorimeter at 17.5$^o$C, the temperature rose to 80.5$^o$C. Determine the heat capacity of the calorimeter. What assumption did you make in your calculations?*

Solution:
Heat given out by water = heat received by calorimeter of heat capacity C.
Heat = MCΔT,
     0.100 x 4180 x (94.0 – 80.5) = C (80.5 – 17.5)
     C = $\underline{0.100 \times 4180 \times 13.5}$
               62.5
      = 90.288Jg$^{-1}$k$^{-1}$
Assumption; specific heat capacity of water is 4180jg$^{-1}$k$^{-1}$

*(b). 250 cm$^3$ of sodium hydroxide were added to 250 cm$^3$ of hydrochloric acid in the calorimeter. The temperature of the two solutions was 17.5$^o$C initially and rose to 20.1$^o$C. Calculate the standard enthalpy of neutralization.*

**Solution:**
- Assuming the specific heat capacities of the solutions is the same as that of water, 4180jg$^{-1}$k$^{-1}$.
Heat from neutralization = heat by calorimeter + solutions.
                = (CΔT)   + MCΔT,
     Mass of solutions = 250+250) =500 cm$^3$
                   = density x volume; = 1gcm$^{-3}$ x 500 cm$^3$=500g

Hat from neutralization = 90(20.1-17.5) + (0.500 x 4180 x (20.1-17.5)
$$= 5670J.$$

4. *The following results were obtained in an experiment to determine the heat of neutralization of 50 cm³ 2M HCl and 50 cm³ 2M sodium hydroxide.*
*Mass of plastic cup = 45.1g*
*Initial temperature of acid = 27.0ºC*
*Initial temperature of alkali = 23.0ºC*
*Mass of plastic cup + HCl + NaOH = 145.1g*
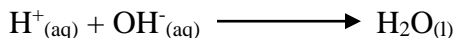*Temperature of the mixture of acid and alkali = 38.5ºC.*

*(a) Define heat of neutralization;*                                                                 *{1mark}*
**Solution:-**
Enthalpy change when one mole of water is formed from a reaction between an acid and a base.

*(b) Write an ionic equation for the neutralization of hydrochloric acid and sodium hydroxide.  {1mark}*
Solution:
$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

*(c) Calculate;*
*(i) The amount of heat produced during the experiment.*                                 *{3marks}*
*(Specific heat capacity of solution=4.2kjkg⁻¹k⁻¹, density of solution= 1gcm⁻³).*

**Solution:**
Amount of heat = MC$\Delta$T
Mass of solution = (145.1 – 45.1) = 100g
Temperature change; $\Delta$T = (38.5)-(27.0 +23.0) = 38.5 – 25 =13.5ºC;
                                                                    2
Heat produced $\Delta$H = 100g x 4.2kjg⁻¹k⁻¹ x 13.5ºC
                    =5670 joules
                    =5.67KJ

*(ii). Molar heat of neutralization for the reaction.*                                        *{3marks}*

**Solution:**
Number of moles involved; taking only NaOH or HCl'
        1000 cm³ = 2moles
        50 cm³= 2 x 50 = 0.1moles
                1000
If 0.1 mole produced 5.67 kg; 1 mol = ?
0.1=5.67kg
1mol= (5.67 x 1) = 56.7 KJMol⁻¹
        0.1

(d). Explain why the molar heat of neutralization of NaOH and ethanoic acid of equal volume and molarity would be less than the value obtained in c (ii) above.                                (1mark)

**Solution:**
- Some of the heat produced during neutralization is used up by the weak acid to dissociate fully hence the lower value.
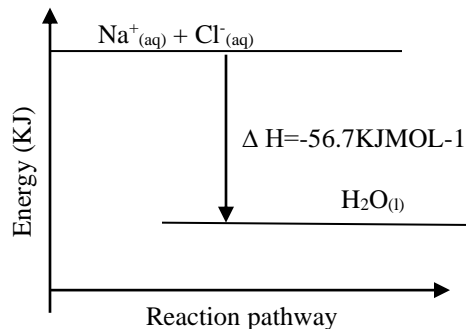
(e). Write down the **Thermochemical equation** for the reaction between NaOH and dilute hydrochloric acid above.

**Solution**

$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$; $\Delta H = -56.7KJMol^{-1}$

(f). Draw an energy level diagram for the neutralization reaction in 4 (c ) above.



**3. Heat of solution/ enthalpy of solution.**
- Is the heat change when a given mass (moles) of a substance is dissolved in a stated amount of solvent (water).

**Molar enthalpy of solution:**
- Is the heat change when one mole of a substance is dissolved in a stated amount of solvent (water).
- Alternatively;
- It is the heat change when one mole of a substance dissolves in water to give an **infinitely dilute solution** i.e.
(a solution which shows no change in its properties when more water is added).

- Is determined as;

$\boxed{\Delta H_{solution} = - \Delta H_{lattice} + \Delta H_{hydration}}$ ; when $\Delta H_{lattice}$ is given as a negative value;

Alternatively;

$\boxed{\Delta H_{solution} = \Delta H_{lattice} + \Delta H_{hydration}}$ ; where $\Delta H_{lattice}$ is given a s appositive value;

Where,
➤ **Lattice energy**
- Is the leaf evolved when one mole of a compound is formed from its separate gaseous ions.
Alternatively;
- It is the energy required to break the ionic bonds within a crystal (solid) lattice.

➤ **Hydration (solvation) energy,**
- Is the heat evolved when one mole of ions are hydrated by water molecules.

Note:
- Water is a good solvent because it has a high negative(-ve) enthalpy of solvation resulting from powerful interaction between polar molecules and solute ions due to large dipoles on water molecules.
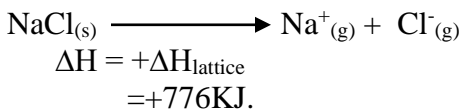
- Therefore,
  - *Heat of solution can either be exothermic or endothermic depending on the magnitude of hydration and lattice energies.*

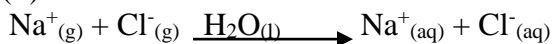- Solution process occurs into two stages.

**Example:**
- Consider the dissolution of sodium chloride solid.
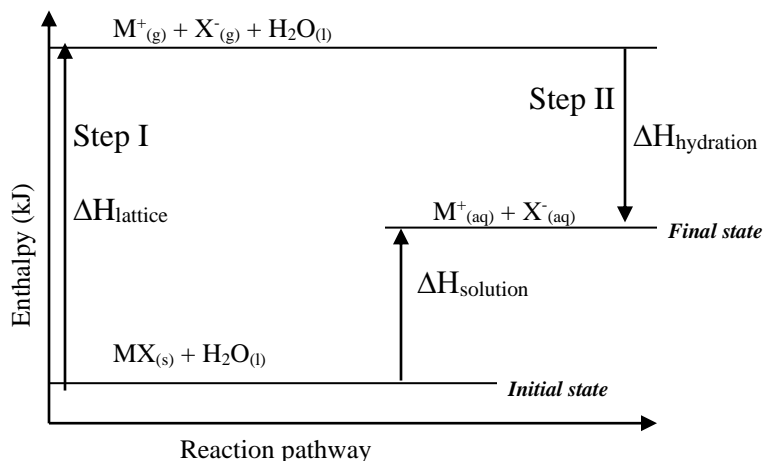(i). Energy is taken in to break the crystalline lattice.

$$NaCl_{(s)} \longrightarrow Na^+_{(g)} + Cl^-_{(g)}$$
$$\Delta H = +\Delta H_{lattice}$$
$$= +776KJ.$$

(ii). Heat is evolved when one mole of icons are hydrated by water molecules.
$$Na^+_{(g)} + Cl^-_{(g)} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + Cl^-_{(aq)}$$

$\Delta H$ hydration$=-771KJ$

**Illustrations:**
**(a) Energy level diagram for an endothermic dissolving process for a solid $MX_{(s)}$**



-The lattice energy is larger than the hydration energy hence;-
$\Delta H_{solution} = +ve$

(b) Energy level for the diagram for an exothermic dissolving process for solid $MX_{(s)}$
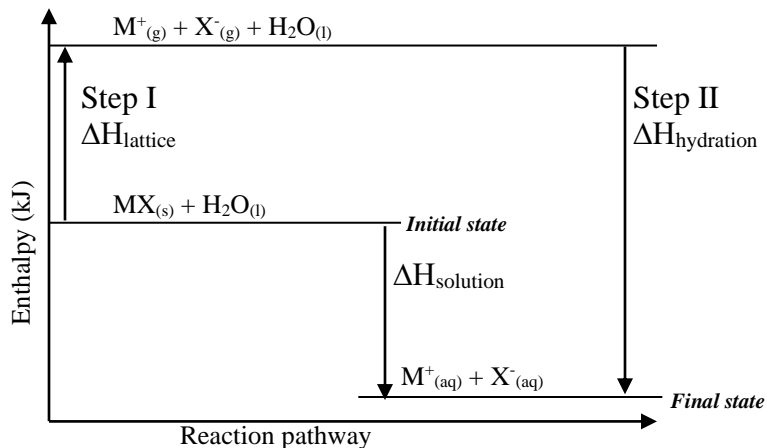


The lattice energy is smaller than hydration energy hence;

ΔH solution = -ve.

**Note:** All gases dissolve with evolution of heat;
**Reason:**
- There are no intermolecular forces or bonds to break before hydration occurs.

**Worked examples:**
*1. The equation below represents changes in physical states for iron metal.*

$Fe_{(s)}$ ⟶ $Fe_{(l)}$; ΔH = 15.4KJMol⁻
$Fe_{(l)}$ ⟶ $Fe_{(g)}$; ΔH = 354KJMol⁻
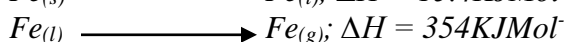
*Calculate the amount of heat required to change 11.2g of solid into iron to gaseous iron. (Fe=56.0)*

**Solution:**
Total heat needed to convert 1 mole of iron from solid to gas = (15.4Kj + 354Kj); = 369.4Kj;
1 mole = 56g;
Thus if 56g requires 369.4Kj;
Then 11.2g =?
$$= \frac{11.2 \times 369.4}{56}; = 73.88Kj;$$

*2. The lattice and hydration enthalpies for lithium chloride and potassium chloride are given below.*

| Salt | $\Delta H_{lattice}$ | $\Delta H_{hydration}$. |
|------|------------|--------------|
| LiCl | -861 | -884 |
| KCl | -719 | -695 |

*(a). Calculate the enthalpy of solution, ΔH$_{solution}$; Kj mol⁻ for;*
*I. Lithium chloride.* *(2 marks)*

**Solution:**

H$_{solution}$ = -ΔH$_{lattice}$ + ΔH$_{hydration}$
= - (-861) + (-884)
= 861- 884;
= -23Kjmol-

*II. Potassium chloride:* *(2 marks)*

**Solution:**

H$_{solution}$ = -ΔH$_{lattice}$ + ΔH$_{hydration}$
= - (-719) + (-695)
= 719- 695;
= -24Kjmol-

*(b) Which of these two salts above has a higher solubility in water? Give reasons for your answer.*

**Solution:**

Potassium chloride; the difference in $\Delta H_{solution}$ is greater;

4. Given that the lattice energy of $NaCl_{(s)}$ is $+77kjmol^{-1}$ and hydration energies of $Na^+_{(g)}$ and $Cl^-_{(g)}$ are $-406kjmol^{-1}$ and $-364kjmol^{-1}$ respectively. Calculate the heat of solution, $\Delta H_{soln}$ for one mole of $NaCl_{(s)}$

**Experiment: To measure the molar enthalpy change for the dissolution (enthalpy of solution) for various compounds.**

**(i) Procedure;**

- A clean 250 $cm^3$ glass or plastic beaker is wrapped with a newspaper leaf.
- About 50 $cm^3$ of tap water is measured into the beaker and the steady temperature noted.
- The beaker is held in a tilted position and 2 $cm^3$ of and sulphuric acid added into the water.

**(ii) Apparatus.**



Conc. Sulphuric acid

Tap water
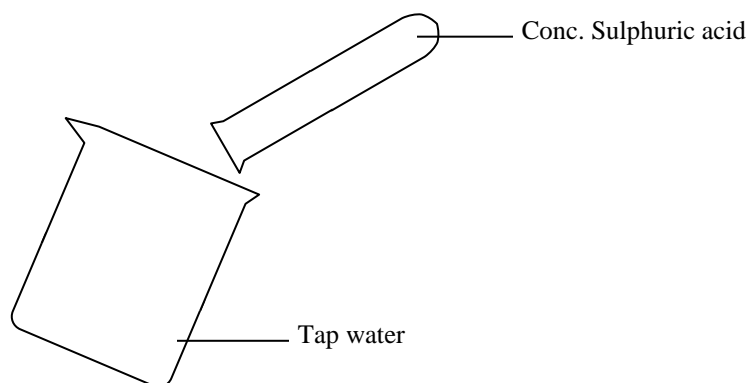
**Caution:**

- Concentrated sulphuric acid should always be added to water and never vise versa.

**Reason:**

- The mixture is then carefully but vigorously stirred using a thermometer and the highest temperature of the solution recorded.
- The experiment is repeated with other compounds:
  ➢ Ammonium nitrate solid
  ➢ Potassium nitrate solid
  ➢ Sodium hydroxide pellets.
  ➢ Sodium nitrate solid

Results and observations.

| | Concentrated sulphuric acid | Ammonium nitrate solid | Potassium nitrate solid | Sodium hydroxide pellets |
|---|---|---|---|---|
| Temperature of water(˚c) | | | | |
| Highest temperature of solution (˚c) | | | | |
| Change in temperature(˚c) | | | | |

Calculate the enthalpy change ($\Delta H_{soln}$) in each experiment done.

**Additional information;**
- Density of concentrated Sulphuric acid $= 1.84 gcm^{-3}$
- Density of water $= 1 gcm^{-3}$
- No change in volume when any of the solids dissolved in water
- The specific heat capacities of the solutions $= 4.2 kjkg^{-1}k^{-1}$

## (a). Sulphuric acid:
- Total volume of solution $= (50 + 2) = 52 cm^3$
- Temperature change = A rise of 1°C
- Enthalpy change; $\Delta H_{soln}$; $= MC\Delta T$

$$M = 52 cm^3 \times 1 gcm^{-3} = 52g = 0.52kg.$$
$$C = 4.2 kjkg^{-1}k^{-1}$$
$$\Delta T = 5K.$$

Thus enthalpy change $= 0.52 \times 4.2 \times 1$
$$= -2.184kj$$

Calculating molar enthalpy of solution of concentrated sulphuric acid:
Mass of acid used = density x volume
$$= 1.84 \times 2 = 3.68g;$$
Formula mass of Sulphuric acid $= 98g$
3.6g of acid liberated 2.184kj
Thus 98g of acid liberated; $\underline{2.198 \times 98} = 56Kj;$
$\phantom{Thus 98g of acid liberated; }3.68$

Because heat was liberated ($+ve$ $\Delta T$), the $\Delta H_{soln} = -56 Kjmol^{-1}$

## (b). Sodium nitrate:
**Data:**
- Volume of water used $= 100 cm^3$
- Mass of sodium nitrate $= 2.5g$
- Initial temperature of water $= 21.0°C$
- Final temperature of water $= 19.5°C$
- Temperature change; = A fall of 1.5°C i.e. (19.5 - 21.0) °C;
- Mass of $100 cm^3$ of water $= 100g = 0.1kg;$

Enthalpy change i.e. heat absorbed $= MC\Delta T$
$$= 0.1 \times 4.2 \times 1.5$$
$$= 0.63Kj.$$
Molar heat of dissolution;
- Molar mass of NaNO3 $= 23 + 14 + 48 = 85g;$
- 2.5g of $NaNO_3$ absorbed 0.63Kj;
- 85g of $NaNO_3$ will absorb =?
$$= \underline{0.63 \times 85}$$
$$2.5$$
$$= +21.42 Kjmol^{-1}$$
Since heat is absorbed (-ve heat change), the reaction is endothermic thus $\Delta H_{soln} = +21.42 Kjmol^{-1}$

**Note:** energy level diagram for the dissolution of sodium nitrate:
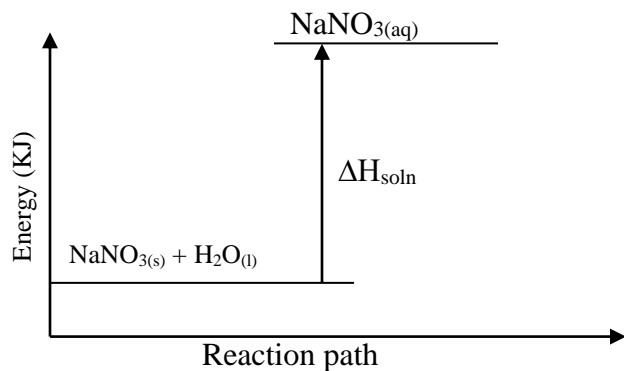


### 3. Potassium hydroxide;
 - Calculate the molar enthalpy of dissolution of potassium hydroxide (based on values obtained).

### 4. Heat of displacement.
- This refers to the enthalpy change that occurs when one mole of a substance is displaced from a solution of its ions.

### Experiment: To determine the molar enthalpy change in the reaction between $Cu^{2+}$ ions and zinc or iron.

### (i) Procedure:
- A plastic cup or glass beaker is wrapped with a newspaper leaf.
- 25 $cm^3$ of 0.2M copper (II) sulphate solution is transferred into the beaker.
- The steady temperature of the solution is noted.
- 0.5g of zinc powder are carefully transferred into the plastic cup and stirred with a thermometer.
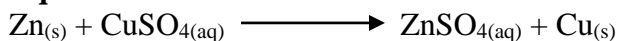- The highest temperature attained by the solution is recorded.

### (ii). Procedure:
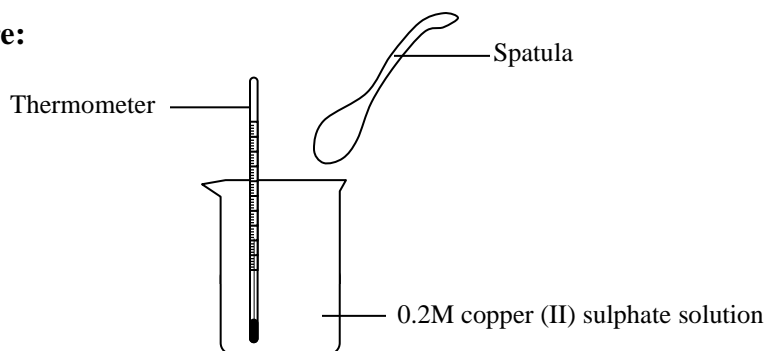


### Observations:
- The blue colors of copper (II) sulphate fades.
- Brown deposits of copper metal are formed in the plastic cup.

### Explanation:

- Zinc is higher in the electrochemical series than copper;
- Zinc therefore displaces copper ions from its solution.

**Equations:**
$Zn_{(s)} + CuSO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$

**Ionically:**
$Zn_{(s)} + Cu^{2+}{}_{(aq)} \longrightarrow Zn^{2+} + Cu_{(s)}$

- During the reaction the blue $Cu^{2+}$ in the solution are replaced by the colorless $Zn^{2+}$.
- Consequently the blue colour of the solution fades, as brown deposits of copper metal are formed in the plastic cup.
- Excess solid (zinc powder) was used to ensure complete displacement of $Cu^{2+}$.

**Results:**
- Initial temperature of copper sulphate solution, $T_1 = 23°C$
- Highest temperature of the mixture $T_2 = 33°C$
- Temperature change, $\Delta T; = T_2 - T_1 = 10°C$
- Volume of copper sulphate solution used = 25.0 $cm^3$.
- Mass of zinc powder taken = 0.6g
- Density of the solution = $1gcm^{-3}$.
- Specific heat capacity of the solution = $4.2Kjkg^{-1}k^{-1}$.

**Assumptions:**
- The volume of the solution remains unchanged after the reaction.
(Cu = 63.5, S = 32, O =16, Zn = 65, Fe =56)

**Question:**
Using the above data, calculate, calculate the;
(i). Heat change for the above reaction.
(ii). The molar heat of displacement of copper (II) ions.

**Solutions:**
(i) Heat change = $MC\Delta T$

Mass = density x volume
$1gcm^{-3}$ x 25$cm^3$ =25g.

$\Delta H = \dfrac{25kg}{1000}$ x 4.2 $kjkg^{-1}k^{-1}$ x 10k

= 1.050Kj;

(ii). Molar heat of displacement of $Cu^{2+}$ displacement.
1000 $cm^3$ = 0.2 moles.

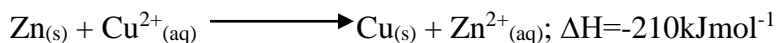25 $cm^3 = \dfrac{0.2 \times 25}{1000} = 0.005$moles

Thus,

0.005moles =1.050Kj

1mole $= \dfrac{1 \times 1.050}{0.005} = \dfrac{1050}{5} = 210Kj$;

- Since the final temperature of the mixture is higher than initial temperature; it means the $H_{products}$ is **lower** than $H_{reactants}$.
- The reaction is thus **exothermic.**

- Thus molar heat of displacement of $Cu^{2+}$ = -210Kjmol⁻

**Thermochemical equation:**

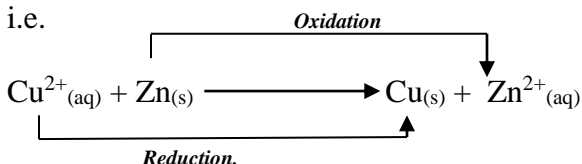$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}; \Delta H = -210kJmol^{-1}$$

**Note:**
- The experimental value for the heat liberated in this reaction is lower than the theoretical value of $216Kjmol^{-1}$.

**Reasons:**
- The heat lost to the surroundings and the heat absorbed by the apparatus is not accounted for in the calculations.
- This reaction is typically a Redox reaction.

i.e.



$$Cu^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

*Oxidation*

*Reduction.*

## 5. Heat of precipitation:
- Is the heat change which occurs when one mole of a substance is **precipitated** from the solution.

**Experiment: To determine the heat of precipitation of silver chloride.**

**Procedure:**
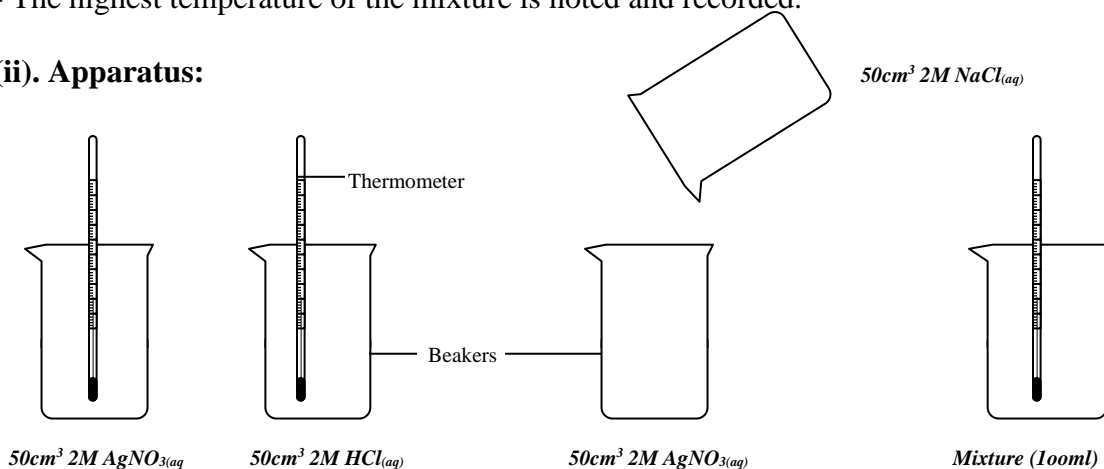- 50 cm³ each of 2M $AgNO_3$ and 2M NaCl are left in separate beakers and their constant temperatures noted and recorded.
- The NaCl solution is added to the silver nitrate solutions.
- The beaker is covered with a card board and shaken gently to allow mixing of the solution.
- The highest temperature of the mixture is noted and recorded.

**(ii). Apparatus:**



*50cm³ 2M NaCl₍ₐq₎*

Thermometer

Beakers

*50cm³ 2M AgNO₃₍ₐq*      *50cm³ 2M HCl₍ₐq₎*      *50cm³ 2M AgNO₃₍ₐq₎*      *Mixture (1ooml)*

**(ii) Data (results)**
- Temperature of $AgNO_3$ solution = 21.0°C
- Temperature of NaCl solution =19.0°C
- Mean temperature of the solutions = $\underline{\{19+21\}}$ = 20.0°C
                                                    2
- Final temperature after mixing = 34.0°C;
- Temperature change = a rise of 14°C;
- Volume of solution mixed =100 cm³
- Mass of solution mixed =100g (assuming density=1gcm⁻³)

**Questions:**
- From the above data, calculate;-

(i) Energy change/ heat change for the reaction
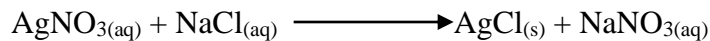(ii) The molar $\Delta H_{precipitation}$ for AgCl.

**Solution:**
(i) Heat change, $= MC\Delta T$

$$= \frac{100}{1000} \times 4.2 \times 14$$

$$= -5.88kj$$

(ii) Equation,

$$AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$$

Mole ratio      1  :     1  :     1  :   1

Moles of $AgNO_3$;

$$1000 \ cm^3 = 2 \ moles$$

$$50 \ cm^3 = 2 \times 50 = 0.1 mole;$$

Since reaction ratio $AgNO_3$: AgCl = 1:1, then moles of $AgCl_{(s)}$ precipitated = 0.1mole
If 0.1mole = 5.88kj
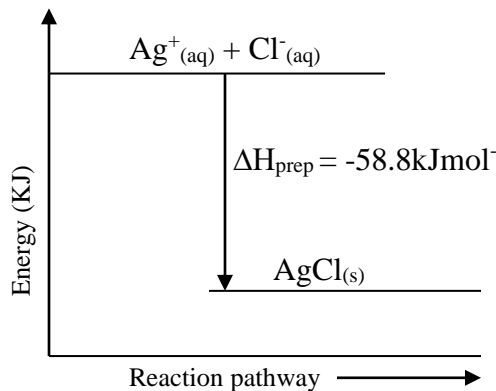
$$1 \ mole = \frac{(1 \times 5.88)}{0.1} = 58.8kJmol^-$$

Reaction being exothermic, $\Delta H_{precip}$ = -58.8kJmol$^-$

**Thermochemical equation:**

$$Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)}; \Delta H= -58.8kjmol-$$

Suitable energy level diagram,



**6. Enthalpy of formation.**
- Is the heat change when one mole of a substance is formed from its constituent elements under standard conditions.
Note: this will be dealt with under thermochemical cycles and Hess's law.

**Standard conditions for measuring enthalpy changes.**
- Experimental evidence shows that enthalpy changes are affected by physical stats of the reactants, temperature, concentration and pressure.

- Consequently, for comparison purposes certain conditions have been chosen as standard for measurement and determination of enthalpy changes.
- These conditions are:
  - ➢ A temperature of 25°C (298K)
  - ➢ Pressure of 1 atmosphere (101.325K)

**Standard enthalpy changes:**
- Are values of enthalpy changes that are measured under standard conditions.
- They are denoted by he symbol $\Delta H^0$
- A subscript is also added to the symbol to indicate the type of enthalpy change involved.

**Common standard enthalpy changes.**
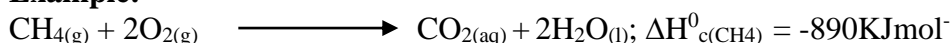
(i). $\Delta H^0_f$; refers to the standard molar enthalpy change of formation.

**Example:**
$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta H^0_{f\ (H2O)} = -286 KJmol^-$

(ii). $\Delta H^0_c$; refers to the standard molar enthalpy change of combustion;

**Example:**
$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(aq)} + 2H_2O_{(l)}$; $\Delta H^0_{c(CH4)} = -890 KJmol^-$

(iii). $\Delta H^0_{neut}$; refers to the standard molar enthalpy change of neutralization.

**Example:**
$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)\ +} H_2O_{(l)}$; $\Delta H^0_{neut} = -58 KJmol^-$

(iv). $\Delta H^0_{soln}$; refers to the standard molar enthalpy change of solution (dissolution).

**Example:**
$NaNO_{3(s)} + H_2O_{(l)} \longrightarrow NaNO_{3(aq)}$; $\Delta H^0_{soln\ (NaNO3)} = +21 KJmol^-$

(v). $\Delta H^0_{hyd}$; refers to the standard molar enthalpy change of hydration.

**Example:**
$Na^+_{(s)} + Cl^-_{(s)} + H_2O_{(l)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$; $\Delta H^0_{hyd\ (NaCl)} = -774 KJmol^-$
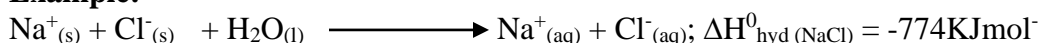
(vi). $\Delta H^0_{latt}$; refers to the molar enthalpy change of lattice formation.

**Example:**
$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(aq)}$; $\Delta H^0_{latt\ (NaCl)} = -774 KJmol^-$

(vi). $\Delta H^0_{at}$; refers to the standard molar enthalpy change of atomization.

**Example:**
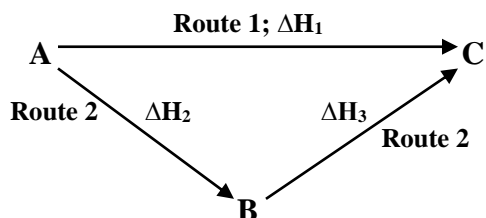$Na_{(s)} \longrightarrow Na_{(g)}$; $\Delta H^0_{at\ (Na)} = 108.4\ KJmol^-$
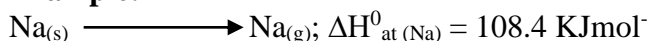
**Energy level diagrams, thermochemical cycles and Hess's law.**
**Hess's law (the law of constant heat summation);**
States that:
  - If a reaction can occur by more than one route the overall change in enthalpy is the same, whichever route is followed.
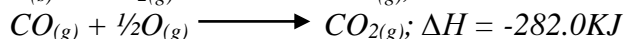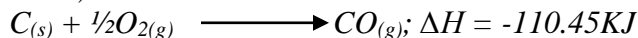
**Illustration:**

$$A \xrightarrow{\text{Route 1; } \Delta H_1} C$$
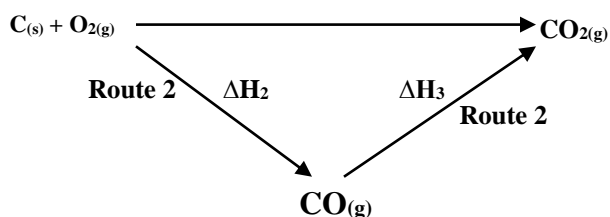
Route 2 $\Delta H_2$ $\Delta H_3$ Route 2 → B

Therefore, $\Delta H_1 = \Delta H_2 + \Delta H_3$

## Worked examples:

*1. Use the information below to determine the enthalpy of combustion of carbon (formation of carbon (IV) oxide).*

$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}; \Delta H = -110.45KJ$

$CO_{(g)} + \frac{1}{2}O_{(g)} \longrightarrow CO_{2(g)}; \Delta H = -282.0KJ$

Solution:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$

Route 2 $\Delta H_2$ $\Delta H_3$ Route 2 → $CO_{(g)}$

Therefore; $\Delta H_1 = \Delta H_2 + \Delta H_3$

$= -110\text{-}45 + (-282.0) = -392.45kJ$

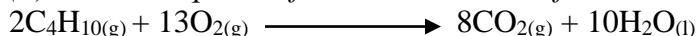$\Delta H_1 = \Delta H_{combustion}$

$= -392.45KJ;$

## Note: - Enthalpy of formation, $\Delta H_f$;

- Is the heat absorbed or evolved when one mole of a substance is formed from its elements under standard conditions.
- This can not be determined experimentally because reactions cannot take place under standard conditions.
- In such cases the enthalpy change is determined theoretically using other measurable enthalpies.
- In the case of enthalpy of formation, the enthalpies of combustion of the compound and that of its constituent elements are linked using an energy level or energy cycle diagram.
- The enthalpy of formation is then calculated using the law of constant heat summation (Hess's law).

## Worked examples:

*1. One mole of butane($C_4H_{10}$) burns completely in oxygen and liberates 2877kj.*
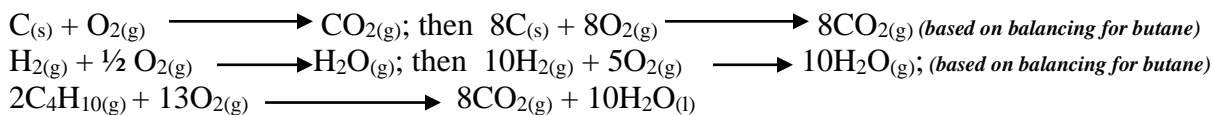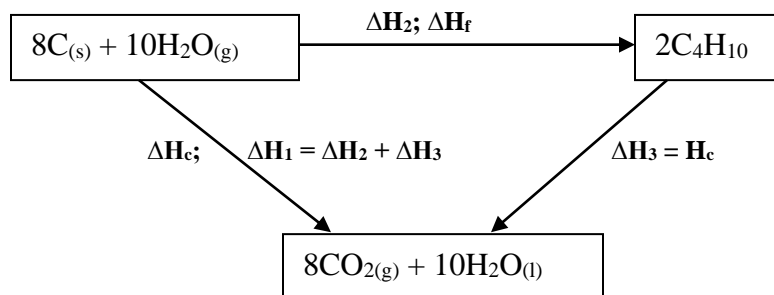
*(a) Write an equation for the combustion of butane.*

$2C_4H_{10(g)} + 13O_{2(g)} \longrightarrow 8CO_{2(g)} + 10H_2O_{(l)}$

*(b) Draw an energy cycle, hence an energy level diagram for the reactions concerned.*

**Solution:**

Equations for combustion:

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$; then $8C_{(s)} + 8O_{2(g)} \longrightarrow 8CO_{2(g)}$ *(based on balancing for butane)*

$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(g)}$; then $10H_{2(g)} + 5O_{2(g)} \longrightarrow 10H_2O_{(g)}$; *(based on balancing for butane)*
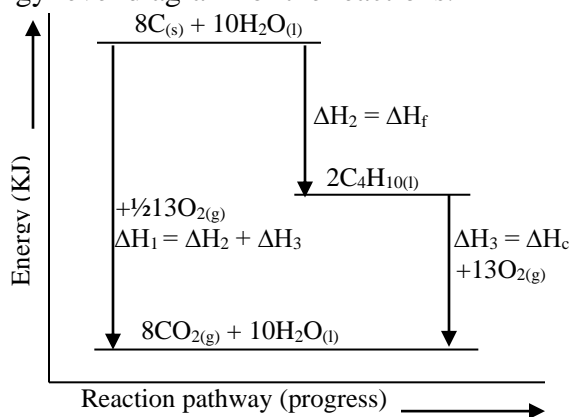
$2C_4H_{10(g)} + 13O_{2(g)} \longrightarrow 8CO_{2(g)} + 10H_2O_{(l)}$

Then, energy cycle for the changes,



Thus energy level diagram for the reactions.



