

TOPIC 1: CHEMICAL EQUATIONS

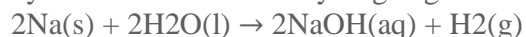
A **chemical equation** is a representation of a chemical reaction with the help of symbols and formulae of the substances involved in the reaction.

It is a chemical shorthand for representing the reacting substance or substances combining (the reactants) and the substance or substances formed as a result of the reaction (the products).

Molecular Equations

A **Molecular equation** is the one which shows the reactants combining and the products formed, in their elemental or molecular forms in a chemical reaction.

An example of a molecular equation is the reaction between sodium and water to produce sodium hydroxide solution and hydrogen gas:



In this context, sodium (in elemental form) reacts with water (in molecular form) to produce sodium hydroxide (in molecular form) and hydrogen gas (in molecular form).

Word Equations for given Chemical Reactions

Write word equations for given chemical reactions

A word equation is a short form of expressing a chemical reaction by word. Chemical reactions can be summarized by word equations that show all the reactants and the products.

This type of equation links together the names of the reactants and the products. For examples, the burning of magnesium in air to produce magnesium oxide can be represented by the following word equation:

Magnesium + Oxygen \rightarrow Magnesium oxide

Another example is the reaction between sodium and chlorine to give sodium chloride (common salt)

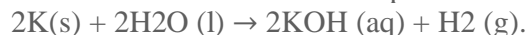
Sodium + Chlorine \rightarrow Sodium chloride

Equations like these sometimes give us some information about the products formed when different substances are reacted together. But equations can be made even more useful by writing them using chemical symbols and formulae.

Any method for representing a chemical reaction must meet basic certain requirements. These are:

- the chemical nature of the reactants as well as those of the products must be clear. The reactants can be in solid, gaseous, liquid or aqueous forms.
- the mole ratios in which the products are combined and the products are formed must be deducible. This means that atoms of the reactants and the products must be balanced.
- the direction of the reaction must be established. This means that it should be clearly shown which substances are the reactants and which ones are the products. This is normally done by separating the reactants from the products by an arrow. The arrow normally points from the reactants to the products.

Consider the reaction between potassium and water:



In this reaction, the three requirements have been met:

- The chemical nature of the reactants [potassium (solid); water (liquid)] and the products [potassium hydroxide (aqueous); hydrogen (gas)] has been shown.

- The mole ratios of the reactants and products are clearly shown: 2 moles of potassium combines with 2 moles of water to produce 2 moles of potassium hydroxide and one mole of hydrogen gas.
- The reactants (potassium and water) and the products (potassium hydroxide and hydrogen) are separated by an arrow (\rightarrow) which also indicates the direction of the reaction

HOW TO PREDICT REACTION PRODUCTS

To predict the reaction products precisely, one needs to take into account the type of reaction occurring. Once you identify the type of reaction that is going to take place, then you will be in a position of telling what possible products of reaction would be. A chemical reaction is said to have taken place when two or more chemical substances called reactants are converted into very different chemical substances called products.

There are a few ways to predict the reaction products.

Firstly, when the reactants are mixed and then isolated, products can be identified. Prediction can also be made when elements from the same group in the Periodic Table show similar reactions. Finally, chemical reactions can be classified into different categories such as combination (or synthesis), decomposition, displacement, precipitation, and redox reactions as described in details below:

Types of Chemical Reactions

When a chemical reaction occurs, it is obvious that the changes have taken place. However, under ordinary conditions it is not easy to see how a reaction goes on. The neutralization of an acid solution with an alkali produces no change that you can see. However, reaction has happened.

The temperature of the mixture increases and the new substances have formed which can be separated and purified. Ideally, we can tell whether a reaction has taken place if one or more of the following changes are observed:

(a) heat change has taken place and can be detected by the change in temperature of the products; (b) a precipitate is formed; (c) there is a change in state of the reactants, i.e. gas, liquid; solid; (d) a colour change has occurred; or (e) a gas is evolved and can be identified by its colour, smell or by effervescence.

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There are very many different chemical reactions. To make it easy to study about these reactions, it is useful to try to group certain types of reactions together. They may be grouped according to certain types of phenomena which accompany them. They can further be subdivided into categories of reactions, each of which has its unique characteristics. Some types of chemical reactions are discussed below:

Combination or synthesis ($A + B \rightarrow C$)

Synthesis reaction occurs when two or more simple substances (elements or compounds) are combined to form one new and more complex substance. The general form of a synthesis reaction is: element or compound + element or compound \rightarrow compound.