*(c) If the following heats of combustion are given*

$\Delta H^o_c$ *(graphite) = -393kjmol*

$\Delta H^o_c$ *($H_{2(g)}$) = -286KJmol*

$\Delta H^o_c$ *($C_4H_{10}$) = -2877kjmol*

*Calculate the heat of formation of butane, $C_4H_{10}$ from its elements in their normal states at S.T.P.*

**Solution:**

$\Delta H_1 = \Delta H_2 + \Delta H_3$ where:

$\Delta H_2 = \Delta H_{formation}$ of $C_4H_{10}$;

$\Delta H_1 = \Delta H^o_{c(graphite)} + \Delta H^o_{c(hydrogen)}$;

While $\Delta H_3 = \Delta H^o_{c(butane)}$

From the equation,

$\Delta H_1 = \Delta H_2 + \Delta H_3$,

$\Delta H_2 = \Delta H_1 - \Delta H_3$

$= \{8(-393) + 10(-286)] - [2(-2877)]$

Dividing all through by 2;

= {4(-393) +5(-286)]-2877]; i.e. *in order to work with 1 mole of butane;*

= (-1572) + (-1430) - (-2877)
= -3002 + 2877
= -125KJmol⁻

*2 (a). Define standard heat of combustion of a substance.*

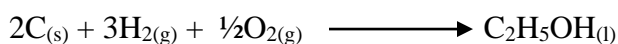**Solution:**
- The heat change when one mole of a substance is completely burnt in oxygen under standard conditions;

*(b). Ethanol, CH₃CH₂OH; cannot be prepared directly from its elements and so its standard heat of formation must be obtained indirectly.*
*(i) Write an equation for the formation of ethanol from its elements in their normal physical states at standard conditions of temperature and pressure.*
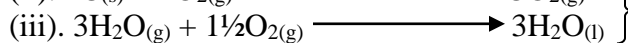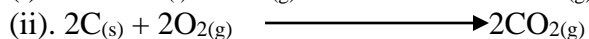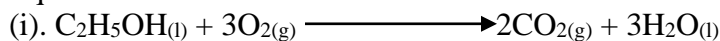
**Solution:**

$$2C_{(s)} + 3H_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow C_2H_5OH_{(l)}$$

(ii). Draw an energy level diagram linking the heat of formation with its heat of combustion and the heats of combustion of its constituent elements.
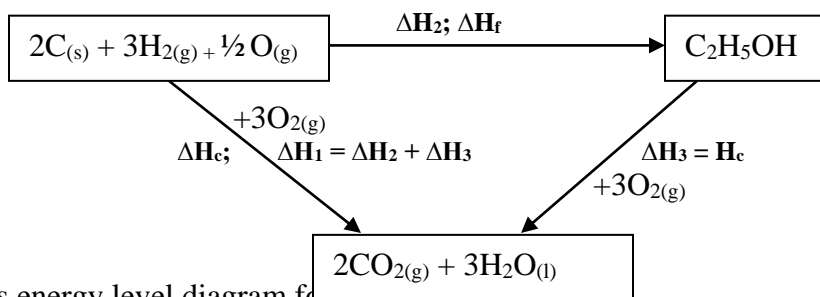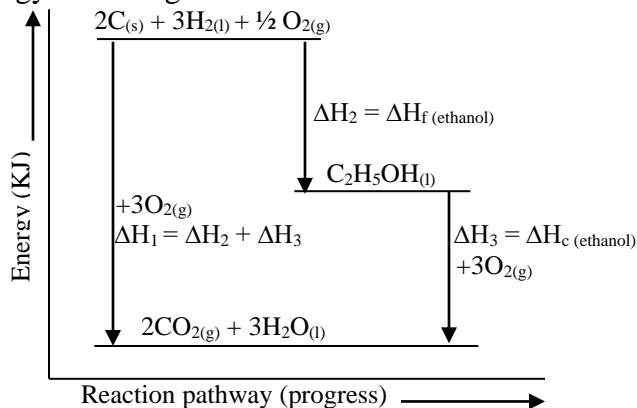
**Solution:**
Equations
(i). $C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$
(ii). $2C_{(s)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)}$ ⎫
(iii). $3H_2O_{(g)} + 1\tfrac{1}{2}O_{2(g)} \longrightarrow 3H_2O_{(l)}$ ⎬ *Balancing based on equation for combustion of ethanol*

Then, energy cycle for the changes,



Thus energy level diagram for the reactions:



*(iii). If the following heats of combustion are given:*
$\Delta H_{c(graphite)} = -393kJmol⁻$

$\Delta H_{c(hydrogen)} = -286kJmol^-$
$\Delta H_{c(ethanol)} = -1368kJmol^-$

*Calculate the heat of formation of ethanol, $\Delta H^0_{f\,(ethanol)}$*

**Solution:**
$\Delta H_1 = \Delta H_2 + \Delta H_3$
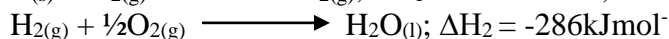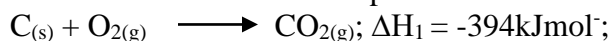$\Delta H_2 = \Delta H_1 - \Delta H_3$
$= [2(-393 + 3(-286)]-[-1368]$
$= [(-786) + (-856)] - [-1368]$
$= -164 + 1368$
$= - 276kJmol^-$

3. Given the standard enthalpies of combustion as
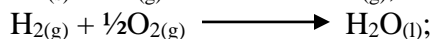$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}; \Delta H_1 = -394kJmol^-$;
$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}; \Delta H_2 = -286kJmol^-$
$C_2H_{2(g)} + 1\frac{1}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(l)}; \Delta H = -1300kJmol^-$.

Find the standard enthalpy of formation of ethyne, $C_2H_{2(g)}$.

**Solution:**
- Considering the $H_{c(ethyne)}$, 2 moles of $CO_2$ and 1 mole of $H_2O_{(l)}$ are produced;
- Rebalancing the equations for $H_{c(carbon)}$ and $H_{c(hydrogen)}$ likewise:
$2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$;
$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$;
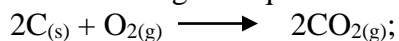
Then, energy cycle for the changes,



Thus energy level diagram for the reactions.

$$+2\frac{1}{2}O_{2(g)}$$
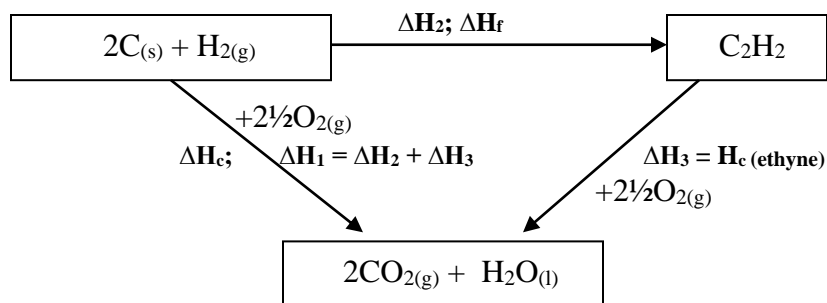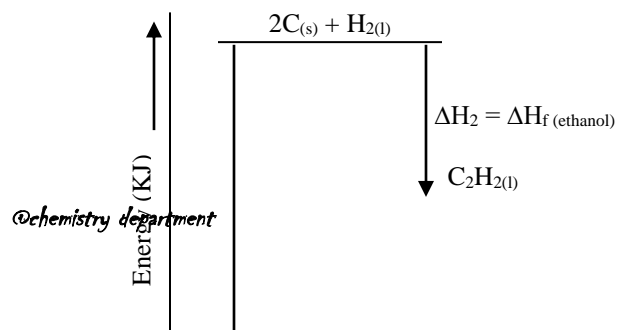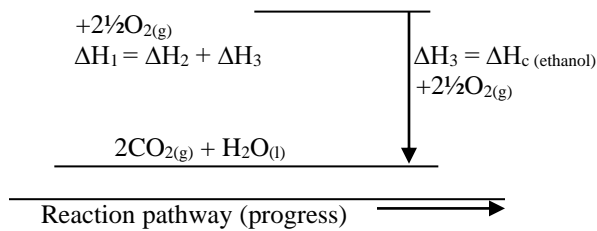$$\Delta H_1 = \Delta H_2 + \Delta H_3 \qquad\qquad \Delta H_3 = \Delta H_{c\,(ethanol)}$$
$$+2\frac{1}{2}O_{2(g)}$$

$$2CO_{2(g)} + H_2O_{(l)}$$

Reaction pathway (progress)

Thus $\Delta H_1 = \Delta H_2 + \Delta H_3$
$\qquad \Delta H_2 = \Delta H_1 - \Delta H_3$
$= [2(-394) + (-286)]-[-1300]$
$= (-788-286) + 1300$
$= -1074 + 1300$
$= +226kJmol^-$

Since $\Delta H_f$ is +ve, ethyne is described as an **endothermic compound.**

**Note:**
- In the determination of $\Delta H_f$ of ethyne, Hess law is used because attempts to make ethyne from carbon and hydrogen $\{2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)} \}$ will result to the formation of a mixture of hydrocarbons.

**Heat of formation and bond energies**
- Chemical reactions involve:
> **Bond breaking**; this requires energy.
> **Bond formation**; releases energy.

**Example:**
- Formation of methane from carbon and hydrogen.
$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$; $\Delta H = -74.9kJmol^-$

Energy level diagonal for the formation of $CH_4$.



Energy (kJ)

$C_{(s)} + 4H_{(g)}$

II $\Delta H_{at};$

$C_{(s)} + 2H_{2(g)}$

I $\Delta H_{at} = +715KJmol^-$        III $\Delta H = -4(C-H)$; *bond energy*
$C_{(s)} + 2H_{2(g)}$

$$\Delta H_{IV} = I + II + III$$
$$= -74.9 Kj$$
$$CH_{4(g)}$$

*Final enthalpy*

Reaction pathway (progress) ⟶
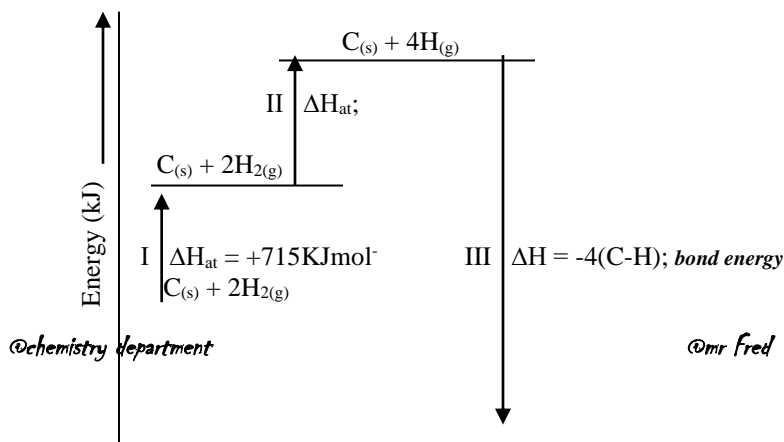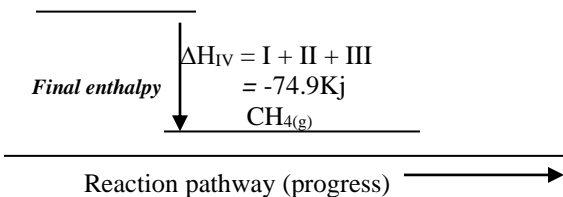
Energy changes involved are:

➤ **$\Delta H_I$; Enthalpy of atomization** – this is the energy absorbed when a substance decomposes to form one mole of gaseous atoms.

➤ **$\Delta H_{II}$; enthalpy of atomization of $H_2$**; i.e. dissociation of hydrogen molecules to free hydrogen atoms.

➤ **$\Delta H_{III}$; enthalpy of formation of four C – H bonds**, during which heat is liberated;

Therefore, enthalpy of reaction $\Delta H_R = \Delta H_{IV}$

$\Delta H_R = \Delta H_1 + \Delta H_{II} + \Delta H_{III}$
$\quad = +715 + 4(218) + -4(C\text{-}H)$
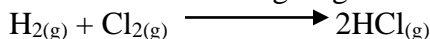$-74.9 = +715 + 872 + -4 \text{ (bond energy)}$
$4 \text{ (C-H)} = 1587 + 74.9$
$= 1661.9$
$C\text{–}H = \dfrac{1661.9}{4} = 415.4 kjmol\text{-}$

- This is the amount of energy released when one C-H bond is formed;

**Worked examples.**

1. Use the bond energies given below to calculate the heat of reaction for;-
$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$$

| Bond | Bond energy |
|------|-------------|
| H-H | 435kjmol⁻ |
| Cl-Cl | 243kjmol⁻ |
| H-Cl | 431kjmol⁻ |

**Solution:**

**Bond breaking,**
$H_{2(g)} = H\text{-}H \dashrightarrow 2H_{(g)}; \Delta H = +435Kj;$    *Total energy absorbed = +678 KJ*
$Cl_{2(g)} = Cl\text{-}Cl \dashrightarrow 2Cl_{(g)}; \Delta H = +243Kj$

**Bond formation,**
$2H_{(g)} + 2Cl_{(g)} \longrightarrow 2(H\text{-}Cl)_{(g)}; \Delta H = 2(-431) = -862Kj;$   *Total energy released = -862 KJ*
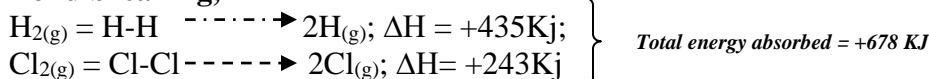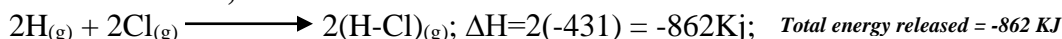
**Heat of reaction:**
Energy absorbed in bond breakage + energy released in bond formation.
$$= [+435 + 243] + [-862]$$

$$= [+678-862] \text{ kJ}$$
$$= -184\text{kj}$$

Thus, H - H + Cl – Cl $\longrightarrow$ 2[H – Cl]; $\Delta H = -184\text{Kj}$

Note: energy level diagram.



2. *Study the information given in the table below and answer the questions that follow;-*

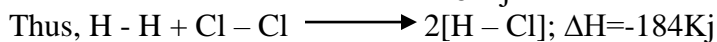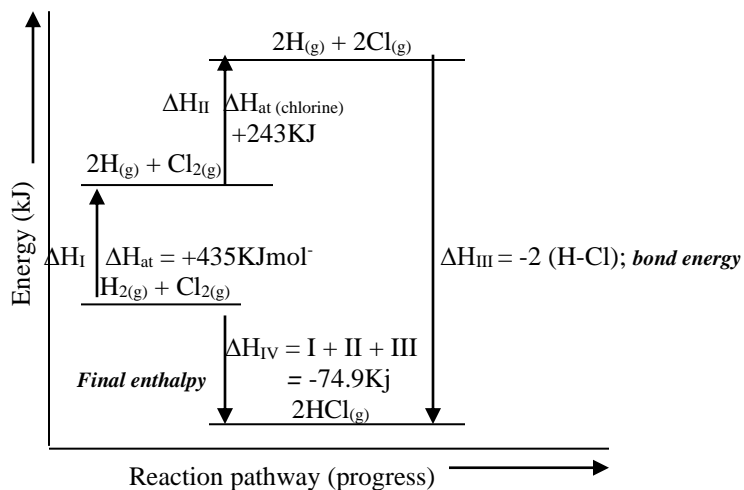| Bond | Bond energy(kJmol⁻) |
|------|---------------------|
| C – H | 414 |
| Cl – Cl | 244 |
| C – Cl | 326 |
| H – Cl | 431 |

*(a). Calculate the enthalpy change for the reaction*
$$CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$$

**Solution:**

Bond breaking
(i). 4(C-H) $\longrightarrow$ 4CH$_{(g)}$; $\Delta H = 4(+414) = +1656\text{kj}$;
(ii). Cl – Cl $\longrightarrow$ 2Cl$_{(g)}$; $\Delta H1 = +244\text{kj}$

**Bond formation**
(i). 3(CH) $\longrightarrow$ 3(C-H); $\Delta H = 3(-414) = -1242\text{kj}$
(ii). CCl $\longrightarrow$ (C-Cl); $\Delta H = -326\text{kj}$
(iii). HCl $\longrightarrow$ (H-Cl); $\Delta H = -431\text{kj}$
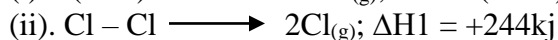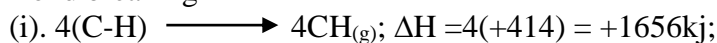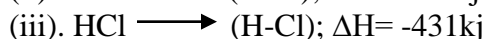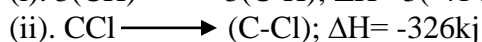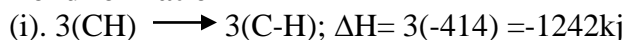
Heat change $= \Delta H_{\text{bond breakage}} + \Delta H_{\text{bond formation}}$
$$= [(+1656) + (+244)] + [(-1242) + (-326) + (-431)]$$
$$= -1900 + (-1999)$$

$\Delta H = -99kJ$

*(b). Draw an energy level diagram for the reaction*



*3. Study the information given in the table below and answer the questions that follow.*

| Bond | Bond energy |
|------|-------------|
| C – C | 346 |
| C = C | 610 |
| C - Br | 280 |
| Br – Br | 193 |
| C – H | 413 |

*(i) Calculate the enthalpy change for the reaction.*

$$CH_2=CH_2 + Br_2 \longrightarrow CH_2\text{-}CH_2$$
$$\qquad\qquad\qquad\qquad\qquad | \quad |$$
$$\qquad\qquad\qquad\qquad\quad Br \quad Br$$

**Solution:**

**Bond breaking,**
$4(C\text{-}H) \longrightarrow 4CH_{(g)}; \Delta H = 4 (+413) = +1652kj$
$Br_2 \longrightarrow 2Br \qquad \Delta H = +193kj$
$C = C \longrightarrow C = C; \Delta H = + 610kj;$

**Bond formation:**
$4(C\text{-}H), \longrightarrow 4CH; = 4(\text{-}413) = \text{-}1662kj$
$2(C\text{-}Br), \longrightarrow 2CBr; = 2(\text{-}280) = \text{-}560kj$
$(C\text{-}C ) \longrightarrow 2C; = \text{-}346kj$

**Heat change:**

ΔH bond breakage + ΔH bond formation
= [+1652 + 193 + 610] + [-1652 + -560 + -346kJ]
= [+2455] + (-2558)
ΔH change = -103kJ;

## Molar heat of fusion, $\Delta H_f$;
- Is the amount of heat required to change one mole of a solid into a liquid at its melting point.
- It is a measure of intermolecular forces between solid particles since it is the heat energy used to separate the solid particles.

## Molar heat of vaporization, $\Delta H_{vap}$;
- Is the amount of heat required to change one mole of liquid into vapor at its boiling point.
- It is a measure of the intermolecular forces between the liquid particles since it is the heat energy used to separate liquid particles.

## Relationship between heats of fusion and vaporization to structure.
They are;-
(a). Higher for substances with giant structures e.g.
  ➢ Ionic solids
  ➢ Metals
  ➢ Giant covalent structures, e.g. diamond, graphite and silicon (IV) oxide
(b). Lower in simple molecular structures whose particles are held together by weak intermolecular forces.
**Examples:**
  ➢ Iodine crystals
  ➢ Sulphur
  ➢ Hydrogen.

**Examples:**

|  | NaCl | $C_{(graphite)}$ | Cu | $H_2O$ | $I_{(s)}$ | S |
|---|---|---|---|---|---|---|
| Structure type | Giant ionic | Giant atomic | Giant Metallic | Molecular | Molecular | Molecular |
| $\Delta H_{fusion}$ kjmol⁻ | 28 | - | 13 | 6 | 8 | - |
| $\Delta H_{vap}$ kjmol⁻ | 171 | 717 | 305 | 41 | 21 | 10 |

**UNIT 4: RATES OF REACTION AND REVERSIBLE REACTIONS**
**UNIT OUTLINE:**

1. Reactions rates:

➢ **Meaning.**

➢ Measurements of reaction rates

➢ Rate of product yield pre unit time

➢ Rate of disappearance of reactants

➢ Apparatus for measuring reaction rates

➢ Collision theory and activation energy

➢ Factors affecting reaction rates

▪ Temperature

▪ **Particles size (surface area)**

▪ Catalysts

▪ Pressure

**2. Reversible reactants**

➢ Meaning

➢ Chemical equilibrium

➢ Factors affecting position of equilibrium

▪ Temperature

▪ Pressure

▪ Concentration (of reactants or products)

▪ Catalysts

➢ Le'Chartaliers principle.

**Reaction rate:**

- The rate of a chemical reaction is taken as the rate at which products are formed or the rate at which reactants disappear.

**Measurements of reaction rates**

Reaction rates are measured in terms of
➢ How much product appears in a given time.
➢ How much reactant disappears in a given time
- Rates curves are then plotted
- These are plots of concentration or properties, which are functions of concentration against time

**Graph: concentration of products against time.**
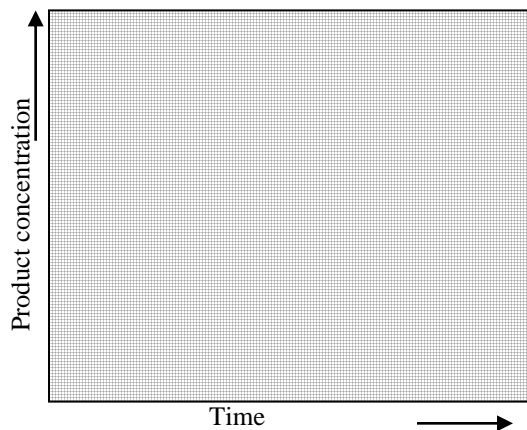


**Graph: concentration of reactants against time.**
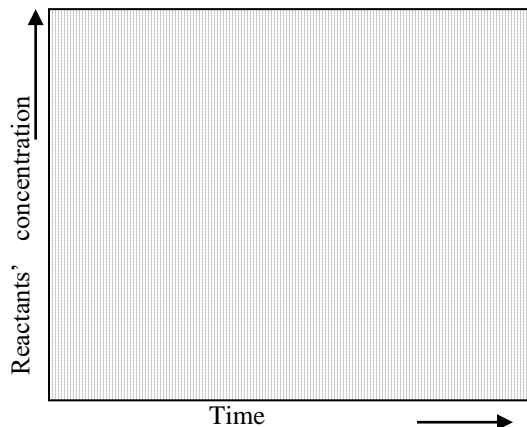


**Apparatus used to determine rates of reaction**
**Examples:**
- Reaction between dilute HCl and marble chips.

- This can be by:

**(a). Measuring the decrease in mass with time**
**Apparatus:**

**Graph:**
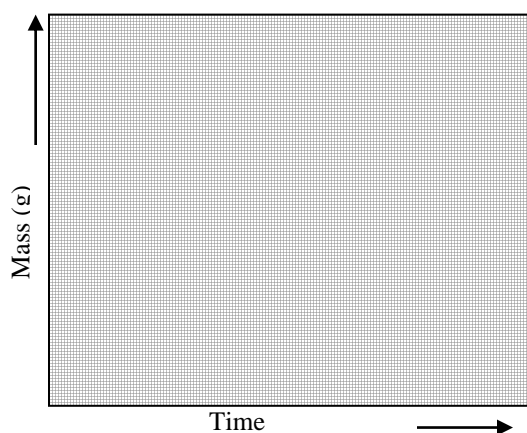


**(b). Measuring the volume of the gas produced with time and then plotting a graph.**
**Apparatus:**
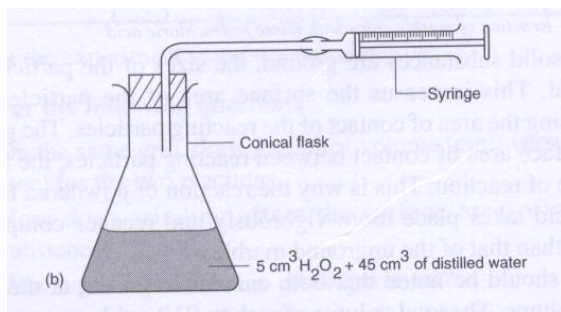


**Graph:**
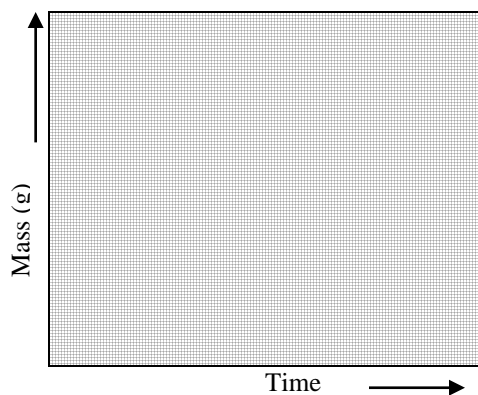


Similar experiments maybe done using zinc granules and zinc powder with an acid

**Worked example:**
Marble chips and dilute hydrochloric acid were mixed. The mass of the reaction mixture was measured and recorded with time. The results are shown in the table below.

| Time (sec) | 0 | 30 | 60 | 90 | 12 | 150 | 180 | 21 | 240 | 270 | 300 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mass of mixture (g) | 42.0 | 41.5 | 41.0 | 40.7 | 40.4 | 4.02 | 40.1 | 40.0 | 40.0 | 40.0 | 40.0 |
| Loss in mass (g) | | | | | | | | | | | |

(a). Complete the table.                                                                          (5 marks)

(b). Draw a graph of loss of mass against time.                                   (3 marks)

(c). On the same axes sketch the curves that would be obtained if:
(i). the acid was more concentrated.                                                      (1mark)

(ii). larger marble chips were used.                                                       (1mark)

**Collision theory and activation energy.**
The collision theory of reacting particles postulates that:
➢  Reacting particles must collide before a chemical reaction occurs
➢  Not all collisions are effective/ result in chemical reaction
➢  **Only those particles with sufficient energy result in effective collisions i.e. energy equal to or greater than the activation energy.**
➢  Any factor, which increases the rate of a chemical reaction, does so by increasing the number of effective collisions;

**Activation energy ($E_A$):**
- Is the minimum amount of energy required by reacting particles to cause a successful collision to form products;
- It refers to the energy an energy barrier that must be overcome by the reactants to be converted to products;
- This energy barrier determines the magnitude of the activation energy of the reactants;

**Factors determining the value of activation energy:**
- Strength of the bonds in the particles of the reactants;
- Whether the reaction is exothermic or exothermic;
- Presence of catalysts;

**Graph: activation energy:**

## Factors affecting the rate of reaction

- Factors that increase the rate of a reaction does so by:
➢ Increasing number of effective collisions;
➢ Lowering the activation energy; since a reaction with high activation energy is slow at ordinary conditions;

These factors are:
➢ Concentration of reactants
➢ Temperature
➢ Surface area (size of the particles
➢ Catalyst Light
➢ Pressure

## (a). Concentration of reactants.

- Increase in concentration of one of the reactants increases the rate of the reaction;
**Reason:**
- Higher concentration results in a greater probability of collision hence a higher rate of reaction

## Example: reaction between Mg $_{s)}$ and 2M and 4M hydrochloric acid.

## Graphical representation
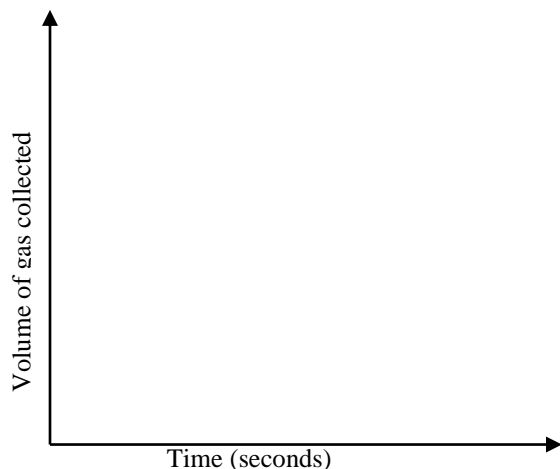


- The maximum volume of a gas collected in both experiments is the same because the number of moles of HCl is the same
- Curve for 4M HCl is steeper indicating a faster rate because the acid is more concentration
- The 4M HCl contains more $H^+$ ions per unit volume than 2M HCl. This reaction takes a shorter time to go to completion
- The start of the flat part of the curve indicates the end of the reaction;

**Diagram:**



Magnesium and hydrochloric acid mixture

**Note:** Rate of reaction can also be verified by measuring the rate of disappearance of reactants per unit time.
- Reactants with 4M HCl will disappear faster;
- Curve for a faster reaction rate is always to the left of the reference curve;

**Worked example:**
In an experiment to determine the effect of concentration on the rate of a reaction, various concentrations of sodium thiosulphate were reacted with equal volume of hydrochloric acid and the time taken for the precipitate to obscure a cross on paper put under the reaction beaker was determined.
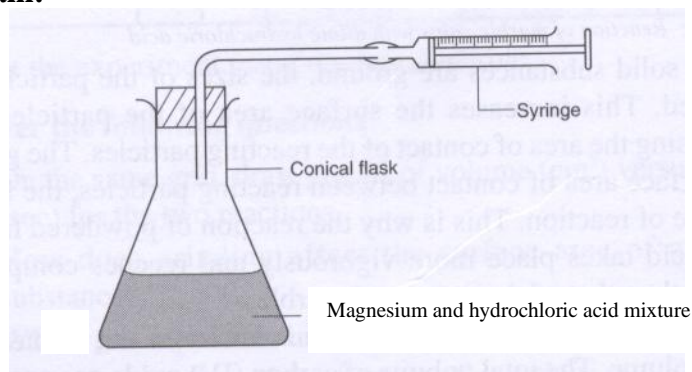The results are shown in the table below.

| Volume of $S_2O_3^{2-}$ (cm$^3$) | Volume of $H_2O$, cm$^3$ | Volume of HCl, cm$^3$ | Time for cross to disappear, (s) |
|---|---|---|---|
| 50 | 0 | 10 | 20 |
| 40 | 10 | 10 | 25 |
| 30 | 20 | 10 | 34 |
| 20 | 30 | 10 | 52 |
| 10 | 40 | 10 | 70 |

(a). Plot a graph of time (vertical axis) against volume of aqueous sodium thiosulphate.        (3marks)

(b). From the graph estimate the time for the cross to disappear when 10 cm$^3$ of hydrochloric acid is added to a mixture of 35cm3 of aqueous thiosulphate and 15cm$^3$ of water.                (2 marks)

(c). What is the effect on the rate of the reaction of adding more water to the aqueous sodium thiosulphate? Explain your answer.                                (2 marks)

(d). On the same graph, plot the curves you would obtain if the experiment were repeated at:
(i). at 45ºC;                                                        (1mark)

(ii). using 10 cm$^3$ of less concentrated hydrochloric acid.                    (1mark)

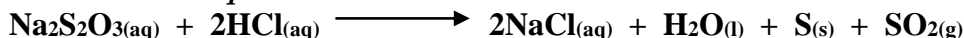**(b). Effect of temperature.**
- An increase in temperature increases the rate of a chemical reaction.
**Reasons:**
- Increase in temperature increases the kinetic energy of the reacting particles;
- The particles therefore move faster leading to more frequent and more effective collisions.
- The rate of reaction therefore increases;

**Example: reaction between sodium thiosulphate and dilute HCl$_{(aq)}$**

*Stoichiometric equation:*

$Na_2S_2O_{3(aq)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + S_{(s)} + SO_{2(g)}$

*Ionic equation:*

$S_2O_3^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \longrightarrow S_{(s)} + SO_{2(g)} + H_2O_{(l)};$
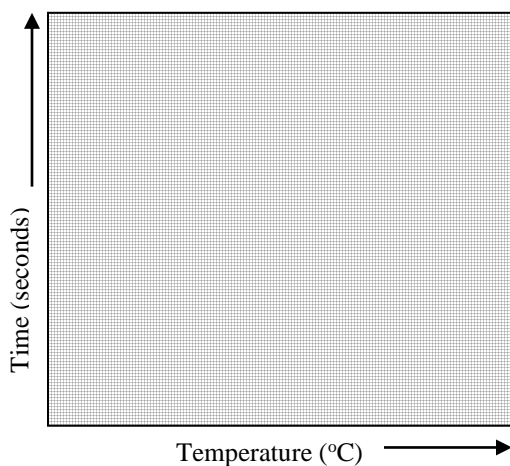
- The time taken to precipitate the same amount of sulphur by the same volume of acid at different temperatures is measured.
- Concentration of thiosulphate solution and the acid are kept constant.