The reaction between iron and sulphur to form iron (II) sulphide is the best example for this kind of reaction. Iron combines directly with sulphur to form iron (II) sulphide:



Another example is the reaction between hydrogen and oxygen to form water:



Decomposition ($A \rightarrow B + C$)

Decomposition occurs when one compound breaks down into simpler substances. All decomposition reactions have one thing in common: There is only one reactant and it breaks down into two or more simpler products. Decomposition can be brought about by heat, light, electricity and even enzymes or catalysts.

Decomposition by heat

Decomposition caused by heat is termed as thermal decomposition. An example is the decomposition of calcium carbonate (limestone) which breaks down into calcium oxide(quicklime) and carbon dioxide gas when heated.



Formula Equations Using Chemical Symbols

Write formula equations using chemical symbols

Essentially, chemical reactions can be expressed in two forms. The chemical reaction can be expressed either as a word equation or as a formula (or symbolic) equation. We have already seen how chemical equations can be represented by words (word equation). The formula equation makes use of chemical symbols and formulae to represent a chemical reaction. An example is the reaction between iron and sulphur to form iron (II) sulphide: $\text{Fe} + \text{S} \rightarrow \text{FeS}$

Steps for writing a chemical equation

These are the steps to follow when writing a chemical equation:

- State the reaction equation in words, for example, carbon reacts with oxygen to form carbon dioxide.
- Write the complete word equation using an arrow to separate the reactants from the products: Carbon + Oxygen \rightarrow Carbon dioxide. Conventionally, the reactants are placed on the left-hand side and the products on the right-hand side of the equation. An arrow from left to right indicates that the reaction proceeds from reactants to products as shown.
- Change the words into the correct symbols and formulae of the reactants and products: $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
- Balance the number of each type of atoms on each side of the equation. It is important to make sure that there is equal number of each kind of atom on the left of a chemical equation as on the right in order for your equation to comply with the Law of Conservation of Mass (or Indestructibility of Matter): Matter can neither be created nor destroyed in the course of a chemical reaction. This means that the total mass of all products of a chemical reaction is equal to the total mass of all reactants. All atoms appearing on the left-hand side must also be presented on the right-hand side. No atom should appear as a product if it is not present as a reactant.
- Add the state symbols: Reactants and products may be solids, liquids, gases or solutions. You show their state by adding state symbols to the equation. The state symbols are, (s) for solid, (l) for liquid, (g) for gas and (aq) for aqueous solution (solution in water). For the two reactions above, the equations with the state symbols are: $\text{Fe}_{(s)} + \text{S}_{(s)} \rightarrow \text{FeS}_{(s)}$; $\text{C}_{(s)} +$

$\text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})}$ All state symbols must be bracketed and placed as subscripts after the reactant(s) and product(s).

Balancing Chemical Equations

Balance chemical equations

A balanced chemical equation has an equal number of atoms of different elements of the reactants and the products on both sides of the equation. A balanced equation gives us more information about a reaction than we get from a simple word equation.

Below is a step-by-step approach to working out the balanced equation for the reaction:

- Write the chemical equation for the reaction with the correct symbols and formulae of the reactant(s) and the product(s).
- Identify different atoms of the different elements of the reactant(s) and the product(s).
- Check whether these different atoms are equal on both sides of the equation. Some atoms may balance each other directly.
- Balance the atoms on each sides of the equation by Hit and Trial Method.
- Add state symbols.

Example 1

The reaction between hydrogen and oxygen to produce water:

Hydrogen + Oxygen \rightarrow Water

$\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$ (not balanced)

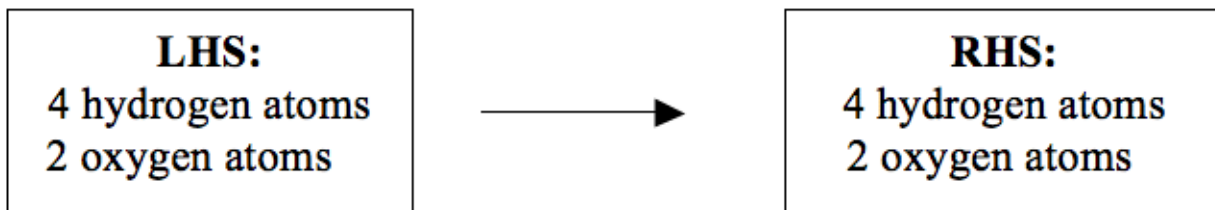
The atoms involved in the reaction are hydrogen and oxygen. It is these atoms that we are going to balance. The atoms must be equal on both sides of the reaction equation. There are two hydrogen atoms on each side of the equation. But, as you can see there are two oxygen atoms on the left-hand side (LHS) of the equation and only one oxygen atom on the right-hand side (RHS). To balance oxygen atoms, we write 2 before water.