**Graph: relationship between time and temperature in a reaction.**



- The rate is proportionate to 1/ t;
  ➢ Hence;
- The higher the temperature the shorter the time for completion of the reaction and the higher the rate of the reaction;
  ➢ Alternatively:
You can plot a graph of 1/ t against temperature;

**Graphically:**



Temperature (ºC)
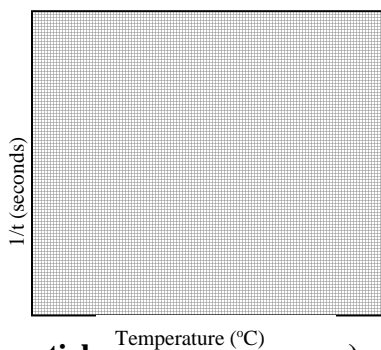
**(c). Effect of particle size (surface area).**
- A decrease in particle size (surface area) increases the rate of a chemical reaction; and an increase in particle size decreases the rate of a chemical reaction.
**Reason:**
- A smaller particle size means a larger total surface area and this offers a large surface on which the reacting particles can collide;
- This means more collisions, hence more chances of effective collisions leading to a higher rate of reaction;

**Example: Reaction between dilute HCl and marble chips**
The larger $CaCO_3$ granules undergo a slower rate of reaction than the finely powdered $CaCO_3$

**Equation:**

$$CaCO_{3(S)} + 2H^+_{(aq)} \longrightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

**Graph 1: volume of gas produced against time (for granules and powder)**

Volume of gas produced (cm$^3$) ↑

Time (seconds) →

## Graph 2: loss in mass of calcium carbonate against time

Total loss in mass (g) ↑

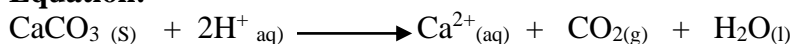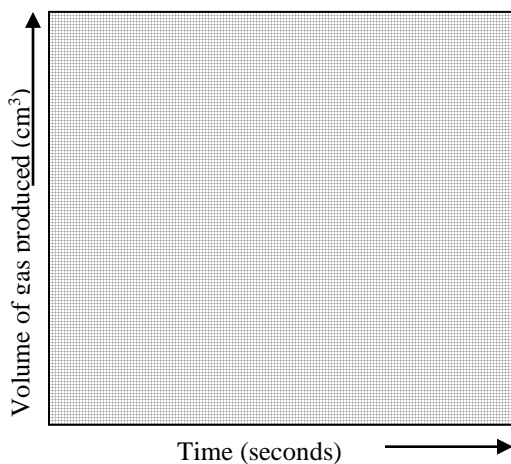Time (seconds) →
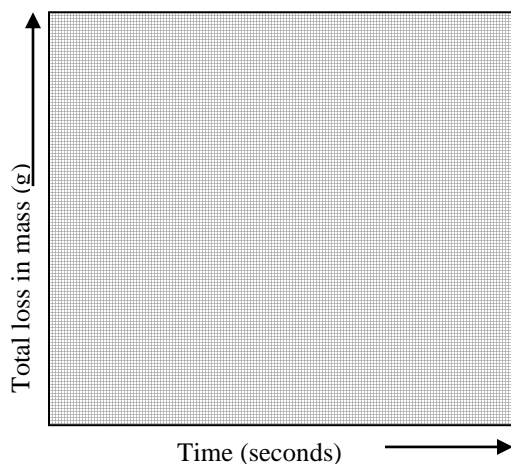
## Worked example:

1. exactly 3.0g of powdered carbonate of metal M of formula $MCO_3$ were mixed with excess dilute hydrochloric acid. The mass of the reaction vessel and its contents were recorded at various times. From these readings, the total loss in mass of the reaction vessel and its contents was calculated and recorded as shown in the table below. The experiment was carried out at room temperature.

| Time (secs) | 0 | 30 | 60 | 90 | 120 | 150 | 180 | 210 |
|---|---|---|---|---|---|---|---|---|
| Total loss in mass (g) | 0 | 0.08 | 0.37 | 0.90 | 1.19 | 1.28 | 1.32 | 1.32 |
| | | | | | | | | |

(a) (i). Plot a graph of total loss in mass against time.                                    (1mark)

(ii). Determine the total loss in mass after 100seconds.                          (2 marks)

(b) (i). Write an equation for the reaction that occurs. (1mark)

(ii). calculate the number of moles of:
  ➢ Carbon (IV) oxide gas produced. (2 marks)

  ➢ $MCO_3$ used. (2 marks)

(iii). Calculate the relative atomic mass of metal M. (3 marks)

(c). On the same axis sketch a curve that you are likely to obtain if the experiment was repeated:
(i)9. at 50°C. Explain. (2 marks)

(ii). Using $MCO_3$ granules instead of the powder. Explain. (2 marks)

## (d). Effect of catalysts
- Catalysts are substances which alter the rate of a chemical reaction without being consumed, e.g. finely divided iron in the harber process;
- They alter the rate of a chemical reaction but remain unchanged at the end of the reaction;
- They can therefore be reused at the end of the reaction;

## Modes of action of catalysts:
➢ Provision of a surface over which particles can react.
**Note:** Due to this solid catalysts are more effective when used in powder form;
➢ Formation of short-lived intermediate compounds with products which then break up to give the products and the catalyst;
➢ By adsorption;

**Note:** - Generally, a catalyst increases the rate of a reaction by providing a different pathway of lower activation energy.
- This means more collisions can overcome this energy barrier and result in a reaction.
- It lowers the activation energy of the reaction;
- Catalysts are also reaction-specific;
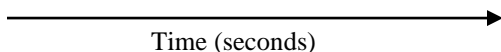
## Some common catalysts:

| Catalyst | Reaction catalyzed. |
|---|---|
| Manganese (IV) oxide | Dissociation of hydrogen peroxide to give oxygen gas and water; |
| Vanadium (V) oxide or platinum | Contact process for the conversion of sulphur (IV) oxide to sulphur (VI) oxide; |
| Platinum | Manufacture of nitric acid in the Oswald's process; |
| Finely divided iron or vanadium | Haber process in the manufacture of ammonia; |
| Nickel | Hydrogenation of oils to make fats; Hydrogenation of unsaturated hydrocarbons |
| Copper (II) oxide | Oxidation of ethanol to produce ethanal; |
| Titanium (IV) chloride | Ziegler method of polymerizing alkenes |

## Graph: reaction rates with and without a catalyst.

Time (seconds) ⟶

**Worked example:**
Hydrogen peroxide decomposes slowly to water and oxygen under normal conditions.
When a little manganese (IV) oxide is added to the solution the rate of decomposition is enhanced. The results of an experiment on the decomposition of hydrogen peroxide in presence of manganese (IV) oxide are shown below. Study the results and answer the questions that follow.

| Volume of oxygen ($cm^3$) | 0 | 19 | 27 | 33 | 36 | 38 | 39 | 40 | 40 |
|---|---|---|---|---|---|---|---|---|---|
| Time (seconds) | 0 | 30 | 60 | 90 | 120 | 150 | 180 | 210 | 240 |

(a). Plot a graph of volume of oxygen produced (vertical axis) against time.                    (3 marks)

(b). What is the rate of reaction:
(i). during the first 30 seconds.                                                                                  (2 marks)

(ii). between 30 seconds and 60 seconds.                                                                      (2 marks)

(c). Explain why: (i). the slope of the curve is steeper at the start of the reaction.         (2 marks)

              (ii). the curve goes flat at the end of the reaction.                                      (2 marks)
(d) (i). Suggest the role of manganese (IV) oxide I the decomposition of hydrogen peroxide.    (1mark)

(ii). Comment on change in mass of manganese (IV) oxide at the end of the reaction. Explain.(2 marks)
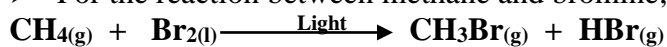
**(e). Effect of light on the rate of reaction**
-The effect of heating and illuminating substances is the same;
- In both cases the constituent particles absorb radiant energy leading to an increase in the number of particles with activation energy resulting in increased rate of reaction;
- Light energizes the particles involved in a reaction;
- This increases the chances of effective collisions per unit time thus increasing the rate of reaction.
- Light of higher frequencies give higher reaction rates e.g. UV Light;
- Examples of reactions affected by light are those involving halogens:

**Examples of reactions affected by light.**
➢ Reaction between $Cl_{2(g)}$ and $H_{2(g)}$ does not take place in the dark but is explosive in bright light;
$Cl_{2(g)} + H_{2(g)} \xrightarrow{\text{bright light}} 2HCl_{(g)}$
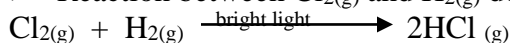
➢ For the reaction between methane and bromine; decolourisation of bromine only occurs in presence of light;
$CH_{4(g)} + Br_{2(l)} \xrightarrow{\text{Light}} CH_3Br_{(g)} + HBr_{(g)}$

**Experiment: Effect of light on the decomposition of silver bromide.**
➢ **Procedure:**

- About 20cm$^3$ of 0.1M potassium bromide is put in a glass beaker.
- 5cm$^3$ of 0.05M silver nitrate solution is added.
- The resulting pale yellow precipitate is divided into three portions in 3 separate test tubes.
- One of the test tubes in immediately placed in a dark cupboard; the second on a bench and the third is placed in a direct source of light e.g. sunlight.

➢ **Observations.**
- Formation of a pale yellow precipitate of silver bromide when silver nitrate reacts with potassium bromide.
    ➢ **Equation:**

$$KBr_{(aq)} + AgNO_{3(aq)} \longrightarrow AgBr_{(s)} + KNO_{3(aq)}$$
*Pale yellow*
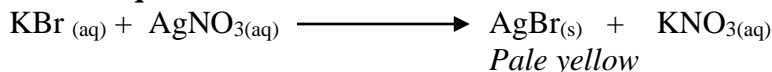
    ➢ **Test tube in light**: precipitate changes colour from pale yellow to grey.
    ➢ **Test tube on the bench**: slight change in colour from pale yellow to slight grey.
    ➢ **Test tube in dark cupboard**: no observable (noticeable) colour change in precipitate.

**Explanation:**
- Light decomposes silver bromide to metallic silver (hence the grey colour) and bromine.

**Equation:**

$$2AgBr_{(aq)} \xrightarrow{\text{Light}} 2Ag_{(s)} + Br_{2(g)}$$
*grey*
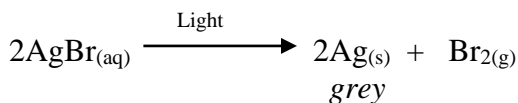
- No observable change in test tube placed in darkness due to lack of light;
- The degree of decomposition and hence change depends on the light intensity falling on the test tubes;
- The rate of decomposition of silver bromide increases with increase in light intensity.
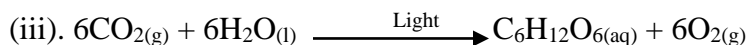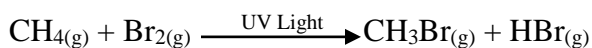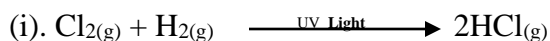
**Conclusion:**
- Light affects the rate of some chemical reactions by energizing the particles involved in a reaction hence increasing the chances of effective collisions per unit time thus increasing the rate of reaction.

**Application of effect of light on reaction rate.**
- Processing of black and white photographic films is done in dark to prevent the decomposition of the silver bromide that is usually used to coat photographic plates;

**Further examples of reactions affected by light:**

(i). $Cl_{2(g)} + H_{2(g)} \xrightarrow{\text{UV Light}} 2HCl_{(g)}$

$CH_{4(g)} + Br_{2(g)} \xrightarrow{\text{UV Light}} CH_3Br_{(g)} + HBr_{(g)}$

(iii). $6CO_{2(g)} + 6H_2O_{(l)} \xrightarrow{\text{Light}} C_6H_{12}O_{6(aq)} + 6O_{2(g)}$

**(f). Pressure**
- Increase in pressure increases the rate of reaction involving the formation of small volume of product because of increase in concentration and slight increase in temperature
- In a given volume the higher the number of molecules of a given gas in a container, the greater the pressure;
- Increase in pressure causes the same effect as increase in concentration;
- Thus the rate of reactions involving gases can be increased by increasing the pressure of the gases

**Note:**

From gas laws, decreases in volume results in increase in pressure. Thus, reactions accompanied by decrease in volume move faster to completion.

**Reversible reactions**
- Are reactions which can be made to go to either direction (forward or backward) by changing conditions such as temperatures, pressure etc.
- In such cases none of the reactants is completely used up and so the reaction does not go into completion.

**Note:**
Reversible reactions are of two types:
  ➢ Reversible physical changes e.g. heating ice, iodine etc.
  ➢ Reversible chemical changes e.g. heating hydrated copper (II) sulphate, Haber process, decomposition of limestone, heating blue cobalt chloride, ammonium chloride etc.
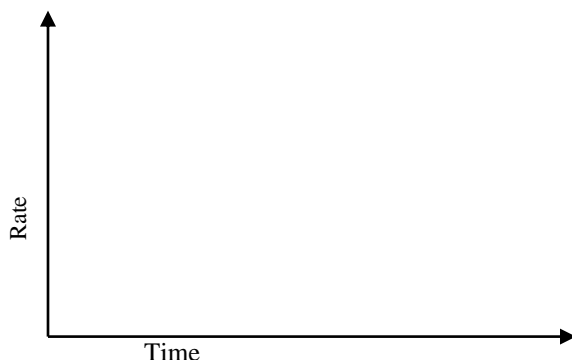
**Examples:**
- Reaction of nitrogen and hydrogen to give ammonia in the **Haber process**.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

- The reversible sign means the reaction can reach a **state of equilibrium** if left undisturbed.

**Explanations of reversible reactions:**
Consider the curves below:



**Point (a): forward reaction.**
- At the start of the reaction, the rate of the forward reaction is faster.
- The concentration of the reactants is greatest at the beginning.
- The rate of forward reaction and the concentration of reactants decreases with time as the reaction proceeds.

**Point (b): backward reaction.**
- At zero time the rate of the backward reaction is zero.
- The concentration of the products is lowest at this time.
- The rate of the backward reaction and concentration of products increases as the forward reaction proceeds.

**Point (c): equilibrium.**
- It comes to a time (t) when the rate of forward reaction is equal to the rate of backward reaction.
- This balance is called equilibrium.

**Equilibrium:**
- Is the state at which the rate of forward reaction is equal to the rate of backward reaction.
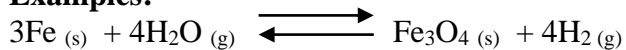
**Types of equilibrium:**
**Static equilibrium:**

- refers to a situation when two opposing forces balance each other and whatever was happening before comes to a standstill.

**Dynamic equilibrium:**
- Refers to a situation when two opposing processes, the forward and reverse, continue taking place but at the same rate.
- The equilibrium is said to be **dynamic** and this **state of balance** can be reached from either direction.

**Examples:**

$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

- The Equilibrium state here is established when:
➢ Either steam is passed over heated iron in a closed container; or
➢ When hydrogen is passed over heated iron oxide;

**Characteristics of equilibrium systems.**
(i) The concentrations of reactants and products do not change after the equilibrium has been reached unless the system is disturbed.

**Note:**
- Observable properties of reactants or products such as colour, mass, volume, PH, temperature etc can be used to detect whether a system is in equilibrium or not.
**Examples:**

| Property | How it can be used to detect attainment of equilibrium |
|---|---|
| Colour | The colour intensity remains constant at equilibrium |
| Volume. | Total volume of solution remains constant at equilibrium; |
| Precipitate | The height of the precipitate remains constant; |

(ii). The equilibrium can be reached from either direction.
(iii). All the reactants and products are present in the system.

**Factors affecting the position of equilibrium**
- Such factors act as a strain on the state of equilibrium and the system reacts in a way to oppose the change.
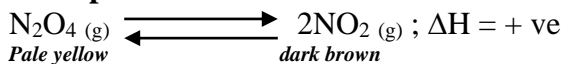- The factors are:
➢ Temperature
➢ Pressure
➢ Concentration
➢ Catalysts.

**(a). Temperature**
➢ **Endothermic reactions**
- Increase in temperature favours the endothermic reactions;

**Example:**
$N_2O_4{}_{(g)} \rightleftharpoons 2NO_2{}_{(g)}$ ; $\Delta H = + ve$
*Pale yellow*           *dark brown*

- Increase in temperature shifts the equilibrium to the right; since the reaction is endothermic and hence more yield of nitrogen (IV) oxide; hence dark brown fumes will be observed;
- Decrease in temperature shifts the equilibrium to the left; since the reaction is endothermic favoured by low temperatures; hence formation of $N_2O_4$; and the pale yellow colour is observed;

➢ **Exothermic reactions:**
- Decrease in temperature favours exothermic reactions.

**Example:**
$2\ SO_2{}_{(g)}\ +\ O_2{}_{(g)} \rightleftharpoons 2SO_3{}_{(g)}$; $\Delta H = -ve$
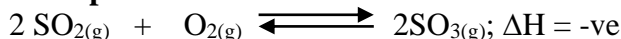
Thus:
- Decrease in temperature causes more yield of sulphur (VI) oxide; because the equilibrium shifts to the right; since the reaction is exothermic favoured by low temperatures;
- Increase in temperature causes $SO_3$ to decompose decreasing its yields. Increase in temperature shifts the equilibrium to the left; because the reaction is exothermic which is favoured by low temperatures;

**(b). Pressure**
-Increase in pressure favours the side with fewer numbers of gaseous molecules since this is the side where pressure is reduced (low).

**Example:**
➢ $N_2{}_{(g)}\ + 3H_2{}_{(g)} \rightleftharpoons 2NH_3{}_{(g)}$
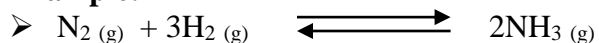
- Increase in pressure favours the production of ammonia; by shifting the equilibrium position to the right; because the volume of gaseous reactants is higher than the volume of gaseous products.
- Decrease in pressure leads to the production of less ammonia (ammonia decomposes); by shifting the equilibrium position to the left; because the volume of gaseous reactants is higher than the volume of gaseous products.

➢ $N_2O_4{}_{(g)} \rightleftharpoons 2NO_2{}_{(g)}$
*Pale yellow*        *dark brown*
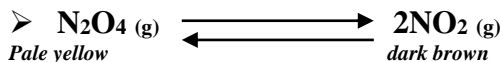
**Increase in pressure:**

- Shifts the equilibrium to the left; leading to formation of more $N_2O_4$ hence mixture turns pale yellow; because the volume of gaseous products ($NO_2$) is higher than the volume of gaseous reactants ($N_2O_4$).
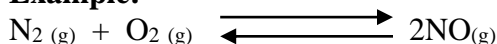
**Decrease in pressure:**
- Shifts the equilibrium position to the right; leading to formation of more $NO_2$ hence colour turns dark brown; because the volume of gaseous reactants ($N_2O_4$) is lower than the volume of gaseous products ($NO_2$);

**Note: -**
➢ Change in pressure has no effect on the equilibrium mixture where gaseous molecules on the two sides are equal

**Example:**

$N_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2NO_{(g)}$

- Increase or decrease in pressure has no effect on position of equilibrium; because the volume of gaseous reactants is equal to volume of gaseous products;
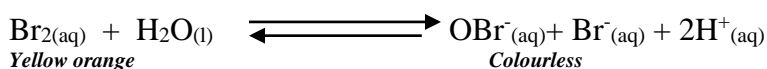
**Note:**
- Generally reactions involving only solids and, or liquids are *not affected by pressure change because they are not compressible;*

**Summary: effects of pressure on equilibrium:**

| Reaction | Effects of pressure change on position of equilibrium | |
|---|---|---|
| | **Increase** | **Decrease** |
| $N_2O_{4(g)} \quad 2NO_{2(g)}$ | Equilibrium shifts to the left; more $N_2O_4$ is formed; | Equilibrium shifts to the right; more $NO_2$ is formed; |
| $N_{2(g)} + 3H_{2(g)} \quad 2NH_{3(g)}$ | - More $NH_3$ is formed; equilibrium shifts to the right; since volume of gaseous reactants is higher than volume of gaseous products | - More $N_2$ and $H_2$ are formed; equilibrium shifts to the left; since volume of gaseous reactants is higher than volume of gaseous products |
| $2SO_{2(g)} + O_{2(g)} \quad 2SO_{3(g)}$ | - More $SO_3$ is formed; equilibrium shifts to the right (forward reaction is favoured); since volume of gaseous reactants is higher than volume of gaseous products | - Less $SO_3$ is formed (more $SO_2$ and $O_2$ are formed); equilibrium shifts to the left (backward reaction is favoured); since volume of gaseous reactants is higher than volume of gaseous products |
| $4NH_{3(g)} + 5O_{2(g)} \quad 4NO_{(g)} + 6H_2O_{(g)}$ | - More $NH_3$ and $O_2$ is formed; equilibrium shifts to the left; since volume of gaseous reactants is lower than volume of gaseous products | - Less $NH_3$ and $O_2$ is formed (more NO and $H_2O$ are formed); equilibrium shifts to the right; since volume of gaseous reactants is lower than volume of gaseous products |
| $H_{2(g)} + Cl_{2(g)} \quad 2HCl_{(g)}$ | - No effect on the equilibrium; because volume of gaseous reactants and volume of gaseous products is the same; | - No effect on the equilibrium; because volume of gaseous reactants and volume of gaseous products is the same; |

**(c). Concentration**
- Consider the equilibrium in bromine water system:

$Br_{2(aq)} + H_2O_{(l)} \rightleftharpoons OBr^-_{(aq)} + Br^-_{(aq)} + 2H^+_{(aq)}$
*Yellow orange*                                    *Colourless*

➢ **Addition of sodium hydroxide to the equilibrium:**

- When NaOH$_{(aq)}$ is added to the equilibrium, the concentration of H$^+$ decrease and the rate of forward reaction are favoured (equilibrium shifts to the right); the reaction of bromine with water increases and there is loss of colour of bromine water.

**Explanation:**
- Addition of sodium hydroxide provides hydroxyl ions into the equilibrium.
- The hydroxyl ions react with the hydrogen ions (on the right of equilibrium) to form water.
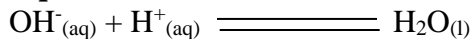
**Equation:**
$$OH^-_{(aq)} + H^+_{(aq)} \rightleftharpoons H_2O_{(l)}$$

- This process removes hydrogen ions from the equilibrium mixture.
- This shifts the equilibrium to the right hence formation of more products;
- This leads to a change in colour from yellow orange to colourless;

➢ **Addition of hydrochloric acid:**
- Addition of HCl$_{(aq)}$ is added concentration of H$^+$ increases; more bromine is formed and the orange-yellow colour of bromine water becomes more intense;

**Explanation:**
- Addition of hydrochloric acid introduces more hydrogen ions into the equilibrium;
- The hydrogen ions react with the **colourless bromide** and **hypobromite** ions to form **yellow-orange** aqueous bromine;
- This shifts the equilibrium to the left hence the increase in the intensity of the yellow-orange colour of bromine water;

**Further examples:**

(i). Given the equilibrium:

$$SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

➢ **Removal of sulphur (VI) oxide:**
- Reducing the concentration of SO$_3$ by removing it causes more sulphur (IV) oxide to be converted to sulphur (IV) oxide.

➢ **Addition of either oxygen or sulphur (IV) oxide.**
- Addition of either sulphur (IV) oxide or oxygen to the equilibrium shifts the equilibrium to the right; due to increase of concentration of products hence more yield of sulphur (VI oxide;

➢ **Addition of pyrogallic acid:**
- Addition of **pyrogallic acid** into the equilibrium shifts the equilibrium to the left; since pyrogallic acid dissolves oxygen gas reducing concentration of reactants on the left hence less yield of sulphur (VI) oxide;
(ii). Given the equilibrium:
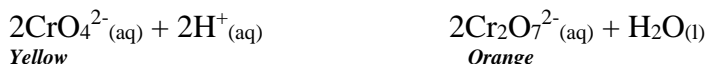
$$2CrO_4^{2-}{}_{(aq)} + 2H^+_{(aq)} \rightleftharpoons 2Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$
*Yellow*                         *Orange*

➢ **Addition of sodium hydroxide to the equilibrium:**
- When NaOH$_{(aq)}$ is added to the equilibrium, the concentration of H$^+$ decrease and the rate of backward reaction are favoured (equilibrium shifts to the left); the reaction of dichromate ions with water to form chromate ions and hydrogen ions increases and there is change in colour to yellow.

**Explanation:**

- Addition of sodium hydroxide provides hydroxyl ions into the equilibrium.
- The hydroxyl ions react with the hydrogen ions (on the left of equilibrium) to form water.
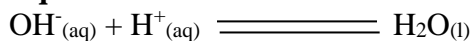
**Equation:**
$$OH^-_{(aq)} + H^+_{(aq)} \rightleftharpoons H_2O_{(l)}$$

- This process removes hydrogen ions from the equilibrium mixture.
- This shifts the equilibrium to the left hence formation of more reactants (chromate and hydrogen ions);
- This leads to a change in colour from orange to yellow;
  ➢ **Addition of hydrochloric acid:**
- Addition of $HCl_{(aq)}$ is added concentration of $H^+$ increases; more dichromate solution is formed and the orange colour of dichromate ions become more intense;

**Explanation:**
- Addition of hydrochloric acid introduces more hydrogen ions into the equilibrium;
- The hydrogen ions react with the **yellow chromate** solution to form **orange** dichromate solution (and water);
- This shifts the equilibrium to the right hence the increase in the intensity of the orange colour of dichromate solution;

**Generally:**
- A change in concentration disturbs the already established equilibrium by making the reaction rate in one direction faster
- The reaction then proceeds predominantly in that direction until equilibrium is re established

**(d). Effect of catalyst**
- Presence of a catalyst has no effect on the position of the equilibrium but alters the rate at which the equilibrium is attained.
- Catalysts usually allow the equilibrium to be reached in a shorter period of time by increasing the rates of the reactions

**Le Chatelier's Principle**
- States that:

> When stress is applied to a system in equilibrium, the system reacts so as to oppose the stress.

- This implies that when a change in condition is applied to a system in equilibrium, the system moves so as to oppose the change.
**Note:**
- The effect of different factors on equilibrium was first investigated in 1888 by a French Chemist; **Henri Louis Le Chatelier.**
- All explanations so far described are based on Le Chatelier's principle.

**Industrial applications of chemical equilibrium.**

- The ability to change the position of an equilibrium by varying the conditions has been important in industrial processes as industrialists aim at obtaining maximum products at minimum cost and shortest time possible.
- Conditions required to obtain **greatest yield** of products at **minimum costs** and **shortest time** possible are called **optimum conditions**.
- Such optimum conditions are obtained by continuous removal of products hence reduction in its concentration or varying external factors like temperature and pressure.

**Summary:**
**Optimum conditions for common industrial processes.**

| Condition | Optimum condition for: | |
|---|---|---|
| | ➢ **Haber process** <br> $N_{2(g)} + 3H_{2(g)}$  $2NH_{3(g)}$; $\Delta H$= - 92KJMol- | ➢ **The contact process** <br> $2SO_{3(g)} + O_{2(g)}$  $2SO_{3(g)}$; $\Delta H$ = -197Kjmol- |
| Temperature | - The reaction is **exothermic** hence favoured by low temperatures; which shift the equilibrium to the right hence more yield of ammonia gas; <br> - However rate at which the $NH_{3(g)}$ will be produced would be too slow and thus uneconomical; an optimum temperature of about $450^{o}C$ is thus normally used; | - Forward reaction is exothermic thus increase in temperature favours backward reaction; shifts the equilibrium to the left hence less yield of $SO_{2(g)}$; <br> - Low temperature will favour forward reaction thus shifts the equilibrium to the right; hence more production of $SO_{2(g)}$; However rate of yield will be too slow and hence optimum temperature for maximum yield are set at about $450^{o}C$; |
| Pressure | Increase in pressure favours the forward reaction; shifting the equilibrium to the right hence more yield of ammonia; because the volume of gaseous reactants is higher than the volume of gaseous products; <br> - However the cost of producing and maintaining high pressures in a system is very high; <br> - Thus for maximum yield the optimum pressure is 200 atmospheres; | - An increase in pressure will shift the equilibrium to the left leading to low yield of sulphur (IV) oxide; since the volume of gaseous reactants is lower than the volume of gaseous products; <br> - Thus the optimum pressure used is atmospheric pressure, which gives a percentage conversion of $SO_{2(g)}$ to $SO_{3(g)}$ of about 96%. |
| Concentration | - Removal of ammonia gas shifts the equilibrium to the right hence more yield of ammonia; since this removal lowers concentration of $NH_{3(g)}$ <br> - thus for maximum yield ammonia is removed as soon as it is produced; so that more $H_{2(g)}$ and $N_{2(g)}$ can continue reacting; | - Removal of sulphur (VI) oxide gas shifts the equilibrium to the right hence more yield of $SO_{3(g)}$; since this removal lowers its concentration; <br> - thus for maximum yield $SO_{3(g)}$ is removed as soon as it is produced; so that more $SO_{2(g)}$ and $O_{2(g)}$ can continue reacting; |
| Catalyst | - Main catalyst used is finely divided iron; platinum is a better catalyst but is very expensive and easily poisoned by impurities, hence may increase cost of production; | - A catalyst of vanadium (V) oxide is used to increase the rate of reaction; |

# UNIT 4: ELECTROCHEMISTRY

**Checklist:**

1. Meaning of electrochemistry
2. Displacement and Redox reactions.
4. Oxidation and Redox reactions in terms of electron gain and electron loss
5. Oxidation numbers (states)
   - ➢ Rules of assigning oxidation numbers
   - ➢ Calculating oxidation numbers
6. Redox reactions involving halide ions (halogens)
   - ➢ Further examples of Redox reactions.
7. Tendency of metals to from ions.
8. Measurements of tendency of metals to ionize
   - ➢ Electrochemical cells
   - ➢ Salt bridge
   - ➢ Cell diagrams
   - ➢ Cell equations
9. Standard electrode potential
   - ➢ Definition
   - ➢ Standard hydrogen electrode
   - ➢ The hydrogen half cell
   - ➢ Electrode potentials (negative and positive values)
   - ➢ Calculating $E^0$ values from Redox reactions.
10. Voltaic cells
    - ➢ Primary cells
        - ▪ Structure
        - ▪ Reactions
        - ▪ Zinc (negative) terminal
        - ▪ Brass (positive) terminal
        - ▪ Functions of various components
    - ➢ Secondary cells (lead acid accumulators)
        - ▪ Structure
        - ▪ Reactions
        - ▪ During discharge
        - ▪ During recharging;
11. Electrolysis
    - ➢ Definition
    - ➢ Terminologies used in electrolysis (basic concepts)
    - ➢ Preferential discharge of ions
    - ➢ Electrolysis of various substances
        - ▪ Dilute sulphuric acid
        - ▪ Dilute sodium chloride
        - ▪ Concentrated sodium chloride (brine)
        - ▪ The mercury cathode cell
        - ▪ Copper (II) sulphate
            - • Using inert electrodes
            - • Using copper electrodes
    - ➢ Factors affecting electrolysis and electrolysis products
    - ➢ Applications of electrolysis
        - ▪ Extraction of reactive metals
        - ▪ Purification of metals
        - ▪ Electroplating
        - ▪ Anodizing aluminium utensils
        - ▪ Manufacture of sodium hydroxide, chlorine and hydrogen;
            - • The mercury cathode cell
            - • Diaphragm cell;
            - • Membrane cell;
    - ➢ Quantitative aspects of electrolysis
        - ▪ Basic terminologies
            - • The ampere
            - • The coulomb
            - • The faraday
        - ▪ Faradays laws of electrolysis
            - • Statements
            - • Calculations.

# Definition:

- Electrochemistry is the chemistry of electrochemical reactions; which deal with the relationship between electrical energy and chemical reactions.
- Electrochemical reactions involve transfer of electrons and are essentially **REDOX** reactions.

**Displacement and REDOX reactions**
**Experiment 1:- Displacement reactions among metals**
**(i). Procedure**
(a). 5 cm$^3$ of 1M CuSO$_4$ $_{(aq)}$ is put in a test-tube and its temperature recorded.
- In the solution, a spatula end-full of iron fillings is added.
- Any observations and temperature change are determined and recorded.
- The procedure is repeated with fresh samples of CuSO$_4$ with Zn, Mg, and Cu powders.

(b). The procedure is repeated with 1M magnesium sulphate solution instead of CuSO$_4$ $_{(aq)}$.

**(ii). Observations:**

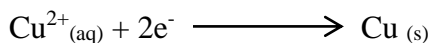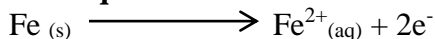| Solution / Metal solid | Copper (II) Sulphate | Magnesium Sulphate |
|---|---|---|
| Iron fillings | - A red brown solid (Cu) is formed<br>- The blue colour of the solution (Cu$^{2+}$) fades then changes to green (Fe$^{2+}$) | - No reaction |
| Zinc powder | - A red brown solid, copper metal is deposited.<br>- The blue colour of the solution (Cu$^{2+}$) fades then turns colourless; | - No observable reaction (change) |
| Copper powder | - No reaction | - No reaction |

**(iii). Explanations**
- Reactions between metals and ions of another metal involve transfer of electrons from the metal to the other metal ion in solution.
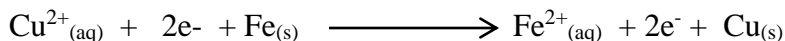
**Examples:**
 ➢ **Fe$_{(s)}$ and CuSO$_4$ $_{(aq)}$**
- Copper being lower in the electrochemical series accepts electrons easier (than Fe) to form copper atoms (brown solid);
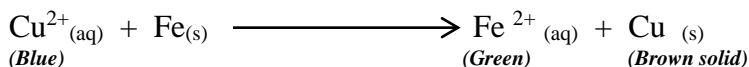
**Half equations**
Fe $_{(s)}$ $\longrightarrow$ Fe$^{2+}$$_{(aq)}$ + 2e$^-$

Cu$^{2+}$$_{(aq)}$ + 2e$^-$ $\longrightarrow$ Cu $_{(s)}$

**Overall reaction**
Cu$^{2+}$$_{(aq)}$ + 2e- + Fe$_{(s)}$ $\longrightarrow$ Fe$^{2+}$$_{(aq)}$ + 2e$^-$ + Cu$_{(s)}$
Then;

Cu$^{2+}$$_{(aq)}$ + Fe$_{(s)}$ $\longrightarrow$ Fe $^{2+}$ $_{(aq)}$ + Cu $_{(s)}$
*(Blue)*                 *(Green)*       *(Brown solid)*

**Oxidation and reduction in terms of electron loss and gain**
- The loss of electrons is **oxidation** and the species that gains electrons (causes electron loss); Cu$^{2+}$ in this case is called **oxidizing agent**; and is itself reduced.
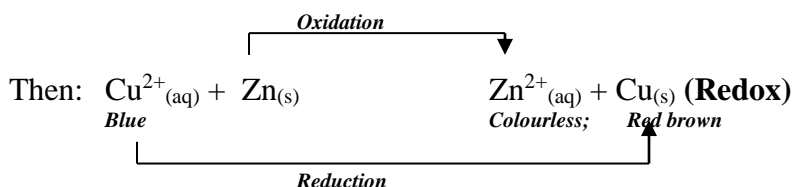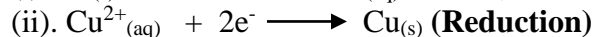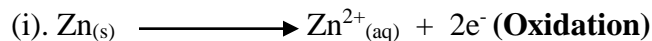
**- Reduction**: refers to gain of electrons, and the species that **donates electrons** (iron solid in this case) is called a **reducing agent** and is itself oxidized.
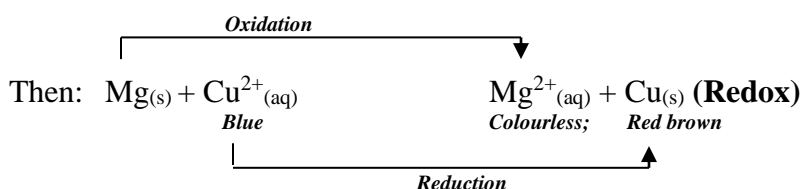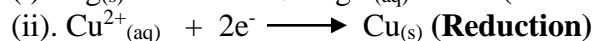- Displacement reactions generally involve reduction and oxidation simultaneously and are thus termed **Redox Reactions.**
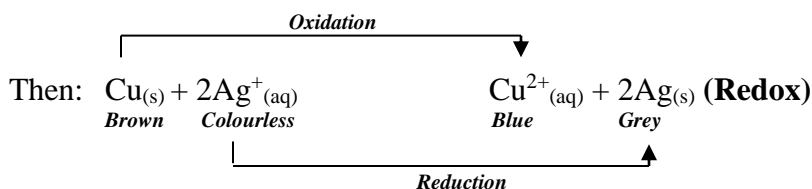
**Further examples**
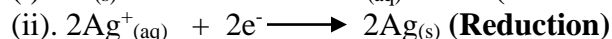**(i). Zinc solid and CuSO$_{4(aq)}$**

(i). $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ **(Oxidation)**
(ii). $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ **(Reduction)**

*Oxidation*

Then: $Cu^{2+}_{(aq)} + Zn_{(s)}$　　　　　$Zn^{2+}_{(aq)} + Cu_{(s)}$ **(Redox)**
　　　　*Blue*　　　　　　　　　*Colourless;*　*Red brown*

*Reduction*

**(ii). Magnesium solid and copper (II) sulphate**

(i). $Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e^-$ **(Oxidation)**
(ii). $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ **(Reduction)**

*Oxidation*

Then: $Mg_{(s)} + Cu^{2+}_{(aq)}$　　　　　$Mg^{2+}_{(aq)} + Cu_{(s)}$ **(Redox)**
　　　　　*Blue*　　　　　*Colourless;*　*Red brown*

*Reduction*

**(iii). Silver nitrate and copper solid.**

(i). $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$ **(Oxidation)**
(ii). $2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)}$ **(Reduction)**

*Oxidation*

Then: $Cu_{(s)} + 2Ag^+_{(aq)}$　　　　　$Cu^{2+}_{(aq)} + 2Ag_{(s)}$ **(Redox)**
　　　*Brown*　　*Colourless*　　　　*Blue*　　*Grey*

*Reduction*

**Note:**
- Amount of heat evolved in these redox reactions depends on the position of the metal in the activity series relative to the metal ion in solution.
- The **closer the metals** are in the activity series; the **less readily displacement** occurs and **the lower the heat evolution** during the displacement.
**E.g.:**　Heat evolved $Mg//Cu^{2+}$ is higher than that evolved between $Fe//Cu^{2+}$.

**Conclusion:**
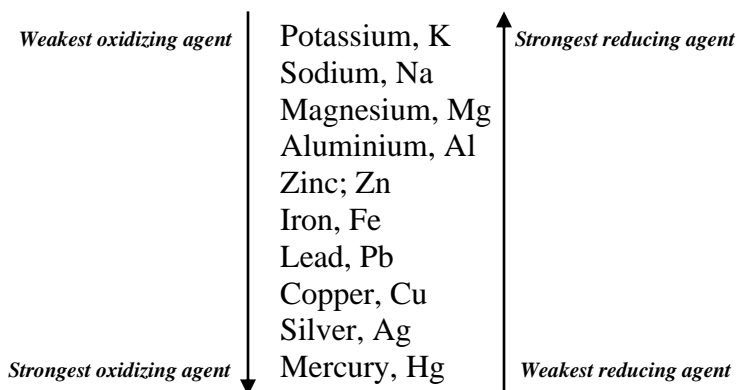- Metals displace from solutions, those metals lower than themselves in the activity series.
**Note:**
- The **more the reactive** a metal is; the **stronger a reducing agent** it is and the **weaker an oxidizing agent** it is.

**Example:**
**-** Potassium is stronger reducing agent; but weaker oxidizing agent than silver, gold etc.

**Summary:**
**Strength of reducing/ oxidizing agent**

| | | |
|---|---|---|
| *Weakest oxidizing agent* | Potassium, K<br>Sodium, Na<br>Magnesium, Mg<br>Aluminium, Al<br>Zinc; Zn<br>Iron, Fe<br>Lead, Pb<br>Copper, Cu<br>Silver, Ag | *Strongest reducing agent* |
| *Strongest oxidizing agent* | Mercury, Hg | *Weakest reducing agent* |

**Summary on displacement reactions**

| Metal / Metal ion (in solution) | Mg | Al | Zn | Fe | Pb | Cu |
|---|---|---|---|---|---|---|
| $K^+$ | X | X | X | X | X | X |
| $Na^+$ | X | X | X | X | X | X |
| $Ca^{2+}$ | X | X | X | X | X | X |
| $Mg^{2+}$ | X | X | X | X | X | X |
| $Al^{3+}$ | ✔ | X | X | X | X | X |
| $Zn^{2+}$ | ✔ | ✔ | X | X | X | X |
| $Fe^{2+}$ | ✔ | ✔ | ✔ | X | X | X |
| $Pb^{2+}$ | ✔ | ✔ | ✔ | ✔ | X | X |
| $Cu^{2+}$ | ✔ | ✔ | ✔ | ✔ | ✔ | X |
| $Ag^{2+}$ | ✔ | ✔ | ✔ | ✔ | ✔ | ✔ |

**Key:**
A cross (x) indicates no reaction hence no redox reaction occurs.
A tick indicates redox reaction occurs.

**Oxidation numbers/ oxidation state.**
- Is the apparent charge that atoms have in molecules or ions.
- For monoatomic ions, the oxidation number (state) is the magnitude and sign of charge;

**Example:**
Oxidation no of Aluminium in $Al^{3+}$ is +3;

**Importance of oxidation numbers:**

- Helps in keeping track of electron movement in redox reactions; hence determination of the reduced and oxidized species.

**Oxidation and reduction in terms of oxidation numbers**
  ➢ **Oxidation**
- Is an increase in oxidation number.

  ➢ **Reduction**
**-** Refers to a decrease in oxidation number

**Rules in assigning oxidation numbers**
1. Oxidation number of an uncombined element is zero (0)
2. The charge on a monoatomic ion is equivalent to the oxidation number of that element;
3. The oxidation number of hydrogen in all compounds is +1 except in metal hydrides where its –1;
4. The oxidation number of oxygen in all compounds is –2 except in peroxides where it is –1 and $0F_2$ where it is +2.
5. In complex ions the overall charge is equal to the sum of the oxidation states of the constituent elements.
6. In compounds, the sum of oxidation numbers of all constituent atoms is equal to zero.

**Worked examples**
*1. Calculate the oxidation number of nitrogen in:*
*(i). $NO_3^-$*

**Solution:**
N + (-2 x 3) = -1
N = -1 + 6
   = +5
**Note:** thus nitric acid with a nitrate ion ($NO_3^-$) is called nitric (V) acid since the oxidation number of nitrogen in it is +5;

*(ii). $NO_2$;*

**Solution:**
N + (-2 x 2) = 0
N = 0 + 4
   = +4
**Note:** Thus the gas $NO_2$ is referred to as nitrogen (IV) oxide because the oxidation umber of nitrogen in it is +4

*(iii). $NO_2^-$;*

**Solution:**
N + (-2 x 2) = -1
N = -1 + 4
   = +3
**Note:** thus nitrous acid containing nitrite ion is called nitrous (III) acid since the oxidation number of nitrogen in it is +3.

*(iii). $AgNO_3$;*

**Solution:**
1 + N + (-2 x 3) = 0
1 + N + (-6) = 0
N = 0 – 1 + 6;
N = +5

*2. Determine the oxidation number of manganese in each of the following, and hence give the systematic names of the compounds.*
*(i). $MnSO_4$*

**Solution:**

Mn + 6 + (-2 x 4) = 0

Mn = 0 – 6 + 8;

Mn = +2

Systematic name: Manganese (II) sulphate;

*(ii). $Mn_2O_3$;*

**Solution:**

2Mn + (3 x -2) = 0;

2Mn = 0 + 6

Mn = ½ x 6;

Mn = +3;

Systematic name: Manganese (III) oxide;

*(iii). $KMnO_4$*

**Solution:**

1 + Mn + (-2 x 4) = 0

Mn = 0 – 1 + 8;

Mn = +7;

Systematic name: Potassium manganate (VII) oxide

(iv). $MnO_3^-$;

**Solution:**

Mn + (-2 x 3) = -1

Mn = -1 + 6;

Mn = +5

Systematic name: Manganese (V) ion;

**Determination of redox reactions using oxidation numbers.**
**Worked examples:**

**Redox reactions involving Halide ions and halogens**
**Experiment**
(i). **Procedure:**
- 2 cm$^3$ of chlorine gas are bubbled into each of the following solutions: - KI, KCl, KBr, and KF.
- The observations are made and recorded.
- The procedure is repeated using fluorine, bromine and iodine in place of chlorine.

**Precaution:**
- Chlorine and bromine are poisonous.

**(ii). Observations**

| Halogen \ Halide | Potassium fluoride | Potassium Chloride | Potassium Bromide | Potassium Iodide |
|---|---|---|---|---|
| Fluorine ($F_2$) | No visible, change | Green-yellow gas is evolved | Colourless solution changes to red brown | Colourless solution turns black; |
| Chlorine ($Cl_2$) | No visible colour change; | No visible colour change; | Colourless solution turns red brown | Colourless solution turns black |
| Bromine ($Br_2$) | No visible colour change; | No visible colour change; | No visible colour change; | Colourless solution turns black; |
| Iodine ($I_2$) | No visible colour change; | No visible colour change; | No visible colour change; | Colourless solution turns black; |

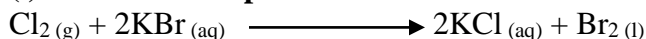**Note:   Colours of halogens in tetra – chloromethane:-**

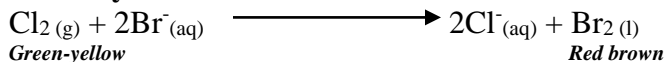| Halogen | Colour in tetrachloromethane |
|---|---|
| Fluorine | |
| Chlorine | Yellow |
| Bromine | Red-brown |
| Iodine | Purple |

**(iii). Explanations**
- Fluorine displaces all the other halogens; $Cl_2$, $Br_2$ and $I_2$ because it has a greater tendency to accept electrons than all the rest.
- Chlorine displaces both Bromine and Iodine from their halide solutions
- $Cl_2$ takes electrons from the bromide and iodide ions i.e. oxidizes them, to form bromine and iodine respectively.
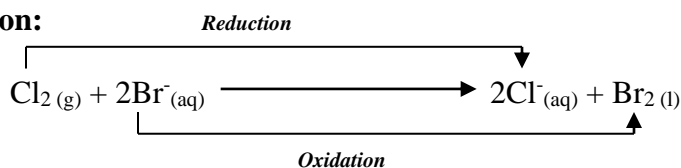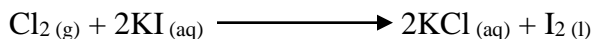
**Equations:**
**(i). Chlorine and potassium bromide:**
$$Cl_{2\,(g)} + 2KBr_{(aq)} \longrightarrow 2KCl_{(aq)} + Br_{2\,(l)}$$

**Ionically:**
$$Cl_{2\,(g)} + 2Br^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + Br_{2\,(l)}$$
*Green-yellow*                         *Red brown*

**Redox equation:**

*Reduction*

$$Cl_{2\,(g)} + 2Br^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + Br_{2\,(l)}$$

*Oxidation*

**(ii). Chlorine and Potasium iodide:**

$$Cl_{2\ (g)} + 2KI_{(aq)} \longrightarrow 2KCl_{(aq)} + I_{2\ (l)}$$

**Ionically:**
$$Cl_{2\ (g)} + 2I^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + I_{2\ (l)}$$
*Green-yellow*                                *Black*

**Half cell reactions:**
- ➤ **Oxidation**: $2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2e^-$
- ➤ **Reduction:** $Cl_{2\ (g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$

**Redox equation:**

*Reduction*

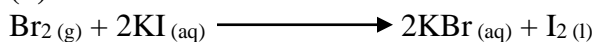$$Cl_{2\ (aq)} + 2I^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + I_{2\ (l)}$$

*Oxidation*

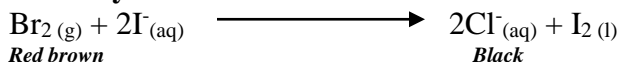- Bromine takes electrons form iodide ions but not from fluorine and chlorine.
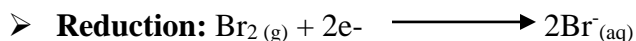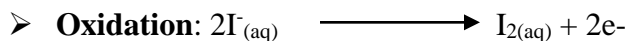- Iodine is formed i.e. due to oxidation of iodide ions by the Bromine.

**Equations**
**(ii). Bromine and Potasium iodide:**
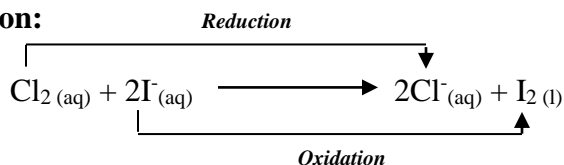$$Br_{2\ (g)} + 2KI_{(aq)} \longrightarrow 2KBr_{(aq)} + I_{2\ (l)}$$

**Ionically:**
$$Br_{2\ (g)} + 2I^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + I_{2\ (l)}$$
*Red brown*                             *Black*

**Half cell reactions:**
- ➤ **Oxidation**: $2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2e^-$
- ➤ **Reduction:** $Br_{2\ (g)} + 2e^- \longrightarrow 2Br^-_{(aq)}$

**Redox equation:**

*Reduction*

$$Cl_{2\ (aq)} + 2I^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + I_{2\ (l)}$$

*Oxidation*

**Note**: oxidation number of chlorine decreases from 0 to -1 hence **reduction**; while oxidation number of iodine increases from -1 to 0; hence **oxidation**;

**(iv). Conclusion:**
- The stronger the tendency of an element to accept electrons, the stronger is its oxidizing power.
- Fluorine is the strongest oxidizing agent of the 4 halogens considered.

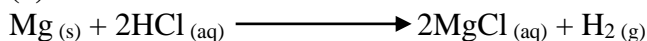**Order of oxidizing power for halogens.**
Fluorine; $F_2$;
Chlorine; $Cl_2$    *Increasing oxidizing power*.
Bromine; $Br_2$

Iodine; $I_2$

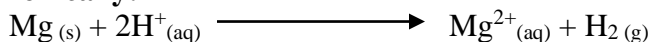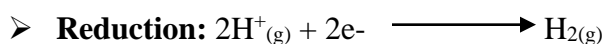**Further examples of redox reactions**
**(a). Action of acid on metals**
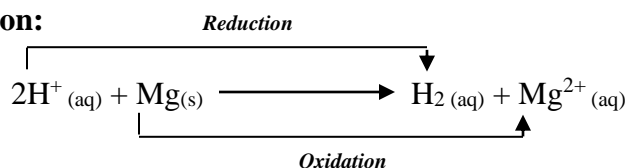$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow 2MgCl_{(aq)} + H_{2(g)}$

**Ionically:**
$Mg_{(s)} + 2H^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_{2(g)}$

**Half cell reactions:**
➢ **Oxidation**: $Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e\text{-}$

➢ **Reduction:** $2H^+_{(g)} + 2e\text{-} \longrightarrow H_{2(g)}$

**Redox equation:**

*Reduction*

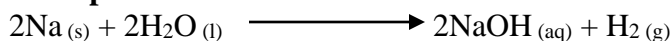$2H^+_{(aq)} + Mg_{(s)} \longrightarrow H_{2(aq)} + Mg^{2+}_{(aq)}$

*Oxidation*

**Note**: oxidation number of hydrogen decreases from 1 to 0 hence **reduction**; while oxidation number of magnesium increases from 0 to 2; hence **oxidation**;

**(b). Reaction of active metals with water**
**Example**
$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$

**Ionically:**
$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_{2(g)}$

**Half cell reactions:**
➢ **Oxidation**: $2Na_{(s)} \longrightarrow 2Na^+_{(aq)} + 2e\text{-}$

➢ **Reduction:** $2H_2O_{(g)} + 2e\text{-} \longrightarrow 2OH^-_{(aq)} + H_{2(g)}$

**Redox equation:**

*Oxidation*

$2Na_{(s)} + 2H_2O_{(aq)} \longrightarrow 2Na^+_{(aq)} + \boxed{2Cl^-_{(aq)} + I_{2(l)}}$

*Reduction*

**Note**: oxidation number of water decreases from 0 to -1(total) hence **reduction**; while oxidation number of sodium increases from 0 to 1; hence **oxidation**;

**(c). Reaction of heated Iron with dry chlorine**
$2Fe_{(s)} + 3Cl_{2(g)} \longrightarrow 2FeCl_{3(s)}$

**Ionically (assumed):**
$2Fe_{(s)} + 3Cl_{2(aq)} \longrightarrow 2Fe^{3+}_{(aq)} + 6Cl^-_{(g)}$

**Half cell reactions:**
- **Oxidation**: $2Fe_{(s)} \longrightarrow 2Fe^{3+}_{(aq)} + 6e^-$

- **Reduction:** $3Cl_{2(g)} + 6e^- \longrightarrow H_{2(g)}$

**Redox equation:**

$$2Fe_{(s)} + 3Cl_{2(g)} \longrightarrow 2Fe^{3+}_{(aq)} + 6Cl^-_{(aq)}$$
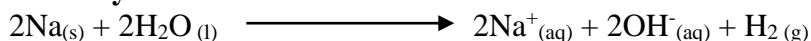
*Oxidation* (top arrow)
*Reduction* (bottom arrow)

**Note**: oxidation number of chlorine decreases from 0 to -1 hence **reduction**; while oxidation number of iron increases from 0 to 3; hence **oxidation**;
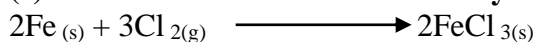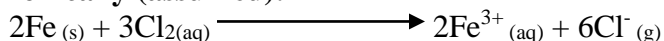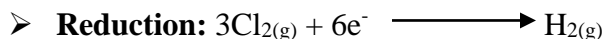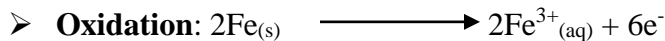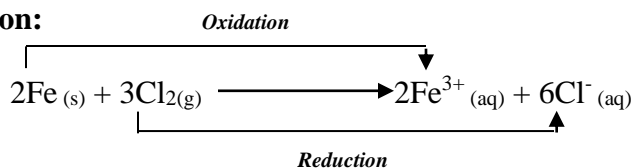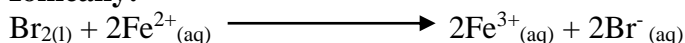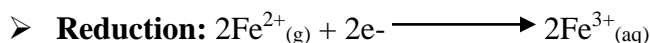
## (d). Reaction between Bromine and Iron (II) ions

**Ionically:**
$$Br_{2(l)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Fe^{3+}_{(aq)} + 2Br^-_{(aq)}$$

**Half cell reactions:**
- **Oxidation**: $Br_{2(l)} \longrightarrow 2Br^-_{(aq)} + 2e-$

- **Reduction:** $2Fe^{2+}_{(g)} + 2e- \longrightarrow 2Fe^{3+}_{(aq)}$

**Redox equation:**

$$Br_{2(aq)} + 2Fe^{2+}_{(s)} \longrightarrow 2Br^-_{(aq)} + 2Fe^{3+}_{(aq)}$$

*Reduction* (top arrow)
*Oxidation* (bottom arrow)

**Note**: oxidation number of bromine decreases from 0 to -1 hence **reduction**; while oxidation number of $Fe^{2+}$ increases from 2 to 3 (in $Fe^{3+}$); hence **oxidation**;

## (e). Oxidation by potassium Manganate (VII) (KMnO₄)

**Procedure:**
- Purple Potassium manganate (VII) is added into a solution containing iron (II) ions in a test tube.
- A few drops of concentrated sulphuric (VI) acid are added.

**Observations:**
- The purple solution (containing Manganate (VII) ions) turns to colourless (manganate (II) ions) i.e. the purple solution is decolourised;

**Explanation:**
- The Manganate (VII) ions which give the solution a purple colour are reduced to Manganese (II) ions which appear colourless. This is a redox reaction.

**Equations**
**Ionically:**
$$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5Fe^{2+}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + 5Fe^{3+}_{(aq)} + 4H_2O_{(l)}$$
*Purple*                     *Colourless*

**Half cell reactions:**
- **Oxidation**: $5Fe^{2+}_{(s)} \longrightarrow 5Fe^{3+}_{(aq)} + 5e^-$; *(since number of electrons is 5)*

- **Reduction:** $MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$

**Redox equation:**

$$\text{MnO}_4^-{}_{(aq)} + 5\text{Fe}^{2+}{}_{(aq)} \longrightarrow \text{Mn}^{2+}{}_{(aq)} + 5\text{Fe}^{3+}{}_{(aq)}$$

*Reduction* (arrow from MnO₄⁻ to Mn²⁺)
*Oxidation* (arrow from Fe²⁺ to Fe³⁺)

**Note**:

➤ oxidation number of Manganate ions in $KMnO_4$ decreases from 7 to 2 (in $Mn^{2+}$) hence **reduction**; while oxidation number of iron increases from 2 (in $Fe^{2+}$) to 3 (in $Fe^{3+}$); hence **oxidation**;

➤ The presence of $Fe^{3+}$ at the end of the reaction can be detected by adding sodium hydroxide solution to form a red brown precipitate of $Fe(OH)_3$;

## (f). Action of potassium dichromate (VI) on iron (II) ions ($Fe^{2+}$):

### (i). Procedure:
- A solution containing iron (II) ions is added into a solution of oxidized potassium dichromate (VI).

### (ii). Observations:
- The orange solution of potassium dichromate turns green.

### (iii). Explanations:
- The iron (II) ions are oxidized to iron (III) ions
- The chromium (VI) ions (orange) are reduced to chromium (III) ions
- This is thus a **REDOX** reaction.

**Equations**
**Ionically:**
$$\text{Cr}_2\text{O}_7^{2-}{}_{(aq)} + 14\text{H}^+{}_{(aq)} + 6\text{Fe}^{2+}{}_{(aq)} \longrightarrow 2\text{Cr}^{3+}{}_{(aq)} + 6\text{Fe}^{3+}{}_{(aq)} + 7\text{H}_2\text{O}_{(l)}$$
*Orange*        *Green*

**Half cell reactions:**

➤ **Oxidation**: $6\text{Fe}^{2+}{}_{(s)} \longrightarrow 6\text{Fe}^{3+}{}_{(aq)} + 6e^-$; *(since number of electrons is 6)*

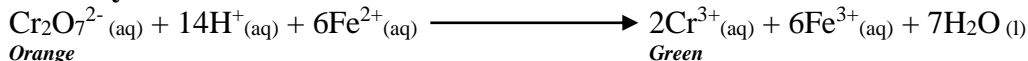➤ **Reduction:** $\text{Cr}_2\text{O}_7^{2-}{}_{(aq)} + 14\text{H}^+{}_{(aq)} + 5e^- \longrightarrow 2\text{Cr}^{3+}{}_{(aq)} + 7\text{H}_2\text{O}_{(l)} + 6\text{Fe}^{3+}{}_{(aq)}$

**Redox equation:**

$$\text{Cr}_2\text{O}_7^{2-}{}_{(aq)} + 6\text{Fe}^{2+}{}_{(aq)} \longrightarrow 2\text{Cr}^{3+}{}_{(aq)} + 6\text{Fe}^{3+}{}_{(aq)}$$

*Reduction* (arrow from Cr₂O₇²⁻ to Cr³⁺)
*Oxidation* (arrow from Fe²⁺ to Fe³⁺)

**Note**:

➤ The oxidation number of dichromate ions in $K_2Cr_2O_7$ decreases from 6 to 3 (in $Cr^{3+}$) hence **reduction**; while oxidation number of iron increases from 2 (in $Fe^{2+}$) to 3 (in $Fe^{3+}$); hence **oxidation**;

➤ The presence of $Fe^{3+}$ at the end of the reaction can be detected by adding sodium hydroxide solution to form a red brown precipitate of $Fe(OH)_3$;

## (g). Action of acidified potassium permanganate on Hydrogen Peroxide.
- The overall reaction is a **Redox reaction**

**Redox equation**
$$2\text{MnO}_4^-{}_{(aq)} + 5\text{H}_2\text{O}_{(l)} + 6\text{H}^+{}_{(aq)} \longrightarrow 2\text{Mn}^{2+}{}_{(aq)} + 5\text{H}_2\text{O}_{(l)} + 5\text{O}_2{}_{(g)}$$
*Purple*        *Colourless*

**Half cell reactions:**
- **Oxidation**: $5H_2O_{2(aq)} \longrightarrow 10H^+_{(aq)} + 5O_{2(g)} + 10e^-$;

- **Reduction:** $2MnO_4^-{}_{(aq)} + 16H^+_{(aq)} + 10e^- \longrightarrow 2Mn^{2+}_{(aq)} + 8H_2O_{(l)}$

**Redox equation:**

$$2MnO_4^-{}_{(aq)} + 5H_2O_{2(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + \boxed{10H^+_{(aq)} + 5O_{2(g)}}$$

*Reduction* (top arrow) *Oxidation* (bottom arrow)

**Note**:
- The oxidation number of manganate ions in $KMnO_4$ decreases from 7 to 2 (in $Mn^{2+}$) hence **reduction**; while oxidation number of hydrogen increases from -1 (in $H_2O_2$) to 1 (in $H^+$); hence **oxidation**;
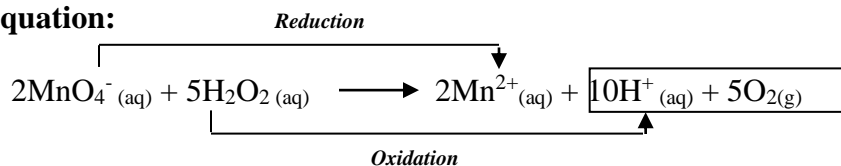- Thus the acidified potassium manganate (VII) oxidizes hydrogen peroxide to water and hydrogen;

## (h). $H_2O_2$ oxidizes Iron (II) salts to Iron (III) salts in acidic medium
**Oxidation:**

$2Fe^{2+}_{(aq)} \longrightarrow 2Fe^{3+}_{(aq)} + 2e^-$

**Reduction:**

$2H^+_{(aq)} + H_2O_{2(aq)} + 2e^- \longrightarrow 2H_2O_{(l)}$

**Overall redox:**

$2Fe^{2+}_{(aq)} + H_2O_{2(aq)} + 2H^+_{(aq)} \longrightarrow 2Fe^{3+}_{(aq)} + 2H_2O_{(l)}$

## Terms used in describing oxidation – reduction

| Term | Electron change | Oxidation number change |
|---|---|---|
| Oxidation | loss of electrons | increases |
| Reduction | gain of electrons | decreases |
| Oxidizing agent | receives electrons | decreases |
| Reducing agent | loses electrons | increases |
| Substances oxidized | loses electrons | increases |
| Substance reduced | gains electrons | decreases |

## The tendency of metals to form ions
- When a metal is placed in an aqueous solution of its ions, some of the metal dissolves;
**Equation:**

$M_{(s)} \longrightarrow M^{n+}_{(aq)} + ne^-$

- Dissolution of the metal causes electron build up on its surface; making it negatively charged, while the surrounding solution becomes positively charged.

**Diagram: dissolution of metal and electron build up.**



— Metal rod

— Solution containing metal ions

- The positive charge of the solution increases and some of the cations start recombining with the electrons on the metal surface to form atoms.

## Equation:

$$M^{n+}_{(aq)} + ne^- \qquad\qquad M(s)$$

- Consequently, an electric potential difference is created between the metal rod and the positively charged ions in solution.
- This arrangement of a metal rod (electrodes) dipped in a solution of its ions constitutes a **half – cell.**

## Note:
- The tendency of a metal to ionize when in contact with the ions differs form one metal to another.
- This difference can be measured by connecting two different Half – cells to make a **full cell**.
- The electrodes of the 2 half – cells are connected by a metallic conductor; while the electrolytes (solutions) of the half cells are connected through a **salt bridge**.

**Diagram: Connection of two half cells to a full cell.**



High resistance voltmeter

Salt bridge

Zinc

Copper

Zinc sulphate solution

Copper sulphate solution

Half-cell A          Half-cell B

## Experiment: - to measure the relative tendency of metals to ionize
### (i). Procedure:
- A Zinc rod is placed into 50 cm$^3$ of 1M zinc sulphate in a beaker;
- Into another beaker containing 50 cm$^3$ of 1M CuSO$_4$ $_{(aq)}$, a copper rod is dipped;
- The two solutions are connected using a salt bridge.

- The two metal rods are connected through a connecting wire connected to a voltmeter
- The experiment is repeated using the following half-cells instead of the Zinc-half cells:-
  - ➢ Mg rod dipped in 1M $MgSO_4$ (aq)
  - ➢ Lead dipped in 1M lead Nitrate
  - ➢ Copper dipped in 1M $CuSO_4$ (aq)

**(ii). Apparatus**
**Diagram:**



**(iii). Observation**
- The zinc rod in the zinc-zinc ions half – cell dissolves;
- The blue colour of the copper (II) Sulphate solution fades/ decrease;
- Red-brown deposits of copper appear on the copper rod in the copper-copper ions half-cell.
- A voltage of 1.10 V is registered in the voltmeter.

**(iv). Equations/ reactions, at each half cell**
  - ➢ **In zinc-zinc ions half cell**
$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

  - ➢ **In the copper-copper ion half cell**
$Cu^{2+}_{(aq)} + 2e- \longrightarrow Cu_{(s)}$;

**(v). Explanations:**
- Zinc rod has a higher tendency to ionize than the copper rod, when the metal rods are placed in solutions of their ions.
- Thus the zinc rod has a higher accumulation of electrons than the copper rod.
- This makes it more negative compared to the relatively more positive copper rod, which has a lower accumulation of electrons.
- On connecting the 2 half cells; **electrons will flow** form the **zinc rod** to the **copper rod** through the **external wire.**
- The copper rod gains the electrons lost by the Zinc rod.

**Roles of the slat bridge:**
Note: It forms a link between the 2 half cells, thereby completing the circuit
- It compete the circuit by:
1. Allowing its ions to carry charge from one half - cell to the other.

2. Maintaining the balance of charge in the two half-cells; by providing the ions which replace those used up at the electrodes.

- The overall reaction in the cells is a Redox reaction

**Half cell reactions:**

$Zn_{(s)} \longrightarrow Zn^{2+}{}_{(aq)} + 2e^-$ (oxidation)

$Cu^{2+}{}_{(aq)} + 2e- \longrightarrow Cu_{(s)}$; (reduction)

**Overall redox equation**



$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \longrightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)}$$

- The voltage of 1.10 V registered in the voltmeter is a measure of the difference between the electrode potential $(E^\theta)$ of Zinc and Copper electrodes, i.e. **the potential difference/ the Electromotive force.**
- Thus: **An electrochemical/ voltaic cell**;
  ➢ Is the combination of two half –cells to give a full cell capable of generating an electric current from a redox reaction.

**Cell diagram for a voltaic cell**
**Rules/conventions for cell representation**
1. A vertical continuous line (/); represents the metal-metal ion or metal ion-metal interphase.
2. Vertical broken line (ˊ); between the 2 half-cells; represents the salt bridge.

**Note**: The salt bridge may also be represented by two unbroken parallel lines (//).

**Example: - cell diagram for the above cell;**
$Zn_{(s)} / Zn^{2+}{}_{(aq)} \; ˊ \; Cu^{2+}{}_{(aq)} / Cu_{(s)}$;

**Alternatively:**
$Zn_{(s)} / Zn^{2+}{}_{(aq)} // Cu^{2+}{}_{(aq)} / Cu_{(s)}$;

**Electrode potential $E^0$, values of other metal – metal ions relative tot he Cu/Cu $^{2+}$ half cell**

| Metal / metal ion half cell | Electrode potential $E^0$ relative to $Cu^{2+}$ / Cu half cell |
| --- | --- |
| $Mg_{(s)} / Mg^{2+}{}_{(aq)}$ | +2.04 |
| $Zn_{(s)} / Zn^{2+}{}_{(aq)}$ | +1.10 |
| $Pb_{(s)} / Pb^{2+}{}_{(aq)}$ | +0.78 |
| $Cu_{(s)} / Cu^{2+}{}_{(aq)}$ | +0.00 |
| $Ag_{(s)} / Ag^+{}_{(aq)}$ | -0.46 |

**Positive and negative E values**

**(i). Positive E values -**
- If the $E^\theta$ value for a metal / metal ion is positive then the metal undergoes oxidation (loses electrons) while the reference electrode undergoes reduction (accepts electrons)

**Example**:
- The $E^\theta$ value for $Zn_{(s)}$ / $Zn^{2+}_{(aq)}$ relative $Cu^{2+}_{(aq)}$ / $Cu_{(s)}$ is positive because the zinc metal is oxidized to zinc ions while the copper ions are reduced to copper metal.