$\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ (not balanced yet)

By introducing 2 before water, another problem has been created. Now we have 4 hydrogen atoms on the RHS but only 2 hydrogen atoms on the LHS. To equalize the number of hydrogen atoms we write 2 before hydrogen on the LHS.

$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ (balanced).

You can still check to find out whether the atoms are balanced or not. Now look at the number of atoms on each side of the equation:



Now, the number of hydrogen and oxygen atoms is the same on both sides of the equation. This is because the atoms do not disappear during a reaction. They are neither created nor destroyed. They obey the Law of Conservation of Mass. When the numbers of different atoms are the same on the both sides, an equation is said to be balanced. Once the equation is balanced you can now add the state symbols.

$2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{H}_2\text{O}_{(\text{l})}$

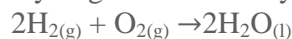
This gives a standard and an acceptable chemical equation.

An equation which is not balanced is not correct. An unbalanced equation implies that the atoms have been created or destroyed. It is therefore, wrong and calculations based on it are certainly unreliable.

Remember that we cannot change the formulae of the substances involved in the reaction. These are fixed by the bonding in the substance itself. For instance, in attempt to balance the number of oxygen in water, H_2O , we cannot write H_2O_2 . We can only put a multiplying numbers before symbols and formulae, e.g. $2\text{H}_2\text{O}$.

Example 2

Hydrogen burns in oxygen to form water. The equation for the reaction is:



- How much oxygen is needed to burn 1g of hydrogen?
 - How much water is formed when 5g of hydrogen is completely burned in oxygen?
- (Atomic weights: H = 1, O = 16)

Solution:

a. Reaction equation: $2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{H}_2\text{O}_{(\text{l})}$

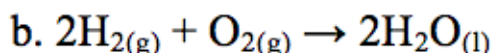
Atoms present: H : O

Molecular weights: 4 : 32

Reacting weights: 1g : Xg

The weight, X, of oxygen = $1 \times 32 / 4 = 8\text{g}$

So, 1g of hydrogen needs 8g of oxygen



H : H_2O

Molecular masses: 4 : 36

Reacting weights: 5g : Xg

$$\begin{aligned} X &= \frac{5 \times 36}{4} \\ &= 45\text{g} \end{aligned}$$

So, the amount of water formed = 45g.

Ionic Equations

The Different Between Molecular Equations and Ionic Equations

Differentiate between molecular equations and ionic equations

Ionic equations are equations in which the reacting substances are represented in ionic forms after the elimination of spectator ions. In other words, ionic equations are those equations represented in such a way that spectator ions are not included in the final equation. Spectator ions refer to those ions, which do not change during the reaction i.e. they do not take part in a chemical reaction.

In order to be able to derive an ionic equation from a molecular equation, one must be acquainted with the solubility rules as outlined below:

- All sodium, potassium and ammonium salts are soluble.
- All nitrates, chlorates and acetates are soluble.
- All binary compounds of the halogens (other than F) with metals are soluble, except those of silver, copper, lead and mercury (lead halides are soluble in hot water).
- All sulphates are soluble except those of silver, lead, mercury (I), barium, strontium and calcium.
- All carbonates, sulphites and phosphates are insoluble except those of ammonium and alkali metal (Group I) cations.
- All hydroxides are insoluble except those of ammonium, barium and alkali metal (Group I) cations.
- All sulphides are insoluble except those of ammonium, alkali metal (Group I) cations and alkali earth metal (Group II) cations.
- All oxides are insoluble except those of calcium, barium and alkali metal (Group I) cations; these soluble ones actually react with the water (hydrolyse) to form hydroxides.

Balanced Ionic Equations

Write balanced ionic equations

Steps for writing balanced ionic equations

- Write a balanced formula equation for the reaction.
- Split all soluble reactants and products into individual ions, clearly indicating their state symbols. Remember that substances that exist as molecules such as water, gases and concentrated mineral acids, precipitates and neutral atoms do not consist of ions and hence do not ionize in water.
- Cancel out all the ions which appear on both sides of the equation (spectator ions). These are the ions which remain unchanged in the reaction.
- Re-write the remaining ions. This is the net ionic equation for that reaction.

Example 3

Consider the reaction for neutralization of hydrochloric acid with sodium hydroxide.

- **Step 1:** $\text{HCl}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow \text{NaCl}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$
- **Step 2:** $\text{H}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})} + \text{Na}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$
- **Step 3:** $\text{H}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})} + \text{Na}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$
- **Step 4:** $\text{H}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})}$

TOPIC 2: HARDNESS OF WATER

The Concept of Hardness of Water

The Concept of Hardness of Water

Explain the concept of hardness of water

As water flows over the land, it dissolves many mineral substances. The dissolved minerals are deposited together with water in rivers, lakes and oceans. Water is said to be hard if it contains some specific type of dissolved minerals. It is important to note that not all dissolved salts make water hard.

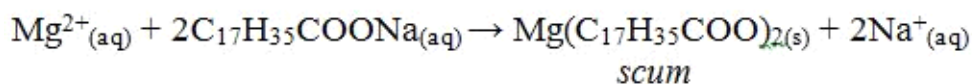
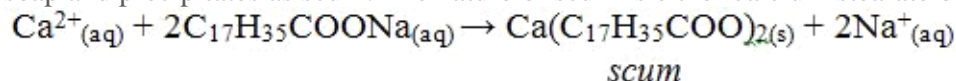
As you learned early, water is treated in water purification plants before being piped to your home. The treatment removes only the insoluble particles and kills bacteria. So the water still is not pure. It contains natural compounds dissolved from rocks and soil. It may also contain traces of chemicals dumped from homes, farms and factories.

Water obtained from an area where the rocks contain chalk, limestone, dolomite or gypsum, contains dissolved calcium and magnesium sulphates and hydrogencarbonates. These salts make the water hard.

One can distinguish between hard and soft water when washing with soap. Hard water does not form lather easily. Instead, it forms a precipitate or scum. It requires much soap to react with all the dissolved minerals before enough lather is formed. Therefore, hard water wastes soap during washing.

When soap is used with hard water a “scum” forms on the surface. This is a result of a precipitation reaction between calcium and/or magnesium ions and soap. Soaps are the sodium or potassium salts of long-chain organic acids. Soaps are made from animal fats by treatment with alkali (NaOH or KOH). Ordinary washing soap is a compound of stearic acid, $C_{17}H_{35}COOH$. The nature of such soaps is the salt, sodium stearate, $C_{17}H_{35}COONa^+$. Sodium stearate is soluble in water but calcium stearate is not.

When soap is mixed with hard water, the calcium or magnesium salts in the hard water react with soap and precipitates as scum. The nature of scum is either calcium stearate or magnesium stearate:



Soap will not form any lather with water until all the calcium and magnesium ions have been precipitated. Hard water, therefore, wastes soap. This means that more soap may be used for an efficient washing. The amount of soap needed to just produce froth can be used to estimate the hardness of water.

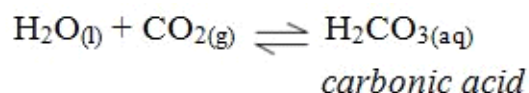
The problem of scum formation only occurs with soaps. Soapless detergents do not produce scum. The trade names for some soapy detergents sold in Tanzania include *Komoa*, *Kuku*, *Taifa*, *Mbuni*, *Mshindi*, *Changu*, *Jamaa* and several other bar soaps. The trade names for some soapless detergents include *Omo*, *Foma*, *Tesa*, *Toss*, *Dynamo*, *Swan*, etc.

Causes of Permanent and Temporary Hardness in Water

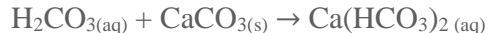
State causes of permanent and temporary hardness in water

Water is generally said to be hard if it contains soluble salts of calcium and magnesium. The salts are calcium and magnesium sulphates and hydrogencarbonates. Hardness of water is caused by higher than usual levels of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in water.

As rain water passes through the atmosphere, it dissolves carbondioxide to form a weak carbonic acid.



As this solution passes over and through rocks containing chalk, limestone or dolomite, the rainwater very slowly dissolves them:



The calcium hydrogencarbonate formed is soluble in water and is responsible for the presence of calcium (Ca^{2+}) ions in water.

Some of the rocks may contain gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4), Kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) or dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) which can dissolve to a limited extent in water. The presence of these dissolved substances also causes the water to be hard. These substances dissolve sparingly in water to form Ca^{2+} and Mg^{2+} ions which are responsible for water hardness as stated early.