**(ii). Negative E values**:
- Implies that the reference half cell undergoes oxidation (donates electrons) while the other metal ions in the other half cell undergoes reduction (accepts electrons)

**Example**:
- The E value for $Ag_{(s)}$ / $Ag^+_{(aq)}$ is negative because Cu is more reactive than silver and gives out electrons (oxidation); while the less reactive Ag has its ions accepting electrons (reduction) to form Ag solid.

**(iii). The 0 (Zero) E value:**
- Always indicate the reference electrode / half-cell; in which case there would be no potential difference (with itself)

**Example:**
- The 2 half cells of $Cu_{(s)}$ / $Cu^{2+}_{(aq)}$ or $Cu^{2+}_{(aq)}$ / $Cu_{(s)}$ have no potential difference in between them hence a zero (0) E value.

**Note:**
1. - Any other element could be chosen as the reference electrode in place of copper Cu and difference electrode potentials values would be obtained for the same elements.

2. - The electrode potential of a single element is usually determined by measuring the difference between the electrode potential of the element and a chosen standard electrode.

3. - This gives the **standard electrode potential ($E^0$)** of the element.

**The standard electrode potential ($E^0$)**
**Definition**
- Is the potential difference for a cell comprising of a particular element in contact with 1 molar solution of its ions and the standard hydrogen electrode.
- It is denoted with the symbol $E^0$.

**Importance**
- It is useful in comparing the oxidizing and reducing powers of various substances.

**The standard Hydrogen Electrode**
- Is the hydrogen half-cell, which has been conventionally chosen as the standard reference electrode.
- It has an electrode potential of zero at:-
  ➢ A temperature of $25^oC$
  ➢ A hydrogen pressure of 1 atmosphere
  ➢ A concentration of 1M hydrogen ions

**Note:** The ions in the other half-cell must also be at a concentration of 1 molar.

**Components of the Hydrogen half – cell;**
- Consist of an inert platinum electrode immersed in a 1M solution of Hydrogen ions
- Hydrogen gas at 1 atmosphere is bubbled into the platinum electrode.
- The hydrogen is adsorbed into the platinum surface and an equilibrium (state of balance) is established between the adsorbed layer of molecular hydrogen and hydrogen ions in the solution.

**Equation:**

$\frac{1}{2} H_{2(g)} \rightleftharpoons H^+_{(aq)} + e^-$

**Platinised platinum**
- Is platinum loosely coated with finely-divided platinum.
- This enables it to retain comparatively large quantity of hydrogen due to its porous state.
- Platinised platinum also serves as a route by which electrons leave or enter the electrode.
- The hydrogen electrode is represented as: $H_{2(g)} / H^+_{(aq)}$; 1M

**Diagram: The standard hydrogen electrode:**

- The electrode potential of any metal is taken as the difference in potential between the metal electrode and the standard hydrogen electrode.

**Negative and positive electrode potentials**
**(a). Negative electrode potential**
- If the metal electrode has a higher/ greater tendency to loose electrons than the hydrogen electrode; then the electrode is negative with respect to hydrogen electrode; and its electrode potential is negative.

**Examples:** Zinc, Magnesium etc.

**(b). Positive electrode potential**
- If the tendency of an electrode to loose electrode is lower than the hydrogen electrode, then the electrode is positive with respect to the hydrogen electrode; and its potential is positive.

**Examples:** copper, silver etc

## Reduction potentials

- Is a standard electrode potential measured when the electrode in question is gaining electrons.
- The lower the tendency of an electrode to accept/ gain electrons; the lower (more negative) the reduction potential and vise versa.

## Examples:

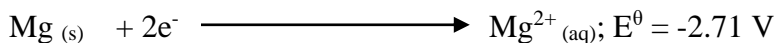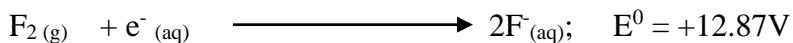$$K^+_{(aq)} + e_{(aq)} \longrightarrow K_{(s)}; \qquad E^0 = -2.92V$$

$$F_{2(g)} + e^-_{(aq)} \longrightarrow 2F^-_{(aq)}; \qquad E^0 = +12.87V$$

$$Mg_{(s)} + 2e^- \longrightarrow Mg^{2+}_{(aq)}; \quad E^\theta = -2.71\ V$$

- Thus potassium ions with $E^0 = -2.92V$ have a lesser tendency to gain electrons than magnesium ions.
- Thus Potassium is the weakest oxidizing agent; but the strongest reducing agent, since it has the greatest tendency to donate electrons.

## Note:
- Oxidation potentials will be the potentials of electrodes measured when they are losing electrons hence undergoing oxidation.

## Standard electrode potentials  reduction potentials) of some elements

| | Reduction equation | $E^\theta$volts |
|---|---|---|
| | $F_{2(g)} + 2e^- \longrightarrow 2F^-_{(aq)}$ | +2.87 |
| Most readily reduced → | $Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$ | + 2.87 |
| | $Br_{2(g)} + 2e \longrightarrow 2Br^-_{(aq)}$ | + 1.36 |
| | $Ag^+_{(aq)} + 2e^- \longrightarrow Ag_{(s)}$ | + 0.80 |
| | $I_{2(g)} + 2e^- \longrightarrow 2I^-_{(aq)}$ | + 0.54 |
| | $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ | + 0.34 |
| | $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ | + 0.00 |
| | $Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)}$ | - 0.13 |
| | $Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$ | - 0.44 |
| | $Zn^{2+}_{(g)} + 2e^- \longrightarrow Zn_{(s)}$ | - 0.76 |
| | $Al^{3+}_{(aq)} + 3e^- \longrightarrow Al_{(s)}$ | - 1.66 |
| | $Mg^{2+}_{(aq)} + 2e^- \longrightarrow Mg_{(s)}$ | - 2.71 |
| | $K^+_{(aq)} + e^- \longrightarrow K_{(s)}$ | - 2.92 |

*- Increasing strength of oxidizing agent*
*- Decreasing strength of oxidizing agent*

Least readily reduced →

## Note:
- The standard electrode potentials in the above table are reduction potentials.
- The greater the tendency to undergo reduction, the higher (more positive) the $E^\theta$ value.

- The reverse reaction (**oxidation**) would have a potential value equal in magnitude but opposite in sign to the reduction potential.

**Example**:
**Zinc**
**Reduction potential**

$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$;  $E^0 = -0.76V$;

**Oxidation potential**

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$; $E^\theta = +0.76V$;

**Uses of $E^0$ values**
1. Comparing the reducing powers and oxidizing powers of various substances;
2. Predicting whether or NOT a stated **REDOX** reaction will take place.

**The $E^0$ value for a REDOX reaction**
- Is usually calculated as the sum of the $E^0$ value for the half cells involved.

Note:
- If the sum is **positive** then the reaction can occur simultaneously;
- If the value of the sum is **negative** the reaction cannot occur;

**Sample calculations**
**1. Cu $^{2+}$ can oxidize Zinc but Zn $^{2+}$ cannot oxidize Cu;**

(a). Cu $^{2+}$/ Cu // Zn / Zn$^{2+}$

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$; $E^0 = +0.34$ V
$Zn_{(s)} \longrightarrow 2e^- + Zn^{2+}_{(aq)}$; $E^0 = +0.76$ V
$\overline{\overline{Cu^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn_{(aq)}}}$; $E^0 = -1.10$ V

- The overall reaction is positive, hence zinc can be oxidized by copper (II) ions, and hence reaction occurs;

(b). Zn $^{2+}_{(aq)}$ / Zn $_{(s)}$ // Cu $_{(s)}$ / Cu $^{2+}_{(aq)}$

$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$; $E^0 = -0.76$ V
$Cu_{(s)} \longrightarrow 2e^- + Cu^{2+}_{(aq)}$; $E^0 = -0.34$ V
$\overline{\overline{Zn^{2+}_{(aq) +} Cu_{(s)} \longrightarrow Zn_{(s)} + Cu^{2+}_{(aq)}}}$ ; $E^0 = -1.10$ V

- The overall $E^0$ is negative; thus Zn $^{2+}$ cannot oxidize Cu to Cu$^{2+}$ (Cu cannot reduce Zn $^{2+}$ to Zn); and hence the reaction cannot occur.

2. Can chlorine displace bromine form bromide solution?

**Cell diagram**: $Cl_{2(g)}$ / $Cl^-_{(aq)}$ // $2Br^-_{(aq)}$ / $Br_{2(g)}$

$$Cl_{2\ (g)} + 2e^- \longrightarrow 2Cl^-_{\ (aq)}; E^0 = +1.36 \text{ V}$$
$$2Br^-_{\ (aq)} \longrightarrow 2e^- + Br_{2\ (g)}; E^0 = -1.09 \text{ V}$$

$$Cl_{2\ (g)} + 2Br^-_{\ (aq)} \longrightarrow 2Cl^-_{\ (aq)} + Br_{2\ (g)}; E^0 = +0.27 \text{ V}$$

- The overall $E^0$ for the reaction is positive, so chlorine can displace bromine from a bromide solution.

**Worked examples**

1. The diagram below represents part of the apparatus to be used for the determination of the standard electrode potential of Aluminum, $E^\theta\ Al^{3+}_{\ (aq)}/Al_{\ (s)}$

*(a). Name the solutions which could be placed in beakers A and B; specifying their concentrations.*
**Answer:**
- In beaker A; 1 M HCl $_{(aq)}$ i.e. any solution with 1 M hydrogen ions
- In beaker B; 1 M Al (NO₃) $_{(aq);}$ i.e. any aqueous solution with 1M $Al^{3+.}$

*(b). One essential part of the cell has been omitted. Name the missing part and give its functions.*
**Answer:-**
**Missing part**: salt bridge
**Function:** completes the circuit by;
1. Allowing its ions to carry charge form one half cell to another.
2. Providing ions which repose those used up of the electrodes, hence maintaining a balance of charge in the 2 half – cells.

*(c). The voltmeter reading was found to be –1.66 V.*
*(i). Give the standard electrode potential for the aluminum electrode.*
**Solution:** it is -1.66 since the Hydrogen-hydrogen ions half-cell = 0.00V.

*(ii). Show the direction of flow of electrons in the circuit;*

**Solution:** From $Al^{3+}$ / Al half cell to the $H_2$ / $2H^+$ (aq) half cell

*(d). Give the half-cell equations and the overall cell equation*
**Solution:**

$3H^+$ (aq) $+ 3e^- \longrightarrow 1\frac{1}{2} H_2$ (g); $E^0 = + 0.00V$;

$Al$ (s) $\longrightarrow 3e^- + Al^{3+}$ (aq); $E^0 = + 1.66V$;

**Overall:**

$Al$ (s) $+ 3H^+$ (aq) $\longrightarrow Al^{3+}$ (aq) $+ 1\frac{1}{2}H_2$ (g); $E^0 = +1.66$ V

*2. You are given the following half-equations;*
$Mg^{2+}$ (aq) $+ 2e$- $\longrightarrow Mg$ (s); $E^\theta = - 2.71$ V
$Zn^{2+}$ (g) $+ 2e$- $\longrightarrow Zn$ (s); $E^\theta = - 0.76$ V

*(i) (a). Obtain an equation for the cell reaction.*

$Mg$ (s) $\longrightarrow 2e^- + Mg^{2+}$ (aq); $E^0 = +2.71V$

$Zn^{2+}$ (aq) $+ 2e^- \longrightarrow Zn$ (s); $E^0 = - 0.76V$

$Mg$ (s) $+ Zn^{2+}$ (aq) $\longrightarrow Mg^{2+}$ (aq) $+ Zn_{(s)}$; $E^0 = +1.95V$

**Thus equation:**
$Mg$ (s) $+ Zn^{2+}$ (aq) $\longrightarrow Mg^{2+}$ (aq) $+ Zn_{(s)}$; $E^0 = +1.95V$

*(b). Calculate the $E^0$ value for the cell.*
$Mg$ (s) $\longrightarrow 2e^- + Mg^{2+}$ (aq); $E^0 = +2.71V$

$Zn^{2+}$ (aq) $+ 2e^- \longrightarrow Zn$ (s); $E^0 = - 0.76V$

$Mg$ (s) $+ Zn^{2+}$ (aq) $\longrightarrow Mg^{2+}$ (aq) $+ Zn_{(s)}$; $E^0 = +1.95V$

*(c). Give the oxidizing species.*
**- Reducing species**
Magnesium i.e. The species that undergoes oxidation since its oxidation number increases (from 0 to 2); as it reduces the other;

**- Oxidizing species**
Zinc/Zinc ions; - the species that undergoes reduction; since its oxidation number decreases (from 2 to 0) as it oxidizes the other species (Mg).

*3. Given the following half-equations*
$I_2$ (g) $+ 2e$- $\longrightarrow 2I^-$ (aq); $E^\theta = + 0.54V$
$Br_2$ (g) $+ 2e$- $\longrightarrow 2Br^-$ (s); $E^\theta = +1.09$ V

*(a). Obtain an equation for the all reaction*

$$2I^-_{(aq)} \longrightarrow 2e^- + I^2_{(g)}; E^0 = -0.54V$$

$$Br_{2(g)} + 2e^- \longrightarrow 2Br^-_{(s)}; E^0 = +1.09V$$

$$Br_{2(g)} + 2I^-_{(aq)} \longrightarrow 2Br^-_{(aq)} + I_{2(g)}; E^0 = +0.55V$$

*(b). Calculate the $E^0$ value for the cell*

$$2I^-_{(aq)} \longrightarrow 2e^- + I^2_{(g)}; E^0 = -0.54V$$

$$Br_{2(g)} + 2e^- \longrightarrow 2Br^-_{(s)}; E^0 = +1.09V$$

$$Br_{2(g)} + 2I^-_{(aq)} \longrightarrow 2Br^-_{(aq)} + I_{2(g)}; E^0 = +0.55V$$

*(c). Give the oxidizing species;*



$$Br_{2(g)} + 2I^-_{(aq)} \longrightarrow 2Br^-_{(aq)} + I_{2(g)}; E^0 = +0.55V$$
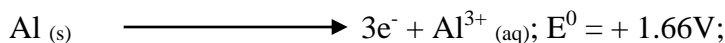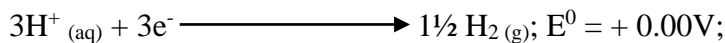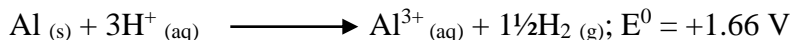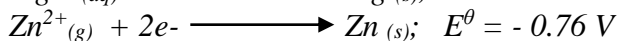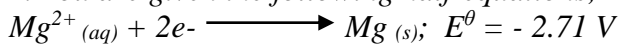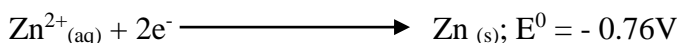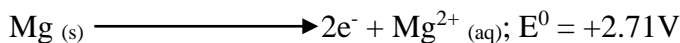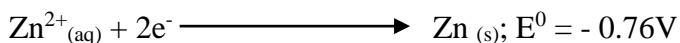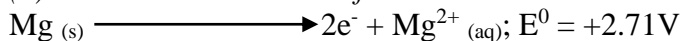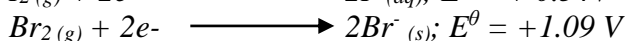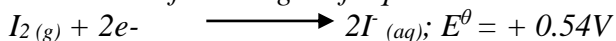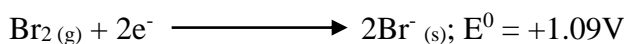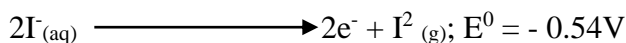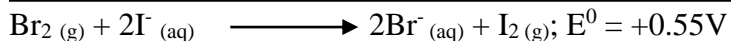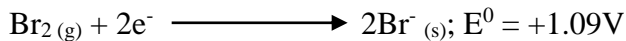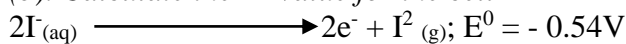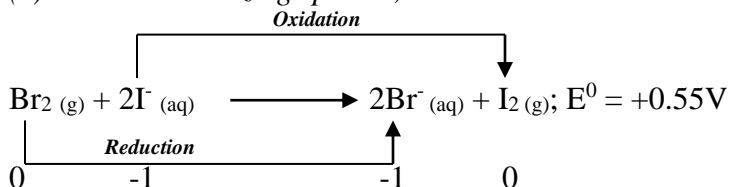
**Oxidizing species**: Bromine; $Br_{2(aq)}$

*4. Consider the following list of electrodes and electrode potential values.*

| Electrode reaction | $E^\theta$ volts |
|---|---|
| $A^{2+}/A$ | +0.34 |
| $B^{2+}/B$ | -0.71 |
| $C^{2+}/C$ | -0.76 |
| $D^+/D$ | +0.80 |
| $E^{2+}/E$ | -2.87 |
| $F^{2+}/F$ | -2.92 |

*(a). Which of the ions is the strongest oxidizer?*
$D^+$; because it is most readily reduced/ have the highest tendency to accept electrons as evidenced by its highest positive $E^\theta$ value when the ions change to element ($D^+/ D^-$)

*(b). Which of the ions is the strongest reducer?*
- Is least readily reduced hence lowest $E^0$ value (-2.92 V); accepts electrons least readily i.e. shows the lowest $E^0$ when its ions gain electrons/ are reduced ($F^+/ F$, = -2.92 V)

*5. The following is a list of reduction standard electrode potentials.*

| Metal | $E^\theta$ volts(standard electrode potential) |
|---|---|
| Magnesium | -2.36 |
| Zinc | -0.76 |
| Iron | -0.44 |
| Hydrogen | 0.00 |
| Copper | +0.34 |
| Silver | +0.79 |

*(a). Which **two** metals, if used together in a cell would produce the largest e.m.f?*

Magnesium-silver cell;

$Mg^{2+}_{(aq)} + 2e^- \longrightarrow Mg_{(s)}$; $E^\theta = -2.36$ V
$2Ag^+_{(g)} + 2e^- \longrightarrow 2Ag_{(s)}$; $E^\theta = -0.79$ V

Thus;

$Mg_{(s)} \longrightarrow 2e^- + Mg^{2+}_{(aq)}$; $E^0 = +2.36V$

$2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)}$; $E^0 = -0.79V$

$Mg_{(s)} + 2Ag^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + 2Ag_{(s)}$; $E^0 = +3.15V$
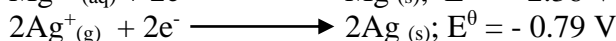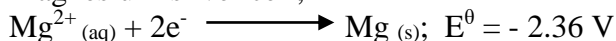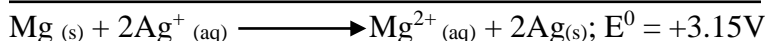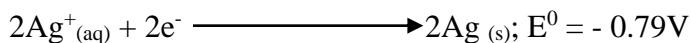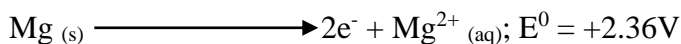
*(b). What would be the voltage produced by:-*
*(i). Zinc-copper cell*

$Cu^{2+}_{(aq)} + 2e- \longrightarrow Cu_{(s)}$; $E^\theta = +0.34$ V
$Zn^{2+}_{(g)} + 2e- \longrightarrow Zn_{(s)}$; $E^\theta = -0.76$ V

Thus; $Zn_{(s)} / Zn^{2+}_{(aq)} // Cu^{2+}_{(aq)} / Cu_{(s)}$;

$Zn_{(s)} \longrightarrow 2e^- + Zn^{2+}_{(aq)}$; $E^0 = +0.76V$

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$; $E^0 = +0.34V$

$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$; $E^0 = +1.10V$

*(ii). Copper-silver cell*

$Cu^{2+}_{(aq)} + 2e- \longrightarrow Cu_{(s)}$; $E^\theta = +0.34$ V
$Ag^+_{(g)} + 2e- \longrightarrow Ag_{(s)}$; $E^\theta = +0.79$ V
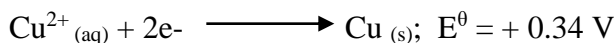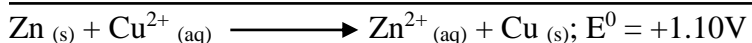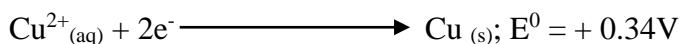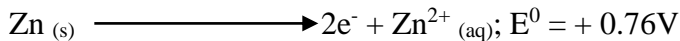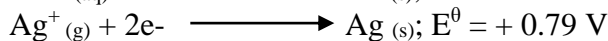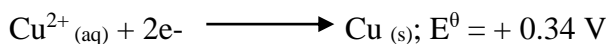
**Thus;** $Cu_{(s)} / Cu^{2+}_{(aq)} // 2Ag^+_{(aq)} / 2Ag_{(s)}$;

$Cu_{(s)} \longrightarrow 2e^- + Cu^{2+}_{(aq)}$; $E^0 = -0.34V$;

$2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)}$; $E^0 = +0.79V$;

$Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$; $E^0 = +0.45V$
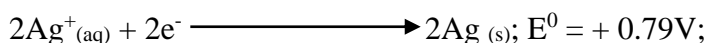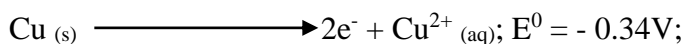
*(c). Explain the meaning of the positive and negative signs;*

**Positive signs**
- The metal in question has a lower tendency to loose electrons than hydrogen hence more relatively positive to hydrogen;
- They are stronger oxidizing agents but weaker reducing agents but weaker reducing agents than hydrogen;

**Negative signs**
- The particular metal has a higher tendency to loose electrons than hydrogen; hence relatively more negative than hydrogen.
- They are weaker oxidizing agents but stronger reducing agents than Hydrogen.

6. The following are some half-cell electrode potentials of some elements.


Reaction

(a). Select two half cells which when oxidized give the burst E value; and fill the cell representation.
Solution:     The silver – copper cell; i.e.
                    Cell representation

(b). Calculate the $E^0$ value

(c). Give the strongest reducing agent and strongest oxidizing agent.

       Strongest reducing agent
       Strongest oxidizer     -     silver   -     has highest reduction potential

7. Study the table below and answer the questions that follow.
(a). Which two metals would form a metallic couple with the highest EMS.

(b). Calculate the e.m.f. of the cell that would be produced by (i) above.

(c). Write down the cell representation for the cell above.

(d). Which metal is the strongest reducing agent in the above list
       Metal A          -          have the lowest reduction potential.

8 (a). The table below gives reduction potentials obtained when the half-cells for each of the metals represented by letters J, K, L, M and N where connected to a copper half- cell as the reference electrode.


(i). What is metal L likely to be?  Give a reason

       Copper          It has an $E^0$ value/ reduction potential of 0.00, with copper as the
       reference electrode

(ii). Which of the metals cannot be displaced from the solution of its salt by any other metal in the table?  Give a reason.

       **Metal J:**     Has the lowest reduction potential; meaning it least readily accepts
       electrons (most readily donates electrons) than any other metal.

(iii). Metal K and M were connected to form a cell as shown in the diagram below;

I. Indicate on the diagram, the direction of flow of electrons.  Explain.
from K to M.
K is a stronger reducing agent than M, as evidenced by its lower reduction potential.
It thus loses electrons faster becoming more Negative than M; hence electrons move from K through  external wires to M.

II. Write the equations for the half-cell reactions that occur at:-
   **Metal K electrode:-**
   **Metal M electrode**

III. If the slat bridge is filled with saturated sodium Nitrate solution, explain how it helps to complete the circuit.

Answer
It allows its ions ($Na^+_{(aq)}$ , and $No^{-3}_{(aq)}$ ) to carry charge from one half cell to another. Providing ions which replace those used up at the electrodes.

**VOLTAIC CELLS**
- Are also called electrochemical cells.
Are cells in which electrical energy is generated from chemical reactions.

**Types of electrochemical cells**
**(i). Primary cells -**
Electrochemical cells which are not rechargeable

**(ii). secondary cells-**
- Voltaic/electrochemical cells which are rechargeable.

**1. Primary cells/dry cells:**
- Are of various types and an example is the Le' clanche dry cell.

<div align="center">The Le'clanche dry cell</div>

**i)  Structure**

-  Consist of a Zinc can with carbon rod at the centre.
-  The central graphite/carbon rod is surrounded by powdered Manganese (IV) oxide and carbon; which are inturn surrounded by a paste of NH4Cl (s)  and Zinc Chloride.
-  The protruding portion of the carbon rod is covered with a brass cap; and the zinc can covered with a sealing material.

**Chemical reaction**
-  The Zinc  can is the negative terminal; while the carbon/graphite rod is the positive terminal;
a)  a the Zinc can/negative terminal
b)  positive  terminal /brass cap

Hydrogen gas
       $(NH_3 (g) + 2e^-$       $2NH_3 (g) + H_2 (g)$
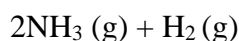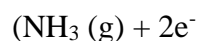
**Note:** These gases ($NH_{3\ (aq)}$ and $H_{2\ (g)}$) are NOT used immediately but are used in more complex reactions.

- The ammonia gas forms a complex with the zinc chloride in the paste.
- The hydrogen gas is oxidised to water by the Manganese (IV) oxide.

**Functions of the various components.**

a)   Brass cap   -   Functions as the positive terminal where the reduction reaction occurs.

b)   Zinc can   -   Is the Negative terminal; where the oxidation reaction occurs.

c)   Carbon rod   -   It serves as the positive electrode.
     -   Acts as the connecting wire between the positive and negative terminal through it electron flow form the Zinc can to the brass cap.

d)   Manganese (IV) Oxide   -   To oxidise the Hydrogen gas produced at the anode/positive terminal/brass cap to water.

-   A single dry cell can produce a potential of 1.5 V

**Note:** Dry ammonium chloride does not conduct electric current.  This explains why a paste, which is a conductor, is used.

The dry cells cannot provide a continuous supply of electricity for an undulate period of time.

**Reason**   -   The reactants (electrolytes) are used up and cannot be replaced.

**1.   Secondary cells**

Are voltaic/electrochemical cells that are rechargeable.
A common example is the lead – acid accumulator.

The lead – acid accumulator.

Structure:   -   The positive plate is a lead grill filled with lead (IV) oxide; while the negative plate consists of a similar lead grill filled with spongy lead.

-   The grills are immersed in sulphuric acid; which serves as the electrolyte.

**Reactions**

i)   During discharge/when in use
-   At the negative terminal/lead -   The lead dissolves forming lead (II) ions

     **equation**

-   At the positive terminal (lead (IV) oxide.
     Lead (IV) oxide reacts with the Hydrogen ions ($H^+$) in sulphuric acid; also forming lead (II) ions.
     Then; the lead (II) ions formed at both electrodes react instantly with the Sulphate ions to form lead (II) Sulphate.

-       The  insoluble lead Sulphate adheres to the electrodes.

        Overall reaction

**Note**:   The Lead Sulphate should NOT be left for too long to accumulate on the electrodes

**Reason**:         The fine $PbSO_{4 (s)}$ will charge to coarse non – reversible and inactive form and            the accumulator will become less efficient.
-       During use/discharge; the lead and the lead (IV) oxide are depleted, and the concentration of sulphric acid declines.

ii)     During recharging     -       Is usually done by applying a suitable voltage to the terminals of the    cell.
                              -       At the negative  terminal     -       the lead ions accept  electrons to form lead solid.

**Overall reaction**

This process restores the original reactants.


# ELECTROLYSIS

## Defination

Is the decomposition of molten or aqueous solutions by passage of electric current through it.

Terminologies used in electrolysis
**i)**     **Electrolyte**
-       Is a solution which allows electric current to pass through while it gets decomposed.
        -       Electric current transfer in electrolyte occur through ions.
        -       The electrolyte can be aqueous solutions or molten solutions
        -       Electrolyte with may ions are called strong electrolyte; while those with few ions are called weak electrolytes.

## Examples

ii)     **Electrodes**    -       Are the solid conductors, usually roots, which usually complete the circuit between electrolytes and cell/battery
                          -       Are of two types

        a)      **Anode** -     The electrode connected to the positive terminal f a battery/cell
        b)      **Cathode**-    Electrode connected to the negative terminal of the battery/cell.

**Note:**  Graphite rods are commonly preferred as electrodes in most access.
**Reasons:**     They are inert/unreactive
                 Are cheap
        -       Platinum is also relatively inert;  but not less preferred  to Graphite because its expensive.


**Preferential discharge  of ions**

- The products of electrolysis of any given electrolyte depend on the ions present in an electrolyte.
- Commonly most molten electrolytes have only two ions; a cation and an anion and are termed Binary electrolytes.
- As the electrolyte decomposes, ions collect/move to the opposite poles.
- Negatively charged ions move to the Anode; the positive electrode, while the positively charged ions move to the cathode, the negative electrode;
- Regardless of how many ions move to an electrode; only one can be discharged ot give a product.
- Both cations and anions have a preferential discharge series.

**a)** **Discharge for cations**

Cations are discharged by reduction (accepting electrons) to form their respective products.

The ease of reduction of cations depends on their position of electrochemical series.

Thus $Ag^+$ is most readily discharged as it's the weakest reducing agent.

**b)** **Discharge for anions**

Anions are discharged by oxidation (electron loss) to form their respective products.

Discharge of anions is viz.

**ELECTROLYSIS OF VARIOUS SUBSTANCES**

1. Electrolysis of various substances
i) Apparatus.

ii) Procedure    -    An electric current is passed through the dilute sulphuric acid.

iii) Observation

**At the Anode**
- A colourless gas; collects
- The gas collected relights a glowing splint; and its volume is half the volume of the gas at cathode. The gas is oxygen.

**At the cathode**
- A colourless gas collects
- The collected gas burns with a pop-sound; and its volume is double the volume of gas at the anode.
- The gas is Hydrogen gas.

i) **Explanations** -    Ions present in the electrolyte
i) Hydrogen ions and Sulphate ions form sulphuric acid.
ii) Hydrogen ions and hydroxide ions from water.

**At the Anode (Positive electrode)**

- The negatively charged Sulphate ions and hydroxide ions migrate to the anode.

**Reason:** $OH^-_{(aq)}$ ions have a greater tendency to loose electrons than the $SO_2^{-4}{}_{(aq)}$ ions

Anode equation


At the cathode (positive electrodes)   -   The positively charged hydrogen ions migrate to the cathode.

Equation


**Note:**

1.   The volume of oxygen produced at the anode is half the volume of hydrogen produced at the cathode.

   **Reason:**   The 4 electrons lost by the hydroxide ions to form 1 mole (1 volume) of   oxygen molecules are gained by the four hydrogen ions which form 2   molecules (2 volumes) of hydrogen  molecules.

2.   During the electrolysis, the concentration of the electrolyte ($H_2SO_4$ (aq), increases

   **Reasons:**   The volumes of hydrogen and oxygen gas liberated are in the same ratio   as they are combined in water.

   Thus the amount of water in the electrolyte progressively decrease; hence the increased electrolyte concentration.

**Conclusion**

Electrolysis of dilute sulphuric acid is thus the electrolysis of water.

Note:  The Hoffmans voltmeter can be used instead of the circuit above.  Viz.



Electrolysis of dilute sodium chloride

i)   Apparatus



ii)   Procedure
   -   An electric  current is passed through dilute sodium chloride solution; with carbon rods    as the electrodes.
   -   Gases  evolved of each  electrode  are collected and tested.

iii)   Observations

- At the anode:
  - A colourless gas is collected
  - The gas relights a glowing splint, and its volume is half the volume of the gas collected at the cathode.
  - The gas is Oxygen, $O_2$

- At the Anode
  - A colourless gas collects
  - The gas burns with a pop sound; and its volume is twice the volume of the gas collected at the anode.
  - The gas is hydrogen gas;

iv)    Explanations
  - The Ions present in the electrolyte

**a)    At the Anode**
  - $Cl^-$ and $OH^-$ migrate to the anode
  - OH- are preferentially discharged – coz they have greater tendency to lose electrons than the chloride ions; - the $OH^-_{(aq)}$ lose electrons to form water and $O_{2\ (g)}$ at anode.

  **Anode equations**

**b)    At the Cathode**
  - The positively charged $Na^+_{(aq)}$ , and $H^+_{(g)}$ migrate to the cathode
  - the $H^+_{(aq)}$ are preferentially discharged.

**Reason:**    They $H^+_{(aq)}$ have a greater tendency to gain electrons than Na+ (aq) ions
The $H^+_{(aq)}$ gain elect5rons to form Hydrogen atoms (H) which ten form molecules of hydrogen which bubble off at the electrode.

**Cathode equations**

**ii)    Conclusion**
Ratio of the volumes of $H_{2\ (g)}$ and $O_{2\ (g)}$ evolved at cathode and anode is 2:1 respectively.

Electrolysis f dilute NaCl is thus the electrolyze of water since only water is decomposed.

3.    Electrolysis of Brine/concentrate sodium chloride.

i)    Apparatus

ii)    Procedure
An electric current is passed though concentrated sodium chloride/brinc

iii)    Observation
**a)**   **At the Anode**
-          A greenish – yellow gas is evolved.
-          The gas has a pungent irritating smell; and its volume is equal to the volume of the gas evolved
           at he cathode.
-          The gas is chlorine $Cl_{2\ (g)}$

**b)**   **At the Cathode**
-          A colourless gas is liberated
-          The gas burns with a pop sound; and its volume is equal to volume of gas evolved at the anode.
-          The gas is Hydrogen gas; $H_2$ (g)

**iv)**   **Explanations**
-          The ions present in the electrolyte are:-
           -          $Na^+_{\ (aq)}$ and $Cl^-$ from sodium chloride
           -          $H+_{\ (aq)}$ and $OH-_{\ (aq)}$ from water.

a)      At the Anode
-          $Cl^-_{\ (aq),}$ and $OH^-_{\ (aq)}$, migrate to the anode
-          The chloride ions are preferentially discharged.

         Reason;        -          $OH^-_{\ (aq)}$ have higher tendency to lose electrons than $Cl^-$ ions.
                        -          However coz of the higher concentration $Cl^-_{\ (aq)}$ , relative to $OH^-_{\ (aq)}$, the $Cl^-_{\ (aq),}$
                                   are preferentially discharged hence the evolution of Chlorine gas.

b)      A the Cathode
-          $Na^+_{\ (aq)}$ and $H^+_{\ (aq)}$ migrate to the cathode.
-          H+ with a higher tendency to gain electrons are preferentially discharged; hence the evolution of
           hydrogen gas at the cathode.

**NB:**   1.      The pH of the electrolyte becomes alkaline/increases with time.

         **Reason:**      The removal of $H^+_{\ (aq)}$ which come form water leaves excess
         hydroxide ions  $(OH^-_{\ (aq),}$ hence the alkalinity.

         2.      Evolution of chlorine gas at anode soon stops after sometime and is replaced by $O_{2\ (g)}$

         **Reason:**      Evolution of $Cl_{2\ (g)}$ decrease/lowers the concentration of $Cl^-_{\ (aq)}$ in                    the
         electrolyte.

                  As soon as the $Cl^-_{\ (aq)}$ concentration becomes equal to that of $OH^-_{\ (aq)}$

**The mercury cathode cell**

Is an electrolytic arrangement commonly used for the large scale manufacture of chlorine and sodium
hydroxide.

**i)**    **Apparatus**
-          Electrolyte in the mercury cell is Brine (concentrated NaCl)
-          Anode is carbon or titanium
-          Cathode is a moving mercury film.

**ii)      Reactions**
a)      At the Anode
-          Both Chloride and Hydroxide ions are attracted
-          Due to their high concentrations the chloride ions are preferentially discharged.
-          The $Cl^-_{(aq)}$ lose electrons to form Chlorine gas. (greenish yellow)

b)      Cathode (moving mercury)
-          The $Na^+_{(aq)}$ and $H^+_{(aq)}$ are attracted
-          The discharge of $H^+_{(aq)}$ is more difficult than expected
-          Hydrogen has a high over voltage at the  moving mercury electrode and so sodium is discharged.

**Equation**

-          The discharged sodium atoms combine with mercury to form sodium amalgam

**Equation**

-          The sodium amalgam reacts with water to form sodium hydroxide, hydrogen and mercury.

Equation

-          Hydrogen is pumped out while the Mercury is recycled.
-          The resultant NaOH is of very high party.


**Limitations/disadvantages of the Mercury Cathode cell.**

1.      Its expensive due to the high cost of mercury.
2.      Pollution form Mercury; i.e. Mercury is poisonous and must be removed from  the effluent.


4.      Electrolysis  of Copper (II) Sulphate solution.

NOTE:         The products of electrolysis of copper (II) Sulphate solution depends on the nature of the elctrodes used.

i)      Apparatus



ii)      Ions present in the elctrolyte:
-          From  copper (II)  Sulphate

-          From  water

-          During electrolysis

a)      Using carbon/platinum electrodes

iii)    Observations

a)    At  the Anode:
    -        A colourless gas is liberated
    -        The gas relights a glowing splint; hence its oxygen.

b)    **At the cathode**
    -        A reddish – brown coating (of Cu solid) is deposited.

c)    **In the electrolyte**
    -        The blue colour of the solution ($CuSO_4$) $_{(aq)}$ / becomes pale and finally colourless after a long time.

**Reason**:        The blue colour is due to Cu2+.  As the $Cu^{2+}$ $_{(aq)}$ are continuously being discharged at the cathode; the concentration of $CU^{2+}$ decreases i.e. decrease in        the concentration of $Cu^{2+}$ $_{(aq)}$ in the solution

            The electrolyte become acidic/pH decreases (declines)

**Reason:**        Accumulation of $H^+$ $_{(aq)}$ in the solution since only $OH^-$ (from water) are being discharged (at the anode).

iv)    **Explanation**

**At the anode**

-        The $SO^{2-}_{4\ (aq)}$ and $OH^-$ $_{(aq)}$ migrate to the anode.
-        The hydroxide ions have a higher tendency to lose electrons than the  $SO^{2-}_{4\ (aq)}$
-        They ($OH^-$) easily loose electrons to form the neutral and unstable hydroxide radical ($OH^-$)
-        The hydroxide radical (OH) decomposes to form water and Oxygen.

**At the cathode**
-        Copper ions and $H^+$ $_{(aq)}$ migrate to the cathode
-        $Cu^{2+}$ $_{(aq)}$ have a greater tendency to accept electrons than $H^+$ $_{(aq)}$
-        The $Cu^{2+}$ $_{(aq)}$ are thus reduced to form copper metal which is deposited as a red-brown coating on the cathode.

    **Cathode equation.**

b)    **Using copper rods electrodes**

i)    observations

    At the anode   -        Mass of the anode (Copper anode) decreases

    At the cathode -        reddish – brown deposit
    -        cathode increases in mass

Electrolyte – no apparent change

Note:   The gain in mass of the cathode is equal to the loss in mass of the anode.

**Explanations**

**At the anode**
-        The $SO_4^{2-}{}_{(aq)}$ and $OH^-{}_{(aq)}$ are attracted to the anode.
-        However, none of them is discharged;
-        Instead; the copper anode itself gradually dissolves; hence the loss in mass of the anode;

**Reason:**        it's easier to remove electrons form the copper anode itself than format the hydroxide ions

**At the cathode**

-        $H^+{}_{(aq)}$ migrate to the cathode
-        The $Cu^{2+}{}_{(aq)}$ are preferentially discharged;  because they have a greater tendency to accept electrons
-        The copper cathode is thus coated with a  reddish brown deposit of copper metal hence increase in mass.

Cathode equation

Factors affecting electrolysis  and electrolytic products.

1.        Electrochemical series
         -        Electrolytic products at the anode and cathode during electrolysis depends on its position in the Electrochemical series.

**Cations:**        The higher  the cation in the electrochemical series; the lower the tendency of discharge at the cathode.

**Reason:**        Most electropositive cations require more energy in order to be reduced and therefore are more difficult to reduce.

**Reduction order**

**Anions:**        Discharge is through oxidation ad is as follows.

**2.        Concentration of electrolytes**
         A cation or anion whose concentration is higher is preferentially discharge if the ions are close in the electrochemical series.

         **Example**:  dilute and concentrated NaCl

         **Product at the anode**.

3.       **The electrodes used:** Products obtained at electrodes depend on the types of electrodes
         used

         **Examples:**      in the electrolysis of $CuSO_{4 (aq)}$ using carbon and copper rods separately.

# APPLICATIONS OF ELECTROLYSIS

1.       **Extraction of reactive metals**

         Reactive metals/elements like sodium, magnesium, aluminum are extracted form their compounds by
         electrolysis.

         **Example**:       Sodium is extracted from molten sodium chloride using carbon
                   electrodes.

2.       **Purification of metals**

         It can be used in refining impure metals

         **Examples:**      Refining copper

         -        The impure copper is made of the anode.
         -        Their strips of copper are used as the  cathode
         -        Copper (II) Sulphate are used as the electrolyte.

-        During the electrolysis the anode dissolves and pure copper is deposited on the cathode.

-        The impurities (including valuable amounts of silver and gold) from the crude copper collect as a sludge
         become the anode.

3.       **Electroplating**

         Is the process of coating one metal with another, using electrolysis so as to reduce corrosion or to
         improve its appearance.

         During electrolysis:
         -        the item to be electroplated is made the cathode
         -        the metal to be used in electroplating is used as the anode
         -        the electrolyte is made from a solution containing the ions of the metal to be sued in
                  electroplating.

**Examples**
         -        Gold-plated watches; silver – plated utensils
         -        Steel utensils marked EPNS. I.e. Electroplated Nickel Silver.

4.       **Anodizing Aluminum**

Is the reinforcement of the oxide coating on Aluminum utensils/articles
Is done by electrolysis of dilute sulphuric acid using Aluminum articles as anode.

**Importance:** Prevention arrosion of Aluminum articles

## 5. Manufacture of sodium hydroxide, chlorine and hydrogen

- Sodium hydroxide is prepared by the electrolysis of brine, for which 3 methods are available
- The method depends o the type of electrolytic cell.
- These cells are
    - The mercury cell
    - The diaphragm cell
    - The membrane cell

## a) The mercury cell

- **Components**
    - The electrolyte is concentrated sodium chloride
    - The anodes are made of graphite or titanium, which are placed above the cathode.
    - The cathode consists of mercury, which flows along the bottom of the cell.

## Chemical reactions

## Anode

- Both chloride and hydroxide ions are attracted.
- Chloride ions are preferentially discharged due to their high concentration
- The chloride ions undergo oxidation to form green – yellow chlorine gas.

## Equation

## At the cathode (flowing mercury)
- $Na^+_{(aq)}$ migrate to the cathode
- Sodium ions are preferentially discharged.
- They undergo reduction to form sodium solid.

## Equation

- the discharged sodium atoms combine with mercury to form sodium diagram

## Equation

- The sodium amalgam is then passed into another reactor containing water.
- The amalgam reacts with water forming hydrogen and sodium hydroxide.

## The mercury is regenerated and it is recycled into the main cell.
- **Main product:**          Sodium hydroxide
- **By products:**          Sodium and chlorine.

**Advantages of mercury cathode cell**
- The resultant sodium hydroxide is very pure; as it has no contamination from sodium chloride.
- It is highly concentrated; i.e. about 50%.

**Disadvantages**
- Some of the mercury said its way into the environment leading to mercury pollution; a common case of brain damage in humans.
- At the operating temperatures ($70^0C - 80^0C$), mercury vapours escape into the atmosphere and cause irritation and destruction of lungs tissues.
- Its operation requires highly skilled man power.

**b) Diaphragm cell**

Components
- An asbestos diaphragm; to separate the electrolytic cell into two compartments; thus preventing mixing of $H_2$ and $Cl_2$ molecules
- The anode compartment contains a graphite rod.
- The cathode compartment contains a stainless steel cathode.

**Diagram**

**Chemical reactions**
- The asbestos diaphragm is permeable only to ions, but not to the hydrogen or chlorine molecules.
- It thus prevents $H_{2\,(g)}$ and $Cl_{(g)}$ form mixing and reacting to yield $HCl_{(g)}$
    - It also separates NaOH and Cl2 which would otherwise react.

**Chemical reactions**

**At the anode**
- Chloride ions undergo oxidation to form chlorine gas.

**Equation**

- At the cathode
    - H= and $Na^+$ (a) migrate to the cathode compartment.
    - The $H^+$ are preferentially discharged.
    - They ($H^+_{(aq)}$) undergo reduction to form hydrogen gas.

    **Equation**

    - the discharge of H+ causes more water molecules to dissociate, thus increasing the concentration of OH- in the solution.
    - therefore, the Na+ and OH- ions also react in the cathode compartment to form sodium hydroxide.

**Equation**

**Advantage**
- Does not result into pollution

**Disadvantage**
- The resultant NaOh is dilute (12% NaOH)
- It is also not pure due to contamination with NaCl – (12% NaOH + 15% NaCl by mass.

**Note: -** The concentration of the NaOH can be increased by evaporating excess water, during which NaCl with a lower solubility crystallizes out first, leaving NaOH at a higher concentration.
- The solid NaCl (Crystals) are then filtered off.
- This is a case of **fractional crystallization**.

**c) The membrane cell**
- Is divided into 2 compartments by a membrane
- Most commonly used type of Membrane is the cation – exchange membrane.
- This membrane type allows only cations to pass through it.

**Components**
- A cation exchange that divides the cell into 2 compartments; an anode and a cathode compartments.
- Both electrodes are made of graphite
- The electrolyte in the anode compartment is purified brine
- The electrolyte in the cathode compartment is pure water.

**Diagram**

Chemical reactions

**The anode**

Chloride ions undergo oxidation to form green – yellow chlorine gas.

**The cathode**

As current passes through the cell H+ and Na+ pass across the membrane to the cathode
- H+ are preferentially discharged.
- They undergo reduction to liberate hydrogen gas.

- Continuos discharge of H+ leaves the OH- at a higher concentration

- The OH- react with Na+ to form sodium hydroxide

**Advantages**

1. Resultant sodium hydroxide is very pure, since it has no contamination from NaCl.
2. The sodium hydroxide has a relatively high concentration; at about 30 – 35% NaOH by mass.

**Uses of sodium hydroxide, chlorine, and hydrogen**

**1.**    **Sodium Hydroxide**

- React with chlorine to form sodium chlorate sodium hypochlorite or I, NaOCl.  This is a powerful oxidising agent which is used for sterilization and bleaching in textiles, paper and textile industries.

  **i.e.** $2NaOH_{(aq)} + Cl_{2(g)} \longrightarrow NaOCl_{(aq)} + NaCl_{(g)} + H_2O_{(l)}$
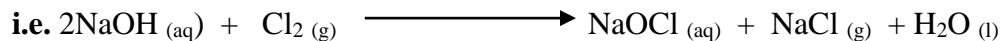
- Manufacture of sodas, detergents and cosmetics.
- Neutralization of acidic solutions in the laboratories.

**2.**    **Hydrogen**

- For hydrogenation in the manufacture of margarine
- Manufacture of ammonia
- Production of hydrochloric acid

**3.**    **Chlorine**
- Formation of sodium chlorate I; for bleaching in pulp, textile and paper industries.
- Sewage and water treatment
- Manufacture of polymers such as polyvinyl chloride.
- Manufacture of pesticides.

**QUANTITATIVE ASPECTS OF ELECTROLYSIS**

# Basic terminologies and concepts

**iii)**    **Ampere**
    Is the standard unit used to measure an electric  current; the flow of electrons
    Is usually abbreviated as amps.

**iv)**    **Coulomb**
    Is the quantity of electricity, when a current of 1 ampere flows for one second. I.e.  1 Coulomb = 1 Ampere x 1 second
    Generally:

| | | | |
|---|---|---|---|
| Quantity of | Electricity | = | current x Time in seconds |
| | A | = | It; Where |
| | Q | = | Quantity of electricity in coulombs |
| | I | = | Current in Amperes |
| | T | = | time in seconds |

**v)**    **Faraday**
    Is the quantity of electricity produced by one mole of electrons; and is usually a constant equivalent to 96487 (approx. 96500) coulombs

    Faradays laws of Electrolysis.
    First law;

The mass of substance liberated during electrolysis is directly proportional to the quantity of electricity passed.

## Worked examples

1.    A current of 2.0 Amperes was passed through dilute potassium sulphate solution for two minutes using inert electrodes.
a)    Write the equation for the reaction at anode.


b)    Work out the mass of the product formed at the cathode. (H = 1.0, Faraday = 96,000 C)
      Solution;     quantity of electricity  =      current x time
                                            =      2 x 2x 60
                                            =      240 coulombs

      cathode reaction

      1 mole of electrons    =       96000 C
              4 moles of e-  =      4 x 96000 C
                             =      384,000 C


2.    What mass of copper would be coated on the cathode from a solution of copper (II) Sulphate by a current of 1 amp flowing for 30 minutes.
      (Cu = 63.5;     Faraday constant = 96487 Cuo/-)

      solution

      Cathode reaction

      Cu 2+ (aq)    +     2e-                    Cu (s)
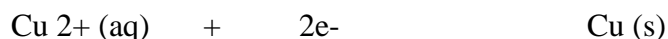
      -     1 mole of Cu requires 2 moles of electrons
      -     Quantity of electricity passed; = 1 x 30 x 60 coulombs; = 1800C
      -     1 mole of electrons carriers a charge of 96487 coulombs = 192974 coulombs
            192.974      coulombs deposit 63.5 g of Cu.

            Thus 1800 C will deposit   63.5 x 1800      =      0.592 grams
                                         192974

3.    An element x has relative atomic mass of 88g. when a current of 0.5 amperes was passed through a solution of x chloride for 32 minutes, 10 seconds; 0.44 g of x was deposited at the cathode. (1 faraday = 96500 c)
      Calculate the charge on the ion of x.


4.    In the electrolysis of dil CuSO4 solution, a steady current of 0.20 Amperes was passed for 20 minutes.
      (1 Faraday = 96, 500 C Mol-, Cu = 64)
      Calculate
      a)     The number of Coulombs of electricity used

      b)     The mass of the substance formed at the cathode.

2 moles of electrons liberate 1 mole of Cu.  i.e.  $Cu^{2+} + 2e$                    Cu (s)

5.      An element p has a relative atomic mass of 44.  When a current of 0.5 Amperes was possed through a
        fused chloride of p for 32 minutes and 10 seconds; 0.22g of p were deposit

## UNIT 5: METALS: EXTRACTION PROPERTIES AND USES.

**Introduction:**
1. Introduction
2. Extraction methods
3. Concentration of the ores
4. Metal extraction
   - **Sodium metal**
     - Main ores
     - Extraction process
     - Properties of sodium
     - Uses of sodium

   - **Aluminium metal**
     - Main ores
     - Qualitative analysis
     - Extraction from bauxite.
     - Electrolysis of purified bauxite
     - Properties of aluminium
     - Uses of aluminium

   - **Zinc metal**
     - Main ores
     - Qualitative analysis
     - Extraction process
     - By oxidation
     - By electrolysis
     - Properties of zinc
     - Uses of zinc

   - **Iron metal**
     - Main ores
     - Qualitative analysis
     - Extraction from haematite
     - Properties of iron
     - Uses of iron

   - **Copper metal**
   - Main ores
   - Qualitative analysis
   - Extraction process from copper pyrites
   - Properties of copper
   - Uses of copper

   - **Lead metal**
   - Main ores
   - Extraction process
   - Properties of lead
   - Uses of lead

**Introduction:**
**-** Only most unreactive metals occur naturally in their elementary form.
**Examples:** - Gold, Silver, Platinum.

- Other elements occur as ores i.e. metal – bearing rocks.

**Examples:**
- Oxides
- Sulphides
- Carbonates
- Chlorides.

**Note:**
An ore is a mineral deposit with reasonable composition of a desired metal.

**Methods of Extraction**
**-** Depend on position of the metal in the reactivity series.
- Main methods are:

**1. Electrolytic Method:**
                 - Used for metals high up in the reactivity series
               E.g. - Sodium and Potassium
                    - Calcium and Magnesium
                    - Aluminium.
                    - These metals occur in very stable ores

**2. Reduction method:**
              - For less reactive metals.
             E.g. Iron, Zinc, and Copper.

            - Is achieved using;
             (i) Carbon in form of coke.
             (ii) Carbon (II) oxide
             (iii) Hydrogen
            - Oxidation is also used followed by reduction.

**Preliminary steps before extraction.**
- Minerals (mineral) are usually mined with several impurities which lower the concentration of the metal per given mass or volume.
- Thus the ore is first concentrated before the actual extraction.
- Concentration is possible due to difference in properties between the mineral compound and the earthy materials.

**Methods of ore concentration.**
**1. Physical methods.**
**(a). Optical sorting.**
- Used to separate ore particles that have sufficiently different colours to be detected by the naked eye.
- It involves physical handpicking of the desired particles.
- Mainly used for minerals containing transition elements such as chromium.

**(b). Hydraulic washing.**
- Also called sink and float separation.
- Utilizes the difference in density between the minerals and the unwanted materials
- The ore is washed with streams of water.
- The denser ore particles will sink to the bottom of the washing container and can then be collected.

- Examples in ores of tin and lead.

**(c). Magnetic separation.**
- Is used when either the ore particles or the earthy materials (unwanted materials) are magnetic.
- A strong magnet is used to attract the magnetic components and leaving the non-magnetic materials behind.
- Examples: in ores like magnetite ($Fe_3O_4$) and chromite which are magnetic.

**(d). Electrostatic separation.**
- Used to separate particles which have different electric charges.
- The particles are subjected into an electric field.
- The oppositely charged particles follow different paths and can then be separated.

**(e). Froth floatation**
- Is mainly use for sulphide ores.
- Takes advantage of two facts.
  ➢ Oil can wet the surfaces of ores.
  ➢ Oil floats on water
**The process:**
- The ore is ground into a fine powder; to increase the surface area for upcoming reactions.
- It is then mixed with water and a suitable oil detergent e.g pine or eucalyptus;
- The mixture is then agitated by blowing compressed air through it;
- Small air bubbles attach to the oiled ore particles; which are thenn buoyed up and carried to the surface where they float.
- A froth rich in mineral is formed at the top while impurities sink at the bottom.
- The froth is skimmed off and dried.
- Froth floatation process is used for copper, lead and zinc metals;

**Diagram: froth floatation apparatus.**

**2. Chemical concentration.**
- Involves the use of chemical reactions to concentrate the ores.
Examples:
- Bauxite, the main aluminium ore is chemically concentrated by a process known as Bayer's process.
- This takes advantage of the amphoteric nature of aluminium oxide, which can thus react with both acids and bases.
- Chemical concentration can also be done by leaching.

- This involves reacting the ore with a compound such as sodium cyanide;
- The cyanide ions form complex ions with the metal.
- The complex ions formed are water soluble, and can be separated by filtration, leaving the unwanted materials in the residue.

**The metals**
**1. Sodium**
**Main ores;**
    i. Rock salt / sodium chloride; NaCl
    ii. Chile saltpetre / sodium Nitrate; $NaNO_3$
    iii. Soda ash/sodium carbonate; $Na_2CO_3$.

**Other ores include;**
(i). Borax; $Na_2B_4O_7.10H_2O$
(ii). Sodium Sulphate, $Na_2SO_4$;

**Extraction;**
- Sodium is obtained by the electrolysis of fused sodium chloride in the electrolytic cell.
- Calcium chloride and calcium fluoride are added to the electrolyte.
**Reasons;**
- To lower the melting point of sodium chloride from 800ºC to 600ºC;

- Once molten, the electrical resistance within the cell is sufficient to maintain the temperature without external heating.
- **Steel or iron** is used as the **cathode**, while **carbon/graphite** is used as the **anode**.
- Thus steel is not used as the anode.
**Reason;**
- At high temperatures, steel would react with chloride formed at the anode, but graphite is inert even at high temperatures.
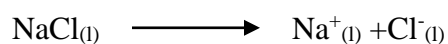
- Steel wire gauze separates the electrodes.
**Reason;**
- To prevent products of electrolysis (sodium and chlorine) from mixing and reacting to form sodium chloride.

- The electrolytic apparatus used in sodium extraction is called the Downs cell.

**Diagram: The Downs cell.**

- During electrolysis, fused sodium chloride dissociates according to the equation;

$$NaCl_{(l)} \longrightarrow Na^+_{(l)} + Cl^-_{(l)}$$

**At the cathode:**
> **Observation;**
- Soft silvery metal

**Explanation**
- $Na^+$ ions are attracted and undergo reduction (accept electrons) to form/ produce molten sodium metal.

**Equation;**
$$Na^+_{(l)} + e^- \longrightarrow Na_{(l)}$$

- Molten sodium is lighter than fused sodium chloride and floats on the surface where it overflows into a separate container / sodium reservoir.

**Note;**
- The resultant sodium is usually collected in liquid / molten state, floating on top of the electrolyte.
**Reasons;**
- Less dense than molten sodium chloride
- Has a low melting point.

**At the anode;**
**Observations;**
- Evolution of a green-yellow gas.

**Explanation:**
- Chlorine gas is evolved as a by – product and collected separately.
- Negatively charged $Cl^-$ ions migrate to the positive anode and undergo oxidation to form chlorine gas;

**Equation:**
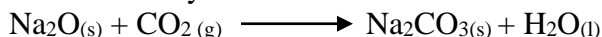$$2Cl^-_{(l)} \longrightarrow Cl_{2(g)} + 2e-$$

**Properties of Sodium;**
- Is a soft silvery metal with low density; $0.979gcm^{-3}$
- Has a low melting point, $97^oC$, and a low boiling point of $883^oC$.

**Chemical reactions**
**(a) With air**
- Na is very reactive and tarnishes in moist air to form an oxide layer.
$$4Na_{(s)} + O_{2(g)} \longrightarrow 2Na_2O_{(s)};$$
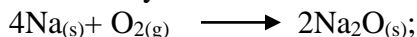
- The oxide layer reacts with more air moisture to form hydroxide
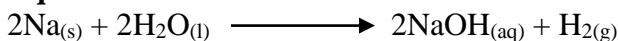$$Na_2O_{(s)} + CO_{2\ (g)} \longrightarrow Na_2CO_{3(s)} + H_2O_{(l)}$$

**Note**
- Due to those series of reactions sodium is stored under a liquid hydrocarbon e.g. petroleum, kerosene.

- Sodium burns in oxygen with a golden yellow flame to form sodium peroxide
**Equation:**
$$2Na_{(s)} + O_{2(g)} \longrightarrow Na_2O_{2(s)}$$
*(White)*
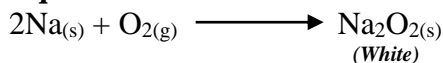
**(b). With water**
- Na reacts vigorously with water to form NaOH and Hydrogen.
**Equation:**
$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

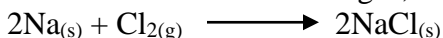- The resulting solution is highly alkaline with a PH of 14.
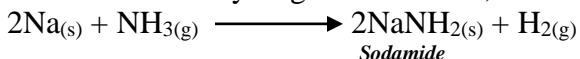- Sodium is stored under oil to prevent contact with moisture from the atmosphere.
**Note:**
- The reaction between Na and dilute acids would be explosive and not safe to investigate
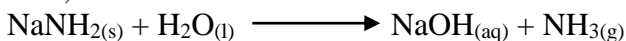
**(c). With chlorine**
- Sodium burns in chlorine gas;
$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$

**(d) With ammonia gas;**
- Sodium forms hydrogen and a solid;
$$2Na_{(s)} + NH_{3(g)} \longrightarrow 2NaNH_{2(s)} + H_{2(g)}$$
$$\textit{Sodamide}$$
And;
$$NaNH_{2(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + NH_{3(g)}$$

**Uses of sodium;**
1. Is alloyed with lead in the preparation tetraethyl (IV) lead, which is added to petrol as an anti-knock.
2. Provides the glow in sodium vapours lamps, for street lighting (orange-yellow street lights).
3. Is an excellent conductor of heat and electricity with low melting point hence used;
   - In nuclear reactors to conduct away heat.
   - Modern aeroplane engines.
4. Manufacture of sodium peroxide, and sodium cyanide used in the extraction of silver and gold.

**Question;**
- Although electrolysis is an expensive way of obtaining metals, it must be used for some metals. Explain.
**Solution;**
- Group 1 and 2 metals together with Al are themselves such powerful reducing agents that their oxides cannot be reduced by chemical reducing agents.
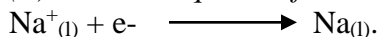
**Worked example**
1. Below is a simplified diagram of the Downs cell in which sodium metal is manufactured.

*(a) (i) Identify; -*
*Electrolyte X: -* Molten sodium chloride
*Gas Y: -* Chlorine gas

*(ii) Write an equation for the reaction at the cathode.*
$Na^+_{(l)} + e- \longrightarrow Na_{(l)}.$

*(iii). In what state is sodium collected?*
- Molten state/liquid state.

*(iv). Give **two** properties of Na that makes it possible to be collected as in (b) (iii) above.*
- Its less dense than molten sodium chloride.
- Has a low melting point.

*(v). The cathode is made of steel but the anode is made of graphite.*
*Why is this yet steel is a better conductor?*
- At high temperature steel would react with chlorine formed but graphite is inert even at high temperatures.

*(vi). In this process, the naturally occurring, raw material is usually mixed with another compound. Identify the compound and state its use.*
*Compound; -* Calcium chloride
*Use;-* To lower melting point of Nacl2 from 800°c to 600°c

*(vii). What is the function of the steel gauze cylinder?*
- Prevents sodium reacting with chlorine forming NaCl

*(viii). Give one industrial use of sodium*
- A coolant in nuclear reactors;
- Alloy with lead in tetraethyl (IV) lead;

*(ix). Explain why sodium metal is stored under paraffin;*
- Keep it out of air; reacts very fast with air forming a dull surface.
- Can react with water.

*(b). State an industry that can be built next to a sodium extracting plant.*

*(c). A current of 100 Amperes flows through an electrolyte of molten sodium chloride for 15 hours. Calculate the mass of sodium produced in kg (Na = 23; 1F = 96500C)*
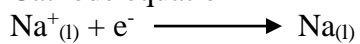**Solution:**
Q = It
=100 x 15 x 60 x 60
=5400000C.

Cathode equation

$$Na^+_{(l)} + e^- \longrightarrow Na_{(l)}$$

96500C = 23g of Na

5400000 C = $\dfrac{23 \times 5400000}{96500}$ = 1287.04g

= 1.287kg

(d) .For the same quantity of electricity as in (c) above ; calculate the volume of the gaseous product produced in the cell at $15^0$c and 800mmhg.(Molar gas volume at s.t.p = 22.4dm$^3$)

## 2. Aluminium
- Forms 7% of the earth's crust and is the most common metal.

**Main ores;**
- Bauxite; $Al_2O_3.H_2O$
- Mica; $K_2Al2S_6O_{16}$.
- China clay;$Al_2S_2O_72H_2O$
- Corundum;$Al_2O_3$.

**Chemical test;**
- Crush the ore into a fine powder;
- Add dilute nitric (V) acid to the powder
- Filter to obtain a solution of the ore;
- To a solution of the ore add $NaOH_{(aq)}$ dropwise till in excess, and then repeat the same procedure using Ammonia solution, $NH_4OH$.

**Observations:**
  ➢ **With NaOH$_{(aq)}$:**
- White precipitate in soluble in excess;

  ➢ **With NH$_4$OH$_{(aq)}$:**
- White precipitate insoluble in excess;

**Extraction from Bauxite;**
-Involves two main processes;-
  ➢ Purification of Bauxite.
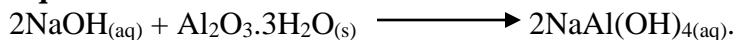  ➢ Electrolysis of purified bauxite (alumina)

**i. Purification of bauxite**
- Chief impurities are small quantities of silica and iron (III) oxide.
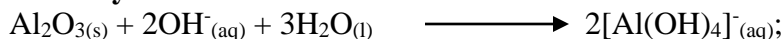- The oxide ore is ground and treated under pressure/ dissolved in hot aqueous sodium hydroxide.

**During the process;**
- The amphoteric bauxite dissolves in NaOH forming sodium aluminate;
**Equation:**
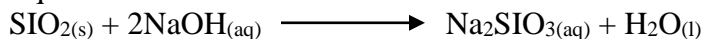$2NaOH_{(aq)} + Al_2O_3.3H_2O_{(s)} \longrightarrow 2NaAl(OH)_{4(aq)}$.

**Ionically:**
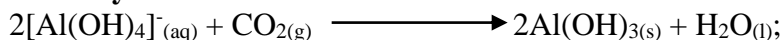$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2[Al(OH)_4]^-_{(aq)}$;

- Silica impurities also dissolve forming sodium silicate
Equation:
$SIO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SIO_{3(aq)} + H_2O_{(l)}$

- The iron impurities (mainly iron (III) oxide) DO NOT dissolve.
- This mixture is then filtered, during which iron (III) oxide remain as residue of red mud while a filterate of sodium aluminate and sodium silicate is collected.
- Carbon (IV) oxide is bubbled through the filterate, followed by dilution then addition of a little aluminium hydroxide to cause precipitation (seeding) of Aluminium hydroxide.
**Ionically:**
$2[Al(OH)_4]^-_{(aq)} + CO_{2(g)} \longrightarrow 2Al(OH)_{3(s)} + H_2O_{(l)}$;

**Alternatively:**

$Al(OH)_4^-{}_{(aq)} \xrightarrow[\text{Al(OH)}_3]{\text{Seeding}} 2Al(OH)_{3(s)} + OH^-{}_{(aq)};$

**General equation:**

$NaAlO_{2(aq)} + 2H_2O_{(l)} \xrightarrow{hydrolysis} NaOH_{(aq)} + Al(OH)_{3(s)}.$
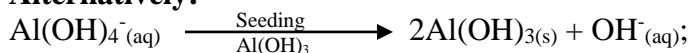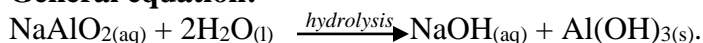
- The precipitated Aluminium hydroxide is then filtered off, washed and ignited to give pure aluminium oxide (Alumina);

**Equation:**

$2Al(OH)_{3(s)} \longrightarrow \underset{Alumina}{Al_2O_{3(s)}} + 3H_2O_{(l)}$
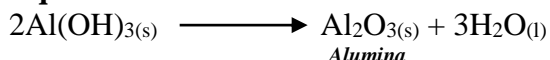
## ii. Electrolysis of purified bauxite (alumina)

- The Alumina ($Al_2O_3$), has a high melting point, 2015$^o$C and a lot of heat would be required to melt it.
- Additionally the molten compound is a very poor conductor of electricity.
- Consequently, cryolite ($Na_3AlF_6$) is mixed with the oxide.

**Reason;**

- To lower the melting temperature of $Al_2O_3$ from 2015$^o$C to around 800$^o$C;
- At this lower temperature the molten oxide also conducts well.

- The molten alumina mixed with bauxite is then electrolysed in a steel cell lined with carbon graphite as the cathode.

**Note;**

- Other than being an electrolyte the *graphite cathode lining* also prevents alloy formation, as it ensures no contact between the resultant aluminium and the steel tank;
-The anodes also made of Graphite dip into the steel tank at intervals.

**Diagram: electrolytic steel cell for the extraction of Aluminium.**

**Electrolytic reactions;**

- The Aluminium oxide dissociates to give constituent ions;

**Equation:**

$Al_2O_{3(l)} \longrightarrow 2Al^{3+}{}_{(l)} + 3O^{2-}{}_{(l)}$
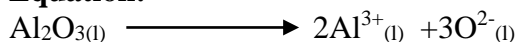
**At the cathode;**
**Observation;**
- A silvery white metal which quickly becomes dulled.

**Explanation:**
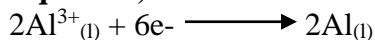- Aluminium ions move to the cathode and are reduced to form aluminium metal.

**Equation;**
$2Al^{3+}_{(l)} + 6e- \longrightarrow 2Al_{(l)}$

**At the anode;**
**Observation;**
- Effervescence of a colourless gas.

**Explanations:**
- Oxygen ions migrate to the anode and get oxidized to form oxygen gas.
- The resultant oxygen gas reacts further with the graphite anode to form carbon (IV) oxide.
- This is due to the high temperatures involved during the process.
**Note;**
- Consequently the carbon anode should be replaced from time to time.

**Equations;**
$3O^{2-}_{(l)} \longrightarrow 3O_{2(g)} + 6e-$
Then;
$C_{(s)\ (anode)} + O_{2(g)} \longrightarrow CO_{2(g)}$
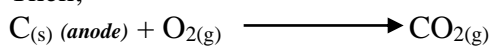
**Note:**
- Cryolite usually adds $Na^+$; and $F^-$ ions into the electrolyte.
- Thus the anions are $O^{2-}$ and $F^-$ ions into the electrolyte.
- However oxygen is discharged in preference to Fluorine.
**Reason;**
- Fluorine is a stronger oxidizing agent than oxygen. Thus oxygen easily gives electrons than fluorine, hence discharge.
- Aluminium is discharged in preference to sodium.

**Summary: - Flow chart on the Extraction of Aluminium from bauxite**.

**Properties of Aluminium**
**Physical properties**
- Is a silvery white metal which quickly becomes dulled with a thin oxide layer.
- Has very low density ($2.7gcm^{-3}$), with ability to be rolled into wires / foil.
- Is a good conductor of heat and electricity.

**Chemical properties.**
**1. Reaction with air;**
- In air it acquires a continuous very thin coating of oxide, which resists further reaction.
- Removal of this protective cover renders the metal reactive.
- Consequently steel wool or wood ash should NOT be used in aluminium utensils.
- Usually, salty water attacks the oxide film allowing the aluminium to corrode and for this reason, *ordinary aluminium is not used for marine purposes*.
- Aluminium will burn in air at $800^{o}C$ to form is oxide and nitrate.
Equations:
$$4Al_{(s)} + 3O_{2(g)} \longrightarrow 2Al_2O_{3(s)};$$
$$2Al_{(s)} + N_{2(g)} \longrightarrow 2AlN_{(s)}$$
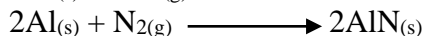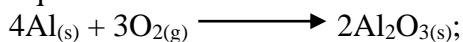
**2. Reaction with Acids.**
**Note:**
- The protective Aluminium oxide (being covalent and insoluble) layer makes its reactivity with acids less than expected.

   ➢ **With nitric (V) acid;**
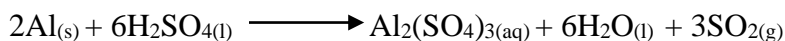- Has hardly any effect on the metal, at any concentration.
**Reason:**
- Being a powerful oxidizing agent, it simply thickens the oxide layer thereby preventing further reaction.

   ➢ **With sulphuric (VI) acid;**
- Only hot concentrated sulphuric (VI) acid breaks down the oxide layer and reacts with the metal.
**Equation:**

$$2Al_{(s)} + 6H_2SO_{4(l)} \longrightarrow Al_2(SO_4)_{3(aq)} + 6H_2O_{(l)} + 3SO_{2(g)}$$

> ➢ **With Hydrochloric acid;**

- Dilute HCl dissolves aluminium slowly; liberating hydrogen.
**Equation:**
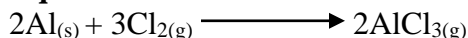$$2Al_{(s)} + 6HCl_{(l)} \longrightarrow 2AlCl_{3(aq)} + 3H_{2(g)}$$
With concentrated HCl the rate of reaction is increased.

## 3. Reaction with chlorine;
- Hot aluminium burns in chlorine gas with a white light, forming dense white fumes of Aluminium (III) Chloride.
-The white fumes cool and collect on the cooler parts of the apparatus as a white solid.
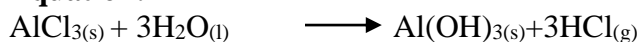**Equation:**
$$2Al_{(s)} + 3Cl_{2(g)} \longrightarrow 2AlCl_{3(g)}$$

**Note:**
- The apparatus for the preparation of $AlCl_3$ is kept very dry.
**Reason:**
- Aluminium chloride is readily/easily hydrolysed by water/moisture, and so it fumes in damp air with the evolution of hydrogen chloride gas.
**Equation:**
$$AlCl_{3(s)} + 3H_2O_{(l)} \longrightarrow Al(OH)_{3(s)} + 3HCl_{(g)}$$

## 4. Reaction with water.
- Aluminium does not react with cold water, due to the formation of an insoluble coating of Aluminium oxide.
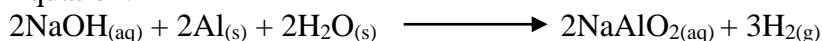**Note;**
- If the oxide film is removed, the metal reacts slowly with cold water.

## 5. Reaction with caustic soda.
- The metal, especially in powder form, reacts with caustic soda solution, liberating hydrogen and leaving sodium aluminate in solution.
- The reaction is exothermic and once started, it is very vigorous.
Equation:
$$2NaOH_{(aq)} + 2Al_{(s)} + 2H_2O_{(s)} \longrightarrow 2NaAlO_{2(aq)} + 3H_{2(g)}$$
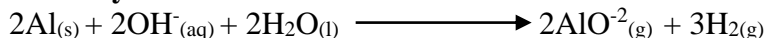
**Ionically:**
$$2Al_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \longrightarrow 2AlO^{-2}_{(g)} + 3H_{2(g)}$$
**Note:**
- Thus aluminium has an amphoteric nature as it reacts with both acids and alkalis.
**Uses of aluminium**
1. Making parts of airplanes, railway, trucks, buses, tankers, furniture, and car e.t.c.
**Reason;**
- It is Very light due to a very low density.

2. Making cooking vessels/ utensils such as sufurias.
**Reason:**
- It is a good conductor of heat and electricity.
- It is not easily corroded by cooking liquids due to the unreactive coating of aluminium oxide.

3. Making overhead cables
**Reason:**

- It is a good conductor of electricity.
- It is light hence can easily be supported by poles and ductile to be rolled into wires (cables).

4. Aluminium powder mixed with oil is used as a protective paint.

5. Making Aluminium foils due to its high malleability. The foil is used in cooking; packaging and for milk bottle tops.

6. Making alloys, which have high tensile strength and yet light.
**Examples:**

| Alloy | Component |
|---|---|
| Duralumin | Aluminium, copper, manganese and magnesium |
| Magnalium | Aluminium (70%) and magnesium (30%) |

7. As a reducing agent in the **Thermite process** in the production of some elements such as chromium, cobalt manganese and titanium.
**Example:**
$Cr_2O_{3(s)} + 2Al_{(s)} \longrightarrow 2Cr_{(s)} + Al_2O_{3(s)}$
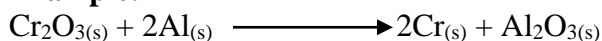
**Note:**
➢ **The thermite process**
- Is a process of reducing oxides of metals which are ordinarily difficult to reduce using Aluminium powder.

**Examples:**
➢ Iron (III) Oxide ($Fe_2O_3$)
➢ Chromium (III) Oxide ($Cr_2O_3$)
➢ Compound oxide of manganese ($Mn_3O_4$)

- The oxide and the Al powder are well mixed together, forming Thermite.
- The thermite is ignited using magnesium ribbon fuse, since the reaction will not start at low temperatures.
- The high heat of formation of Aluminium oxide , results into a vigorous exothermic reaction that leads to a molten metal.

Example: -In the reduction of chromium (III) Oxide.
$Cr_2O_{3(s)} + 2Al_{(s)} \longrightarrow 2Cr_{(l)} + Al_2O_{3(s)} + Heat.$

**Sample question:**

**3. Zinc**
**Main ores;**
(i). Zinc blende; ZnS
(ii). Calamine; $ZnCO_3$.

**Extraction:**
- Is done by electrolysis or reduction of its oxide using carbon.

**Preliminary steps:**
- The ore is first concentrated by froth floatation.
- The ore is roasted in air to convert it to the oxide.
**Equations:**
  ➢ **From Zinc blende:**
$2ZnS_{(s)} + 3O_{2(g)} \longrightarrow 2ZnO_{(s)} + 2SO_{2(g)}$
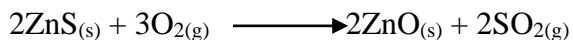
  ➢ **From Calamine:**
$ZnCO_{3(s)} \longrightarrow ZnO_{(s)} + CO_{2(g)}$
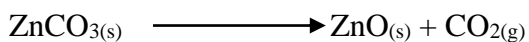
- After obtaining the oxide the metal is extracted by either reduction or reduction:

**(a). The reduction method.**
- The oxide is mixed with coke and limestone and heated in a furnace.

**Diagram: Furnace for zinc extraction by reduction:**

- The limestone ($CaCO_3$) decomposes to liberate $CO_2$ which is then reduced by coke to form carbon (II) oxide.

**Equations:**

$$CaCO_{3(s)} \xrightarrow{\text{Heat}} CaO_{(s)} + CO_{2\,(g)}$$
Then:
$$CO_{2\,(g)} + C_{(s)} \longrightarrow 2CO_{\,(g)}$$

- The resultant carbon (II) oxide and coke are the reducing agents in the furnace, at about $1400^{\circ}C$.
- They reduce the oxide to the metal; which is liberated in vapour form.
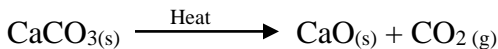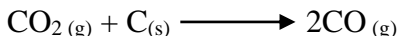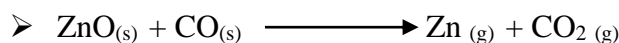
**Equations:**

➢ $ZnO_{(s)} + C_{(s)} \longrightarrow Zn_{\,(g)} + CO_{\,(g)}$

➢ $ZnO_{(s)} + CO_{(s)} \longrightarrow Zn_{\,(g)} + CO_{2\,(g)}$

- At the furnace temperatures zinc exists in vapour form, and leaves at the top of the furnace.
- Liquid zinc being lighter settles above molten lead and is run off;
- The vapour is condensed in a spray of molten lead to prevent re-oxidation of zinc.
- The resultant zinc is 98-99% pure and can be further purified by distillation.
- $SO_2$ is a by-product and is the main source of pollution in the extraction of zinc.
- Usually it is channeled to a contact process plant for the manufacture of sulphuric acid.
- Alternatively it can be scrubbed off to prevent pollution of the environment.
- Less volatile impurities remain in the furnace.
- The silica impurities combine with the quicklime/ calcium oxide (CaO) from limestone to form calcium silicate.

**Equation:**
$$CaO_{(s)} + SiO_{(s)} \longrightarrow CaSiO_{3(s)}$$
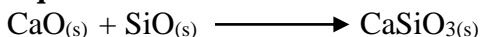
- The silicates together with other less volatile impurities form **slag**, at the bottom of the furnace from where it is run off.

**Summary: Flow chart and the extraction of zinc**
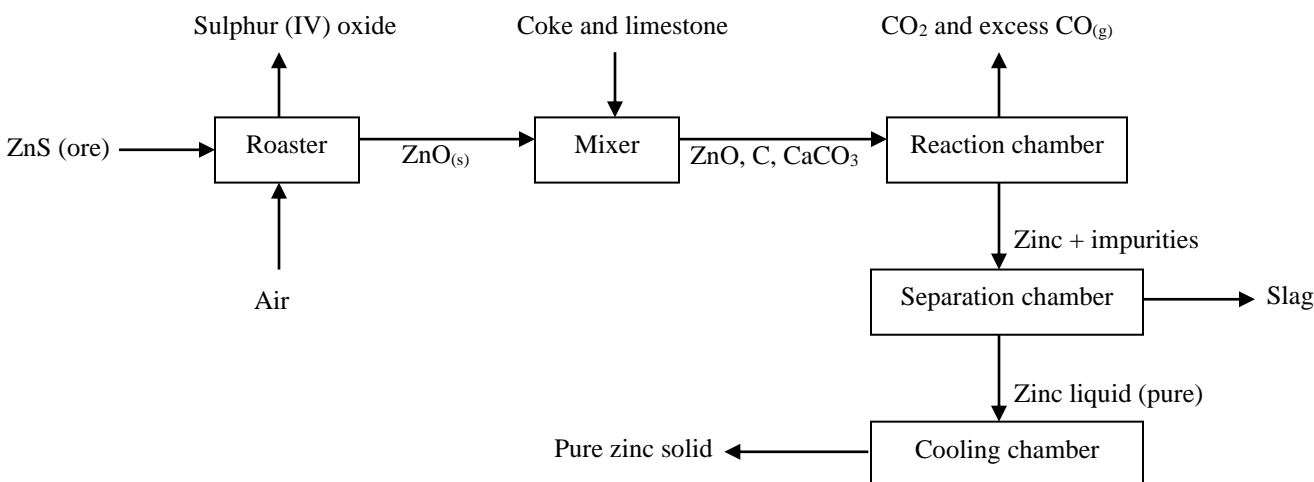


**(b). Electrolytic extraction of zinc.**
- Zinc metal is obtained from the oxide via a series of steps:

**Step I: Preparation of electrolyte:**
- The ZnO obtained from roasting the ore is converted to zinc sulphate by reacting it with dilute sulphuric (VI) acid.

**Equation:**
$$ZnO_{(s)} + H_2SO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + H_2O_{(l)}$$

- Any lead (II) oxide impurity present in the zinc oxide reacts with the acid to form lead (II) sulphate.
**Equation:**
$$PbO_{(s)} + H_2SO_{4(aq)} \longrightarrow PbSO_{4(s)} + H_2O_{(l)}$$

- The insoluble lead (II) sulphate is then precipitated and separated by filtration;
- The zinc sulphate is then dissolved in water and the solution electrolysed.

**Step II: The electrolytic process:**
**Electrolyte:**
- Zinc (II) sulphate solution;

**Ions present:**
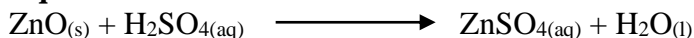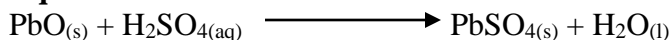- $Zn^{2+}$ and $H^+$ as cations; and $SO_4^{2-}$ and $OH^-$ as anions;

**Cathode:**
Lead containing 1% silver.

**Anode:**
- Aluminium sheets;

**Chemical reactions:**
**Cathode:**
**Observations:**
- Deposits of a grey solid.

**Explanations:**
- $Zn^{2+}$ and $H^+$ migrate to the cathode.
- The $Zn^{2+}$ are discharged in preference to $H^+$;
**Reason:**
- The cathode is relatively reactive. Thus since zinc is more reactive thn hydrogen, its ions undergo reduction faster;

**Equation:**
$$Zn^{2+}_{(aq)} + 2e- \longrightarrow Zn_{(s)};$$
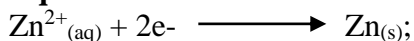
**Note:**
If graphite electrodes were used, hydrogen gas would have been evolved instead;

**Anode:**
**Observations:**
- Evolution of a colourless gas that relights a glowing splint;

**Explanations:**

- OH⁻ and SO₄²⁻ migrate to the cathode.
- The OH⁻ are discharged in preference to SO₄²⁻; giving off oxygen gas

**Reason:**

The OH⁻ ions have a higher oxidation potential than SO₄²⁻ and therefore easily giving electrons for reduction at the cathode

**Equation:**

$$4OH^-_{(aq)} \longrightarrow 2H_2O_{(l)} + O_{2(g)} + 4e\text{-}$$

**Note:**
- Over 80% of zinc is extracted by the electrolytic method.
- Zinc extracted by the electrolytic method is much more pure.

**Note: - Industrial plants that can be set up near the zinc extraction plant.**
- Contact process plant, to make use of the $SO_2$ by-product.
- Lead accumulators factories, to utilize the zinc produced.
- Paper factory using, $SO_3$ and hence $SO_2$ in bleaching.
- Brass factory for alloying zinc and copper.
- Steel factory to use zinc in galvanization.

**Properties of zinc**
**Physical properties**
- Is a blue-grey lustrous metal with:
  ➢ Density of $7.1gcm^{-3}$
  ➢ Melting point of $420^oC$
  ➢ Boiling point of $907^oC$

**Chemical reactions**
**(a). with air;-**
- Zinc tarnishes slowly forming a protective layer which prevents further reaction i.e. oxide layer or basic carbonate.

**Equations:**

$$2Zn_{(s)} + O_{2(g)} \longrightarrow 2ZnO_{(s)}$$
Then;
$$ZnO_{(s)} + CO_{2(g)} \longrightarrow ZnCO_{3(s)}$$
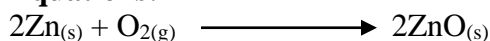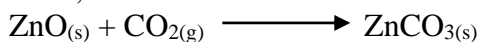
- It burns with a blue-green flame when strongly heated in air to form an oxide which is yellow when hot and white when cold.
**Equation:**
$$2Zn_{(s)} + O_{2(g)} \longrightarrow 2ZnO_{(s)}$$
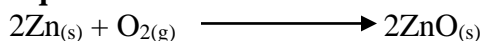
**(b). With water**
- Zinc does not react with water
- Steam reacts with red-hot zinc, forming zinc oxide and liberating hydrogen gas.
**Equation:**
$$Zn_{(s)} + H_2O_{(g)} \longrightarrow ZnO_{(s)} + H_{2(g)}$$

**(c). with dilute acids**

- Zinc is above hydrogen in the reactivity series hence displaces hydrogen from steam (water) and dilute acids like $H_2SO_4$ and $HCl$.
**Equation:**

$$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$

- Pure zinc reacts slowly while impure zinc reacts faster/ more quickly.
- Copper (II) sulphate is used as a catalyst to speed up the reaction.

**(d). Concentrated acids.**
**(i). Concentrated sulphuric (VI) acid.**
**Equation:**

$$Zn_{(s)} + 2H_2SO_{4(l)} \longrightarrow ZnSO_{4(aq)} + 2H_2O_{(l)} + SO_{2(g)}$$

**(ii). 50% concentrated nitric (v) acid.**
- It reacts with 50% concentrated nitric (V) acid to liberate nitrogen (II) oxide.
**Equation:**

$$3Zn_{(s)} + 8HNO_{3(l)} \longrightarrow Zn(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{(g)}$$

**(iii). Concentrated nitric (V) acid.**
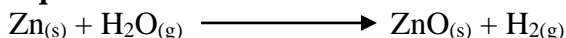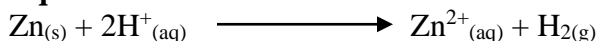- It reduces concentrated nitric (V) acid to nitrogen (IV) oxide.
**Equation:**

$$Zn_{(s)} + 4HNO_{3(l)} \longrightarrow Zn(NO_3)_{2(aq)} + 4H_2O_{(l)} + 2NO_{2(g)}$$
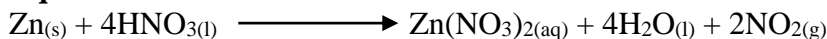
**(e). with alkalis.**
- Zinc is amphoteric and dissolves in hot alkalis to give the zincate ion and hydrogen gas.
Equation:

$$Zn_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \longrightarrow H_{2(g)} + [Zn(OH)_4]^{2-}_{(aq)}$$
*(Zincate ion)*
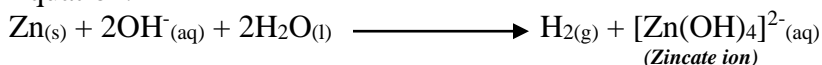
**(f). Other reactions.**
(i). Zinc burns in chlorine to give zinc chloride

$$Zn_{(s)} + Cl_{2(g)} \longrightarrow ZnCl_{2(s)}$$
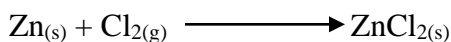
(ii). Zinc combines with sulphur

$$Zn_{(s)} + S_{(s)} \longrightarrow 2ZnS_{(s)}$$
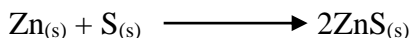
**Uses of zinc:**
1. Galvanization of iron sheets to prevent corrosion and rusting.
**Note:**
Rusting does not occur even when galvanized iron sheets are scratched and exposed.
**Reason:**
- The rest of the zinc protects the iron from rusting. This is because zinc being more reactive gets oxidized in preference to iron, and is hence "sacrificed" in the protection of iron.
- This method is referred to as cathodic or sacrificial protection.
2. Making brass; an alloy of copper and zinc.

3. Making outer casings of dry batteries;
4. Die-castings contain zinc and aluminium, and are used for making radio and car parts;
5. Zinc cyanide is used for refining silver and gold;

**Sample question:**

## 4. Iron
- Is the second most abundant metal after aluminium, forming about 7% of the earth's crust.

### Main ores
- Haematite, $Fe_2O_3$;
- Magnetite, $Fe_3O_4$;
- Siderite, $FeCO_3$;

### Qualitative analysis for presence copper in an ore sample.
- Crush the ore into fine powder;
- Add dilute nitric (V) acid to the ore, to dissolve the oxide filter to obtain the filtrate.
- To the filtrate add aqueous sodium hydroxide / ammonium hydroxide dropwise till in excess.
- Formation of a red brown / brown precipitate in both cases indicates presence of $Fe^{3+}$

### Extraction from haematite ($Fe_2O_3$).
### Summary of the process
- The ore-haematite is crushed and mixed with coke and limestone.
- The mixture is called **charge.**
- The charge is loaded into the top of a tall furnace called **blast furnace**.
- Hot air-the blast is pumped into the lower part of the furnace.
- The ore is reduced to iron as the charge falls through the furnace.
- A waste material called slag is formed at the same time.
- The slag floats on the surface of the liquid iron produced.
- Each layer can be tapped off separately.

### Details of the extraction process.
### (i) The blast furnace
Is a tall, somewhat conical furnace usually made of silica and lined on the inside with firebrick**.**

### Details of the extraction process
### Raw materials.

- Iron ore; i.e. haematite
- Coke; C
- Limestone; $CaCO_3$;
- Hot air;

## Conditions
- Temperature at the bottom of furnace, 1400-1600°C
- Temperature at the top of the furnace, 400°C

## Reactions and processes
### Step-1 – crushing and loading
- The ore is crushed into powder form, to increase the surface area for the upcoming reduction/ redox reactions.
- It is then mixed with coke and limestone and then fed at the top of the furnace using the double bell (double-cone devise) changing system

**Note**:
- The double bell charging system ensures that the furnace can be fed continuously from the top with very little heat loss, by preventing any escape of hot gases.
- This in turn reduces production costs.

### Step 2: -Pre heating of the blast furnace.
- Air that has been preheated to about 700°C is blown/ fed into the base of the blast furnace through small pipes called *tuyers.*
- This provides the required temperatures for the reactions in the blast furnace.
- This results into highest temperatures, about 1600°C at the hearth (bottom of the furnace) which then decreases upwards the furnace.

### Step 3: -Generation of reducing agents.
- Two reducing agents are used in this process: Coke and carbon (II) oxide; with carbon (II) oxide being the main reducing agent.

### (i). Oxidation of coke;
- Coke burns in the blast at the bottom of the furnace.
- The reaction temperatures is about 1600°C and the product is **Carbon (IV) oxide gas**
- This reaction is exothermic, producing a lot of heat in the blast furnace.

**Equation:**
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$
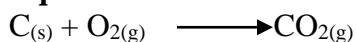
### (ii). Decomposition of limestone;
- The limestone in the charge decomposes in the blast furnace to calcium oxide (Quicklime) and carbon dioxide.

**Equation:**
$$CaCO_{3(s)} \xrightarrow{\text{Heat}} CaO_{(s)} + CO_{2(g)}$$
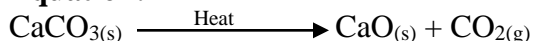
- The calcium oxide will be used in the removal of the main ore impurity/ silicates/ silica in the form of silicon (IV) oxide.
- The $CO_2$ then moves up the blast furnace to regenerate carbon (II) oxide, the chief reducing agent.

### (iii). Production of carbon monoxide
- The $CO_2$ from oxidation of coke and decomposition of limestone (calcium carbonate) react with (excess) coke, to form carbon (II) oxide

- The reaction occurs higher up in the blast furnace at about 700°C;

**Equation:**

$$CO_{2(g)} + C_{(s)} \longrightarrow 2CO_{(g)}$$

**Step 4: The actual reduction process**
- Reduction of the ore is by either CO or coke, depending on temperatures.

**(i). Reduction by coke**
- This occurs much lower down the furnace at higher temperatures of about 800°C and above.
- This reaction is ordinarily slow and thus serves to only reduce the part of the ore reduced by CO at lower temperatures in the upper parts of the furnace.

**Equation:**

$$2Fe_2O_{3(s)} + 3C_{(s)} \longrightarrow 4Fe_{(s)} + CO_{2(g)}$$

**Note:**
- The resultant $CO_2$ is quickly reduced to CO by the white-hot coke to more carbon (II) oxide as per step 3(iii) above.

**(ii). Reduction by carbon (II) oxide**
- This is the main reducing agent.
- The reaction between CO and $Fe_2O_3$ is relatively faster and occurs at lower temperatures of 500°C-700°C, higher up the furnace.

**Equation:**

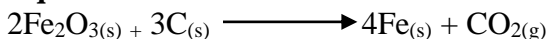$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + CO_{2\,(g)}$$
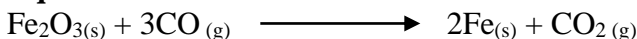
- The resultant carbon (IV) oxide is also quickly recycled by being reduced to CO by coke to from more reducing agent

**(iii). Melting**
- The iron produced in both of the reduction processes is in solid state.
- As the iron drops / falls down the furnace, it melts as it passes through the **melting zone/ molten zone (1500°C-1800°C)**
- The molten iron runs to the bottom of the furnace.
- Temperatures at the hearth (bottom of the furnace) is maintained at approx. 1400°C and yet pure iron melts at about 1525°C.
- Consequently the molten iron would easily solidify at the base (Temp =1400°C)
- However this is not usually the case;
**Reason:**
-Impurities absorbed by iron during melting (**mainly carbon**) reducing the melting point to below **1400°C.**
- The molten iron is then easily tapped off.

**Step 5: -Removal of earthy impurities.**
- The earthy impurities in the ore (mainly silica) react with calcium oxide from decomposition of limestone to form calcium silicate.

**Equation:**

$$CaO_{(s)} + SiO_{2(s)} \longrightarrow CaSiO_{3(s)}$$
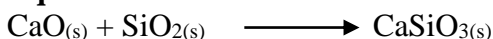
- These earthy impurities form **molten slag** whose main component is **calcium silicate**.

- The slag does not mix with iron but rather floats on top of it, at the base of the furnace.

**Importance of the slag**
- As it floats on top of molten iron it protects it from being re-oxidized by the incoming hot air.

**Uses/application of the slag**
1. Light-weight building material.
2. Manufacture of cement.
3. Road building material.

**Step 6:- Removal of furnace (waste) gases.**
- Hot unreacted/waste gases leave at the top of the furnace.
- Main components include Nitrogen, unreacted $CO_2$, unreacted CO, oxygen and Argon (Noble gases)
- Additionally they contain dust particles.
**Note:**
- Upon removal of dust particles, the furnace gases, being hot can be used to pre-heat the air blown in at the base.

**Summary: flow chart for the extraction of iron.**

**Properties of iron:**
**Physical properties:**
- It has a melting point of 420oC and a boiling point of 907°C;
- Have a good thermal and electrical conductivity;
- It is ductile and malleable;

**Chemical properties.**
**(i). Reaction with air.**
- It readily rusts in presence of moist air hydrated brown iron (III) oxide; $Fe_2O_3.H_2O_{(s)}$
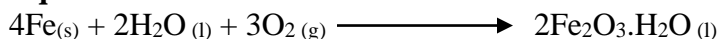**Equation:**
$$4Fe_{(s)} + 2H_2O_{(l)} + 3O_{2\,(g)} \longrightarrow 2Fe_2O_3.H_2O_{(l)}$$

- When heated it reacts with oxygen to form tri-iron tetroxide; $Fe_3O_4$;
**Equation:**

$$3Fe_{(s)} + 2O_{2\,(g)} \longrightarrow Fe_3O_{4(s)}$$
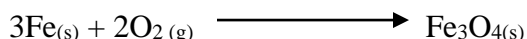
**(ii). Reaction with water.**
- It does not readily react with cold water.
- It however reacts with steam liberating hydrogen gas and forming tri-iron tetroxide.
**Equation:**
$$3Fe_{(s)} + 4H_2O_{(g)} \longrightarrow Fe_3O_{4(s)} + 4H_{2(g)}$$
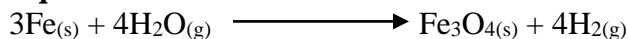
**(iii). Reaction with chlorine.**
- Hot iron glows in chlorine without further heating, forming black crystals of iron (III) chloride;
- Iron (III) chloride sublimes on heating and will thus collect on the cooler parts of the apparatus;
**Equation:**
$$2Fe_{(s)} + 3Cl_{2(g)} \longrightarrow 2FeCl_{3(s)}$$
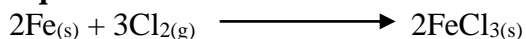
**Note:**
- Iron (III) chloride fumes when it is exposed to damp (moist) air;
Reason:
- It is readily hydrolysed by water with evolution of hydrogen chloride gas;

**Equation:**
$$FeCl_{3(s)} + 3H_2O_{(l)} \longrightarrow Fe(OH)_{3(s)} + 3HCl_{(g)}$$
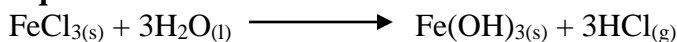
**(iv). Reaction with acids:**
  ➢ **Hydrochloric acid:**
- Iron reacts with hydrochloric acid to liberate hydrogen gas.
**Equation:**
$$2Fe_{(s)} + HCl_{(aq)} \longrightarrow FeCl_{2(aq)} + H_{2(g)}$$

  ➢ **Sulphuric (VI) acid:**
$$Fe_{(s)} + H_2SO_{4\,(aq)} \longrightarrow FeSO4_{\,(aq)} + H_{2\,(g)}$$
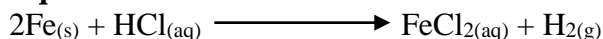
**Note: With hot concentrated H₂SO₄;**
- The iron reduces hot concentrated $H_2SO_4$ to sulphur (IV) oxide and it is itself oxidized to iron (III) sulphate.
**Equation:**
$$2Fe_{(s)} + 6H_2SO_{4\,(l)} \longrightarrow Fe_2\,(SO_4)_{3(aq)} + 6H_2O_{(l)} + 3SO_{2\,(g)}$$

> ➢ **Nitric (V) acid.**

- Iron reacts with dilute nitric (V) acid to form nitrogen (IV) oxide and ammonia which then forms ammonium nitrate.

**Equation:**

$$10HNO_{3\ (aq)} + 4Fe_{(s)} \longrightarrow 4Fe(NO_3)_{2(aq)} + NH_4NO_{3(aq)} + 3H_2O_{(l)}$$
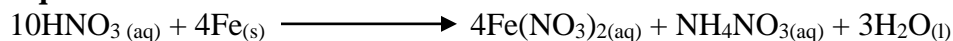
- Warm dilute nitric (V) acid gives iron (II) nitrate.
- Concentrated nitric (V) cid renders the iron unreactive.

**Reason:**

- Formation of iron oxide as a protective layer on the metal surface.

## (vi). Reaction with sulphur.

- Iron when heated in sulphur forms iron (II) sulphide.

Equation:

$$Fe_{(s)} + S_{(s)} \longrightarrow FeS_{(s)}$$

## Uses of iron.

- Iron exists in different types and alloys, depending on percentage composition of iron, and other elements.
- Each type of alloy of iron has different uses depending on properties.

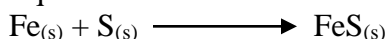| Iron alloy or type | Properties. | Uses |
|---|---|---|
| Cast iron | - Refers to iron just after it has been produced in the blast furnace;<br>- Contains 3-5% carbon, 1% silicon, and 2% phosphorus;<br>**Disadvantage:** very brittle hence easily breaks;<br>**Advantage**: It is extremely very hard; | - Making:<br>  ➢ Furnaces;<br>  ➢ Grates;<br>  ➢ Railings;<br>  ➢ Drainage pipes;<br>  ➢ Engine blocks;<br>  ➢ Iron boxes;<br>**Note:** This is due to its very hard nature;<br>- Manufacture of wrought iron and steel; |
| Wrought iron | - Refers to cast iron with 0.1% carbon.<br>- It is malleable hence can easily be moulded or welded; | - making iron nails; horse shoes; agricultural implements like pangas;<br>**Note:**<br>Its use is declining due to increased use of mild steel |
| Steel | - Are alloys whose main component is iron;<br>- Other components may be carbon; vanadium; manganese; tungsten; nickel and chromium;<br>**Examples:**<br>**Mild steel**: has about 0.3% carbon, 99.75% iron;<br>**Special steel**: has a small percentage of carbon together with other small substances;<br><br>**Stainless steel:**<br>-Contains 74% iron, 18% chromium, and 8% nickel;<br><br><br>**Cobalt steel:**<br>- Contains about 97.5% iron and 2.5% cobalt;<br>- Very tough and hard;<br>- Slightly magnetic; | - Mild steel is used for making:<br>  ➢ Nails; Car bodies;<br>  ➢ Railway lines; Ship bodies;<br>  ➢ Rods for reinforced concrete, pipes;<br>**Note:** Advantage of mild steel:<br>- It is easy to work on;<br><br>- That with 10-12% chromium and some nickel is used to make: cutlery; sinks; vats;<br>- Steel containing 5-18% tungsten is used for: making high speed cutting and drilling tools;<br><br>- For making electromagnets; |

## 5. Copper

**Description:** - A red brown metal.

**Distribution: -** Canada, USA, Zambia, and Tanzania.

**Main ores;**

- Copper pyrites, $CuFeS_2$;
- Cuprite, CuO
- Chalcocite, $Cu_2S$
- Malachite, $CuCO_3.Cu(OH)_2$

**Qualitative analysis / test for presence in an ore sample.**
- Crush the ore and then add dilute nitric or hydrochloric or sulphuric acid to dissolve the ore.
- Filter to obtain $Cu^{2+}$ filtrate.
- Divide filtrate into 2 different test tubes.
- To one sample add aqueous Ammonium hydroxide dropwise till in excess formation of a pale blue precipitate soluble in excess NaOH to form a deep blue solution.

**Equations**
**With little NaOH:-**
$$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Cu(OH)_{2(s)}$$
*Pale blue ppt.*

**In excess:**
$$Cu(OH)_{2(aq)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)}$$
*Deep blue solution*
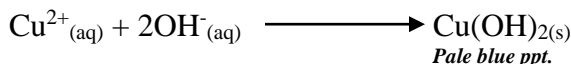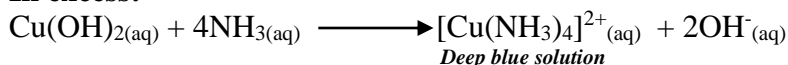
-To the second portion add sodium hydroxide solution dropwise till in excess, formation of a pale blue precipitate insoluble in excess confirms presence of $Cu^{2+}$.

**Extraction- from copper pyrites.**
**1. Crushing the ore**
- The ore is crushed to increase the surface area for the succeeding chemical reactions.
- The ore is then concentrated.

**2. Concentration of the ore.**
- The ore is concentrated by **froth floatation**.
- The fine ore powder is mixed with water and oil, after which air is blown into the mixture, usually from below.
- Bubbles of the air forms froth, resulting to concentration of the ore.
- The lighter oil floats on top of the water, with the ore floating on top of the oil.
- The denser water sediments the earthy impurities like soil particles.
- The concentrated ore is then tapped off.
- This process involves formation of an oil froth onto which the ore floats hence the name *froth formation*.

**3. First Roasting**
-The concentrated copper pyrite, $CuFeS_2$ is then roasted in air to remove some of the sulphur impurities as sulphur (IV) oxide.
**Equation:**
$$2CuFeS_{2(s)} + 4O_{2(g)} \longrightarrow 3SO_{2(g)} + 2FeO_{(S)} + Cu_2S_{(s)};$$
**Note:**
- During $1^{st}$ roasting limestone and silica ($SiO_2$) are added to the roasted ore and the mixture heated in the absence of air.
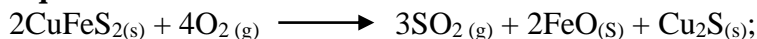
**Importance**
- Removal of iron impurities.
- The iron (II) so formed during roasting is converted to iron (II) silicate, $FeSiO_3$.
- The iron (II) silicate constitutes the major portion/component of the **slag**.

**Equation:**

$$FeO_{(s)} + SiO_{2(g)} \longrightarrow FeSiO_{3(s)}$$
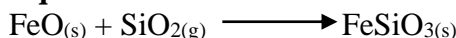
- The slag separates itself from the copper (I) sulphide.
- The sulphur (IV) oxide escapes into the atmosphere and is the **major pollutant** in this process.

**Pollution control mechanisms.**
- Scrubbing the gas using calcium hydroxide;

**Equation:**

$$SO_{2(g)} + Ca(OH)_{2(s)} \longrightarrow CaSO_{3(s)} + H_2O_{(l)}$$

- Construction of a contact process nearby.

## 4. Second Roasting.
- The CuS is heated in a regulated supply of air where some of it is converted to $Cu_2O$

**Equation:**

$$2Cu_2S_{(s)} + 3O_{2(g)} \longrightarrow Cu_2O_{(s)} + 2SO_{2(g)}$$
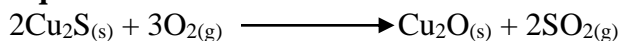
## 5. Reduction of copper (II) oxide
**Note:** - Not all the $Cu_2S$ was oxidized to copper (I) oxide $Cu_2O$.
- The unreacted (unoxidized) $Cu_2S$ serves as the reducing agent in this step.
i.e. The copper (I) oxide formed in step 4 is reduced to copper metal by the (unreacted) copper (I) sulphide.
- This is called **blister copper**.

**Equation:**

$$Cu_2S_{(s)} + 2Cu_2O_{(s)} \longrightarrow 6Cu_{(s)} + SO_{2\ (g)};$$

## 6. Electrolysis
-The copper metal from reduction in step 6 is impure and is thus purified by electrolysis.

**Main impurities**
- Traces of gold
- Traces of silver
- Iron
- Sulphur

**Electrolytic apparatus**
**Anode:** Impure copper
**Cathode:** Pure copper plates/ sheets;
**Electrolyte:** Dilute copper (II) sulphate solution (containing $Cu^{2+}$; $H^+$; $SO_4^{2-}$ and $OH^-$)

**Diagram of electrolytic apparatus.**

**Electrolytic reactions;**
**At the cathode.**
**Observations:**
- Deposition of a brown solid.

**Explanations:**
- The copper (II) ions, $Cu^{2+}$ move to the cathode, where they accept electrons and undergo reduction.
- Cations in the electrolyte are $Cu^{2+}$ and $H^+$ but $Cu^{2+}$ are preferentially discharged due to their easy tendency to undergo reduction.

**Equation:**
$Cu^{2+}_{(aq)} + 2e- \longrightarrow Cu_{(s)}$;
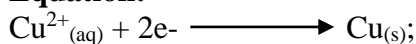
**At the anode**
**Observations:**
- Dissolution of the anode, hence the impure copper rod decreases in size.

**Explanation**
- Since the metal rod is dipped into a solution of its ions, the copper solid undergoes oxidation, losing electrons to form copper ions, $Cu^{2+}$
- Consequently as more copper ions, $Cu^{2+}$ get reduced at the cathode; more are released by the dissolving anode.

**Equation:**
$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e-$
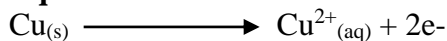
**Overall reaction**
$Cu_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$
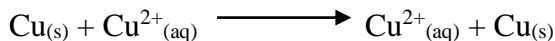
- The electrolytic product is 99.98% copper.
- Traces of silver and gold collect as sludge at the bottom of the cell.
**Note**:-To improve purity of the product of electrolysis, the following steps are advisable;
(i). Increase the dilution of the electrolyte/ use a very dilute electrolyte.
(ii). Reduce the amount of current / use a low current.

**Summary of extraction of copper from copper pyrites.**

**Uses of copper**

1. Making copper wires and contacts in switches, plugs and sockets
**Reason:**-Copper is a good conductor of electricity
**Note:**-For this purpose, pure copper is necessary, since impurities increase electrical resistance.

2. Making soldering instruments.
**Reason:**-Copper has a high thermal conductivity.

3. Manufacture of alloys.
**Examples**

| Alloy | Components |
|---|---|
| Brass | Copper and zinc |
| Bronze | Copper and tin |
| German silver | Copper, zinc and nickel; |

4. Making coins and ornaments.
**Reason:**-it is durable and aesthetic.

**Properties of copper.**
**a. Physical properties**
- Soft red-brown metal.
- Melting point of $1083^{o}C$ and a boiling point of $2595^{o}C$
- Density is $8.92 gcm^{-3}$ and electrical conductivity is about $5.93 \times 10^{-9} \Omega^{-1}m^{-1}$

**b. Chemical properties**
(i). It does not react with cold water or steam.

**(ii). Heating in air**
- When heated in air it forms a black layer of copper (II) oxide on its surface.
- Finely divided copper burns with a **blue flame**.

**Equation:**
$$2Cu_{(s)} + O_{2(g)} \longrightarrow 2CuO_{(s)}$$
*(Red brown)*         *(Black)*

**(iii). Reaction with chlorine**

- Cu reacts with chlorine in presence of heat to form *green copper (II) chloride.*

**Equation:**

$Cu_{(s)} + Cl_{2(g)} \longrightarrow CuCl_{2(s)}$
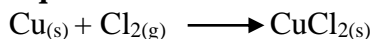
**(iv). Reaction with Acids.**
- Copper does not react with dilute hydrochloric, nitric and sulphuric acids.
- However it reacts with 50% Nitric acid, concentrated Nitric acid and concentrated sulphuric acid.

  ➢ **With 50% Nitric (V) acid**
- Copper reduces the nitric acid to nitrogen monoxide.

**Equation;**

$3Cu_{(s)} + 8HNO_{3(l)} \longrightarrow 3Cu(NO_3)_{2\ (aq)} + 4H_2O_{(l)} + 2NO_{(g)};$

  ➢ **With concentrated Nitric (V) acid**
- Copper reduces the acid to brown nitrogen (IV) oxide/Nitrogen dioxide gas.

**Equation:**

$Cu_{(s)} + 4HNO_{3(l)} \longrightarrow Cu(NO3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)}$
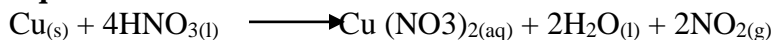
  ➢ **With concentrated sulphuric acid.**
-The sulphuric acid is reduced to sulphur (IV) oxide.

**Equation:**

$Cu_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CuSO_{4\ (aq)} + 2H_2O_{(l)} + SO_{2\ (g)}$
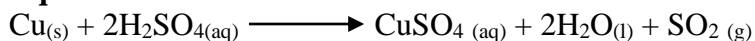
**Worked example.**

*The flow chart below outlines some of the processes involved in the extraction of copper from copper pyrites. Study it and answer the questions that follow.*
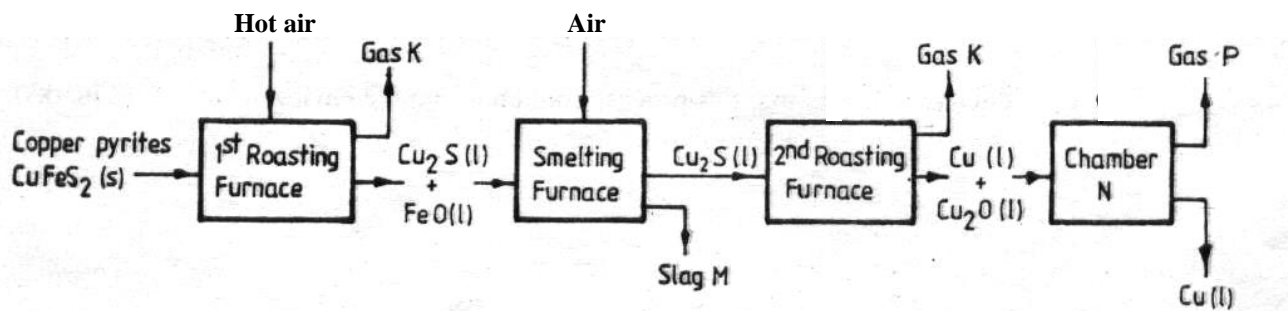


*(a) (i). Write an equation for the reaction in the first roasting chamber.* (1mark)

*(ii). Name gas K.* (1mark)

*(iii). Give the name and formula of slag M.* (1mark)

*(iv). Give the name of the reaction in chamber N.* (1mark)

*(v). Name the impure copper X.* (1mark)

*(b). Pure copper is obtained from impure copper by electrolysis.*
*(i). Name the anode the cathode and the electrolyte.* (3 marks)

*(ii). Write equations for the reactions at the anode and cathode.* (2 marks)

*(iii). calculate the time taken for a current of 10 amperes to deposit 32kg of pure copper. (Cu = 64, 1F = 96000C)* (3 marks)
*(c). Draw a diagram to show how you would plate an aluminium spoon with copper*

## 6. Lead.
- Is a transition element that combines with other elements to form compounds with 2 oxidation states.
- It is among the group 4 elements;

## Main ores:
- Galena, PbS (lead sulphide); the main ore;
- Cerrusite, $PbCO_3$ (lead carbonate)
- Anglesite, $PbSO_4$ (lead II) sulphate);

## Qualitative analysis / test for presence of $Zn^{2+}$ in an ore sample.
- The ore is crushed and then dilute nitric or hydrochloric or sulphuric acid added to dissolve the ore.
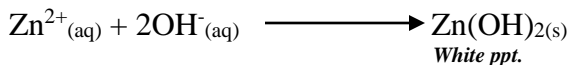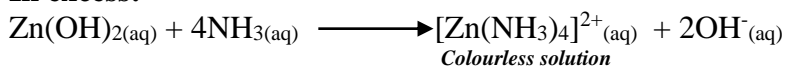- It is then filtered to obtain $Zn^{2+}$ filtrate.
- The filtrate is divided into 2 different test tubes.
- To the first portion sodium hydroxide solution is added dropwise till in excess, formation of a white precipitate soluble in excess confirms presence of either $Zn^{2+}$; $Al^{3+}$ or $Pb^{2+}$.
- To the second sample aqueous ammonium hydroxide is added dropwise till in excess; formation of a white precipitate soluble in excess $NH_4OH_{(aq)}$ confirms presence of $Zn^{2+}$ only;

## Equations
## With little $NH_4OH$:-

$$Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Zn(OH)_{2(s)}$$
*White ppt.*

## In excess:

$$Zn(OH)_{2(aq)} + 4NH_{3(aq)} \longrightarrow [Zn(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)}$$
*Colourless solution*

## Extraction of lead:
- Occur in three main steps:
  ➢ Ore concentration;
  ➢ Extraction by reduction;
  ➢ Purification (refining) by electrolysis;

## 1. Ore concentration:
- Is done by selective froth floatation;
- The ore is ground into a fine powder, then water and a suitable oil added;
- Air is then blown into the mixture; facilitating formation of a low density froth that floats on top;
- Additionally, chemicals such as sodium cyanide and zinc sulphate are added to facilitate separation of zinc sulphide present in the ore.
- The separated PbS is then dried and broken into smaller pieces, then subjected to reduction;

## 2. Reduction:
## Step I: Roasting the ore:
- The crushed and concentrated ore is roasted in a furnace to convert it to lead (II) oxide;
## Equation:

$$2PbS_{(s)} + 3O_{2(g)} \longrightarrow 2PbO_{(s)} + 2SO_{2(g)}$$
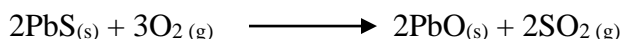
- During roasting some of the lead (II) sulphide is converted to lead (II) sulphate;
**Equation:**

$$PbS_{(s)} + 2O_{2(g)} \longrightarrow PbSO_{4(s)};$$
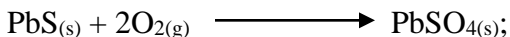
- Any lead sulphate formed is converted to **lead silicate** by silicon (IV) oxide;
- The fate of lead (II) silicate;
**Note:**
- Additionally the lead (II) sulphate may further react with lead sulphide to form lead metal;

## Step II: Ore reduction:
- The lead oxide obtained is mixed with coke, limestone and silica and some scrap iron;
- The mixture is fed into the top of the Imperial smelting furnace (ISF); where it is melted using hot air blasts introduced near the bottom of the furnace;

**Diagram: The Imperial Smelting furnace for Lead extraction.**
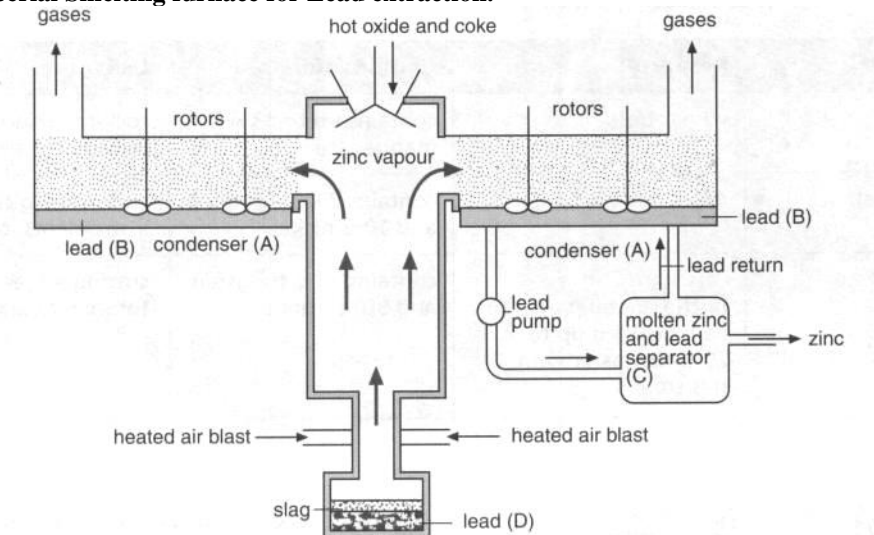


## Main reactions:
(i). The lead (II) oxide is reduced to lead by the coke.

**Equation:**
$$PbO_{(s)} + C_{(s)} \longrightarrow Pb_{(s)} + CO_{(s)};$$
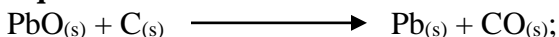
(ii). The resultant carbon (IV) oxide produced in reaction (i) above further reduces any remaining lead (II) oxide;

**Equation:**
$$PbO_{(s)} + CO_{(s)} \longrightarrow Pb_{(s)} + CO_{2(g)};$$
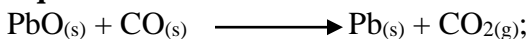
(iii). The scrap iron is added so as to react with any lead sulphide that may be present.

**Equation:**
$$Fe_{(s)} + PbS_{(s)} \longrightarrow Pb_{(s)} + FeS_{(s)}$$
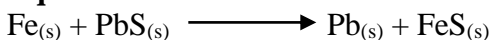
(iv). The limestone undergoes decomposition to give calcium oxide and liberate carbon (IV) oxide;

**Equation:**

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2\,(g)};$$
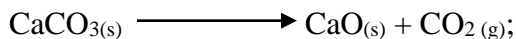
- The carbon (IV) oxide gets reduced by coke to form more carbon (IV) oxide for reduction as in reaction (ii);

**Equation:**
$$CO_{2\,(g)} + C_{(s)} \longrightarrow 2CO_{\,(g)};$$
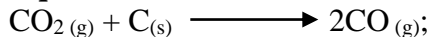
(v). The calcium oxide reacts with silica in form of $SiO_2$ to form calcium silicate;

**Equation:**
$$CaO_{(s)} + SiO_{2\,(g)} \longrightarrow CaSiO_{3\,(l)};$$
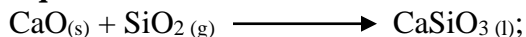
**Waste gases and residues.**
- The iron sulphide and calcium silicate form a molten slag which is less dense and floats on top of molten lead at the bottom of the furnace;
- From here the slag is separately tapped off;
- Excess gases and air that did not react in the blast furnace escape through outlets at the top of the furnace;
- These waste gases can be trapped and recycled;
- These gases include: excess $CO$; excess $CO_2$; oxygen; nitrogen; some $SO_2$; and argon;

**Pollution effects:**
- Main pollutant is sulphur (IV) oxide from roasting of the ore.

**Pollution control:**
- It is directly fed into a contact process plant or scrubbed using calcium hydroxide forming calcium sulphite;

**3. Purification (refining) of lead:**
- The molten lead obtained in this process contains impurities such as gold, silver, copper, arsenic, tin and sulphur;
- The impure lead is refined by electrolysis.

**Electrolysis of molten lead.**
**(i). Electrolyte:**
Any aqueous solution containing lead ions;

**(ii). The anode:**
- Impure lead;

**(iii). The cathode:**
- Pure lead;

**Electrolytic reactions;**
**At the cathode.**
**Observations:**
- Deposition of a grey solid.

**Explanations:**
- The lead (II) ions, $Pb^{2+}$ move to the cathode, where they accept electrons and undergo reduction.

- Cations in the electrolyte are $Pb^{2+}$ and $H^+$ but $Pb^{2+}$ are preferentially discharged due to their easy tendency to undergo reduction.

**Equation:**
$Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)};$
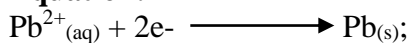
**At the anode**
**Observations:**
- Dissolution of the anode, hence the impure lead rod decreases in size.

**Explanation**
- Since the metal rod is dipped into a solution of its ions, the impure lead solid undergoes oxidation, losing electrons to form lead (II) ions, $Pb^{2+}$
- Consequently as more lead (II) ions, $Pb^{2+}$ get reduced at the cathode; more are released by the dissolving anode.

**Equation:**
$Pb_{(s)} \longrightarrow Pb^{2+}_{(aq)} + 2e^-$

**Overall reaction**

*Oxidation at anode;*

$Pb_{(s)} + Pb^{2+}_{(aq)} \longrightarrow Pb^{2+}_{(aq)} + Pb_{(s)}$

*Reduction at cathode;*
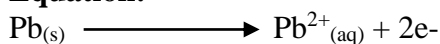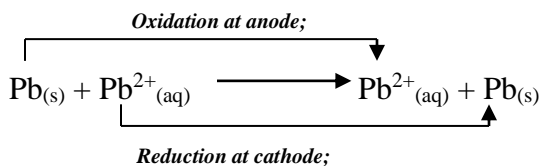
**Summary: flow chart on extraction of lead.**

**Properties of lead:**
**Physical properties;**
- Has a low melting point but a high density;
- The unusually low melting point of lead is difficult to explain using simple metallic bonding theory;
- It is rather soft and pliable;
- Relatively malleable;

**Chemical properties.**
**Note:** - Lead is fairly unreactive to most other metals;

### 3. Uses of lead:

1. It is used in several alloys e.g. solder and also added to bronze alloys to make them stronger;
2. Lead ingots are used in the manufacture of accumulators;
3. Being so malleable and so chemically inert lead sheeting was used for roofing (look at roofs of old churches and cathedral)-cost and pollution effects have however brought this to a stop;
4. Making lead pipes for water supply; this is also discouraged particularly in soft water areas due to threat of lead poisoning;
5. Making tetraethyl lead (IV) which for many years was used as a fuel additive to increase octane rating of fuels;
6. Used in weights, clock pendulums, plumb bobs etc; due to its high density;
7. It absorbs X-rays and hence lead aprons and lead glass are used to shield hospital radiographers;
8. Used for safe disposal or storage of radioactive substances since no radioactive emission has been known to pass through thick lead blocks;

**Sample question:**

# UNIT 6: RADIOACTIVITY

Checklist
1. Meaning of radioactivity
2. Natural and artificial radioactivity
3. Nuclear equations and chemical equations.
4. Types of radiations
   - Alpha particles
   - Beta particles
   - Gamma rays
5. Half life of a radioisotope
6. Radioactive decay curves and half life
7. Radioactive disintegration and nuclear equations.
8. Radioactive decay series, nuclear fission and nuclear fusion;
9. Uses of radioactivity;
10. Dangers and pollution effects of radioactivity;

Definitions:
- ➢ Radioactivity is an automatic spontaneous disintegration of nuclei of some heavy elements emitting some kinds of radiant energy
- ➢ Elements which exhibit this are said to be radioactive and emit different types of radiation

**Types of radiation from radioactive elements**
**They can be identified by**
  i. Measuring their penetration power
     - They were directed to thin leaves of paper, aluminium, lead plates of varying thickness.
     - Observations:
     A. One penetrated only thin foils of paper but not aluminium of 0.05mm thick and lead
     B. One penetrated both paper and Al but not lead
     C. One penetrated paper Al and lead
  ii. Directing them to air
     - Observations
     (a) Penetrated less through air but caused a lot of ionization to the air molecule
     (b) Penetrated more through air but caused less ionization
     (c) Penetrated most through air but caused less ionization
     These penetrated just as far as X-rays
     Directing through magnetic /electric fields
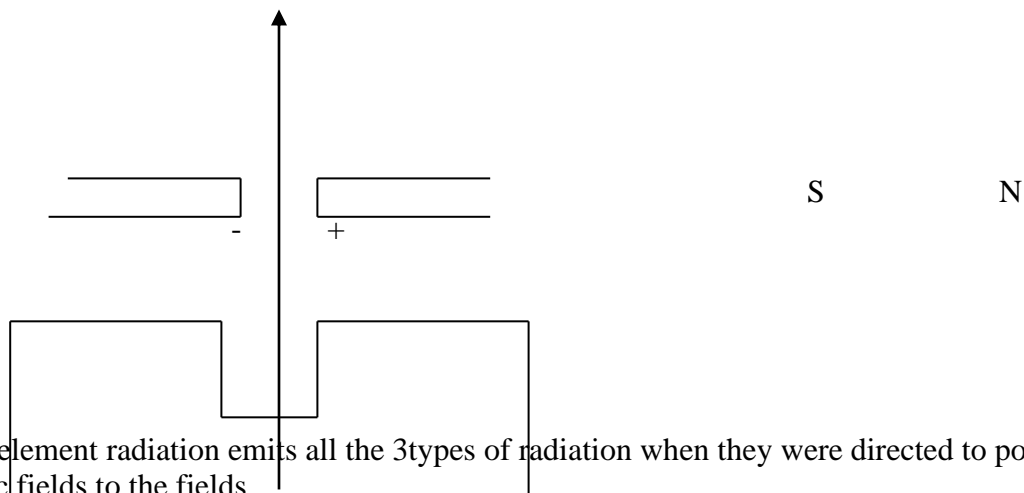


The radioactive element radiation emits all the 3types of radiation when they were directed to poss through electric magnetic fields to the fields
**Were slightly deflected towards the negative**
**Were strongly deflected towards the positive**
C. Were not deflected
Therefore
A and B –are charged particles
-Have opposite charges
A is positive, B is negative
And
Deflections obeyed through L.H Rule
  - A were deflected less because they were moving with higher momentum (MV) because of high mass
       Experimental evidence
  - Experiments carried out by Rattlerford revealed
  A. Were positively charged and had a mass of 4 units and thus a charge of +2 these are Alpha- particles therefore double charged helium ions,
  B. Were negatively charged and had similar properties to cathode rays. Measurement of charge/ mass confirmed they were electrons and carries a unit of –1
  They are beta particles

C. Were carrying no charge. They are electromagnetic waves similar to light rays and X- rays with a wave length of only 10 metres

Their emission enables a nucleus to lose surplus energy

They are gamma rays

Evidence for the nature of gamma rays

- Gamma rays
1) Are unaffected by an electric field
2) Are an affected by a magnetic field
3) Can penetrate several centimeters of lead
4) Can be diffracted by the lattice of a crystal
5) Have no change in atomic number mass of the atoms emitting them

NATURE AND PROPERTY OF α , β ,AND γ

| Nature | α- particles helium nuclei $^4He$ (He ) | B-particles electrons | Rays electromagnetic waves radiation |
|---|---|---|---|
| Relative penetrating power | Least 5cm in air stopped by paper and Al foils | Several metres of air thin Al foil (100) | Penetrate air, Al and many mm of Pb (10000) |
| Range in air | A few cm | A few m | A few km |
| Effect of electric and magnetic fields | Small deflection | Large deflection | No deflection |
| Ionization of gases | Cause much ionization Discharges electroscopes rapidly | Cause less ionization Discharges electroscopes slowly | Negligible ionization |

Radioactive decay curve
Is always a symptotic to the x-axis

Number of atoms of the
Radioactive element
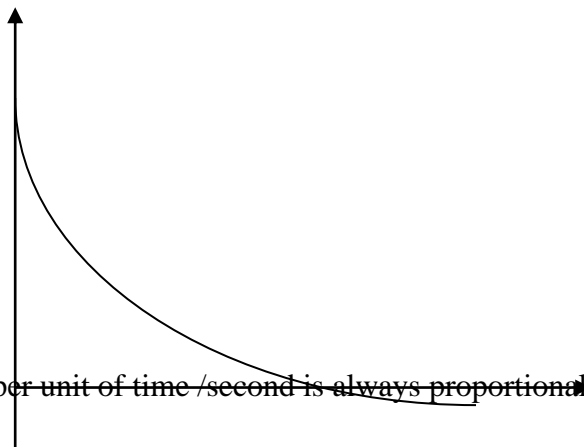
- The number of atoms disintegrating per unit of time /second is always proportional to the number of atoms, N at that time

This number N decreases slowly / exponentially with time

- At any time to the number of atoms of a radioactive element is N/ No and at time T½, only ½ the total number of atoms of the original radioactive element will be present i.e.

   T½ = ½N

This time is referred to as the half-life period of a radioactive element

Therefore
Half-life period T½ of a radioactive element is defined as the time taken for ½ the atoms to disintergrate
Thus
In T½ the radioactivity of the element diminishes to half its value
Example
Radioactive decay curve of radon
With half life of 4 days

$No = 6 \times 10^3$ atoms
$T½ = 4days$

No. Of atoms
$10^3 \times 6$

$10^3 \times 5$

$10^3 \times 4$

$10^3 \times 3$

Radon emits α- particles
Initial no of radon atoms $= 10^3 \times 6$
After 4 days the number of atoms present$=10^3 \times 3$
" " " "8 days " " " " " " " " " " " " " " " " $=10^3 \times 1.5$
" " " "12 days "" " " " " " " " " " " " " " $= 10^3 \times 0.75$
It is impossible to predict the atoms that will disintergrate next

The half lives of some radioactive isotopes

| Radioactive isotopes | Half life |
|---|---|
| Uranium-238 | $4.5 \times 10^9$ years |
| Radium-226 | $1.6 \times 10^3$ years |
| Carbon-14 | $5.7 \times 10^3$ years |
| Strontium-90 | 28 years |
| Iodine-131 | 8.1days |
| Radon-222 | 4days |
| Bismuth-214 | 19.7minutes |
| Polonium-218 | 3minutes |
| Polonium-214 | $1.5 \times 10^{-4}$sec |

-The half-life of a radioactive isotope provides aquantitave measure of its stability
Thus
-The shorter the half-life the faster the isotope decays and the more unstable it is
-The longer the half-life the slower the decay process and the more stable the isotope
     RADIOACTVE DISINTERGRATION EQUATIONS
-Different radioactive elements disintergrate to emit different radiations
a) Emission of α particles

-Occurs in isotopes with an atomic number greater than 83 (Z> 83) because they are unstable since their nuclei are so heavy and their atomic mass is too large
-They attain stability by ejecting an alpha particle containing two protons and two neutrons
Examples
     (1)    $^{238}$U-α partially-

(b) Emission of β particles
- Occur in isotopes with more neutrons than stable isotopes of the same element, therefore heaviest isotopes of an element are likely to emit β particles to attain stability
- During the β-decay process, a neutron splits up forming a proton &an electron

The proton remains in the nucleus while the electron /β particles is ejected.
Result
  Number of neutrons in the isotope decreases by one while number of protons increase by one.

© Emissions of α-& β alternatively

(2) Emissions of beta particles in two –stage

Application of Radioactivity /Using radioactive isotopes.
1. Carbon dating
- Radio active Carbon –14 nuclide produced when Nitrogen –14 is bombarded with radiocum from the sum is used.
- When they die carbon-14 resent starts to reduce as decay takes place by emission of β particles.
- Using the decay curve of carbon –14 it is possible to estimate age of the animals/plants since the carbon –14 is present in their tissues.

2.Medication/treatment of cancer
- Gamma rays are used to treat /kill cancer cells when the tumour is subjected to the radiations
E.G Gamma rays /penetrating from CO are used in treating inaccessible growths.

Superficial /skin cancers can be treated by less penetrating radiation from or in plastic sheets strapped on the affected

3.Studying metabolic pathways
-Radioactive Isotopes can be used to trace the uptake of metabolism of various elements by animals /plants.
E.g Uptake of phosphate & metabolism of phosphorus by plants can be studied using a fertilizer containing
Radioactive tracer studies using have helped in the exudation of photosynthesis and protein synthesis
have been used in the diagnosis & treatment of thyroid diseases &in research into thyroid gland functioning.

4.Thickness gauge and empty packet detectors
-Radiation passing through a material decreases as the material gets thicker
Hence:
Amount of penetrating Beta –or-gamma- radiation can be used to estimate the thickness of various materials like paper, metal or plastic
-Radiation thickness gauges can be used to control the thickness of sheet steel emerging from a high-speed rolling mill.
-β –Rays measure thickness upto ~ 0.2cm of steel γ-rays can be used with steel upto 10cm thick.
-Level gauges are used to measure amount of liquid in fire extinguisher &gas cylinders
-Empty –packet detectors can be set to reject empty/insufficiently filled packets filled packets of biscuits/cigarettes.  \
5.decting pipe bursts
- Can be underground pipes carrying water /oil
- If the water / oil is mixed with radioactive substances form the mixture will leak at the point where there is a burst and the radiations can be detected if a detector is passed
6. Effect on static electricity
- In textile industry the presence of static charges can attract dust and cause fires
- When a radioactive element is placed in such industries the radiations emitted will ionize air and ions formed will attract the static charges : this minimises problems due to static charges

### Hazards of radioactive
- Arise from
i. Exposure of the body to external radiation
ii. Ingestion/ inhalation of the radioactive matter
- They damage body cells/ tissues
- Cause mutation/deformities

### Precautions
- Protect the body with lad/ concrete shielding
- Never pick/ hold radioactive elements with bare hands ; use forceps and well protected tongs
- Use radiation absorbers

SAMPLE QUESTIONS
(a) Particles from a radioactive source move through 7cm in air at ordinary pressure
(b) The radioactive emission of radium are α-, β- and γ. Draw labelled diagram to show how the rays can be separated
(c) the table below shows nuclides which are radioactive products of   Their ½ lives and K.E during decay are shown

| nucleide | Half life | energy |
|---|---|---|
| Th | $1.39 \times 10^{10}$ | 3.98 |
| Th | 1.9yrs | 5.42 |
| Ra | 3.64days | 5.66 |
| Rn | 54.5 sec | 6.28 |
| Po | 0.16 sec | 6.77 |

| At | $3 \times 10^{-4}$ sec | 7.64 |
|---|---|---|
| Bi | 60.5 min | X |
| Po | $2.9 \times 10^{-7}$ sec | 8.78 |


i. Identify pairs of isotopes of same element
ii. Identify 2 nuclides by in this table, which have been produced directly by α- decay of other nuclides in the table. Use equations
iii. Identify 2 nuclides in this table, which have been produced by β- decay of other nuclides in the table. Use equations
iv. Suggest a series of decays for formation of
v. Deduce how ½ life varies with energy of emitted rays
    Suggest the value of X for