Activity 1

Investigation of the causes of water hardness

Materials:

- Test tube rack-
- Five clean test tubes
- Measuring cylinder (100cm^3)
- Calcium sulphate solution (1 mol dm^{-3})
- Soap solution
- Magnesium sulphate solution (1 mol dm^{-3})
- Sodium sulphate solution (1 mol dm^{-3})
- Potassium sulphate solution (1 mol dm^{-3})
- Distilled water

Procedure:

- Label five clean and dry test tubes as A, B, C, D and E. 2
- Add 10 cm^3 of 1.0M calcium, magnesium, sodium and potassium sulphate solutions and distilled water in each of the test tubes respectively.
- Add 5 cm^3 of soap in each test tube
- Shake the test tubes well and place them in a test tube rack
- Observe the amount of lather formed in each test tube, and if there is any precipitate (scum) formed.

Results:

Results of experiment showing minerals which cause water hardness

Test tube	Salt present	Ions present in solution of salt	Lather or scum formed?	Water hard or soft?
A	calcium sulphate	Ca^{2+} , SO_4^{2-}	scum is formed	Hard
B	magnesium sulphate	Mg^{2+} , SO_4^{2-}	scum is formed	hard
C	sodium sulphate	Na^+ , SO_4^{2-}	lather is formed	soft
D	potassium sulphate	K^+ , SO_4^{2-}	lather is formed	soft
E	distilled water	no ions	lather is formed	soft

Interpretation of the results

From the result of experiment, we can conclude that scum is produced when either calcium or magnesium salt is present in water. So, high levels of calcium or magnesium ions in water are responsible for water hardness.

When the concentration of either of these minerals is over 150 milligrams per cubic decimeter (150 mg/dm³), water is considered to be hard. The upper limit allowed is 300 mg/dm³

Types of Hardness of Water

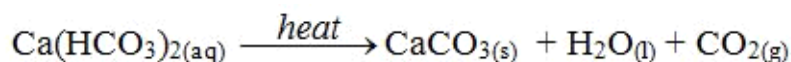
Types of Hardness of Water

Identify types of hardness of water

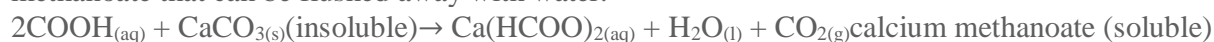
The hard water in some areas can be softened simply by boiling the water, but this is not true in all cases. This means that the hardness in water can be divided into two types – temporary and permanent hardness.

Temporary hardness

Temporary hardness in water is caused by dissolved calcium or magnesium hydrogencarbonates. The most important characteristic of temporarily hard water is that it can be softened by simply boiling. When the water is boiled, the soluble sodium hydrogencarbonate is decomposed to form the insoluble calcium carbonate.



The decomposition causes the “furring” of kettles, hot water pipes and shower heads. This means that the inside of kettles, pipes and shower heads become coated with a layer of calcium carbonate (*limescale*) caused by the decomposition of the hydrogencarbonate according to the equation above. In many supermarkets, it is possible to buy a limescale remover. This is often a solution of methanoic acid (formic acid). This weak acid is strong enough to react with limescale but not with the metal. The insoluble limescale (carbonate) is probably dissolved to a soluble compound, calcium methanoate that can be flushed away with water.



Permanent hardness

Permanent hardness in water is caused by soluble sulphates and chlorides of calcium and magnesium (CaSO₄, MgSO₄, CaCl₂ and MgCl₂). This type of hardness cannot be removed by boiling the water. This is because boiling does not decompose the chlorides of calcium or magnesium. Such water may only be softened by chemical treatment or ion exchange methods

The Difference between Soft and Hard Water

Differentiate soft from hard water

Activity 2

Distinction between temporarily and permanently hard water

Materials:

- Calcium carbonate
- Dilute hydrochloric acid
- 4 test tubes
- Test tube rack
- 1 litre of distilled water
- Calcium chloride
- Soap solution
- Beaker
- Heat source

Method:

- Prepare carbon dioxide gas in the laboratory by mixing calcium carbonate with hydrochloric acid in a gas generator.
- Bubble the gas through a suspension of calcium carbonate in water. Shake well as you bubble the gas until most of calcium carbonate has dissolved. Filter and divide the filtrate into two test tubes M and N.
- Prepare a 0.5M solution of calcium chloride and divide it in two test tubes P and Q.
- Prepare soap solution in a large beaker.
- Arrange the four test tubes in a rack
- Heat the solutions in test tubes M and P to boiling. Allow them to cool.7. Add 10cm³ of the soap solution to each of the four test tubes, M, N, P and Q. Shake well and allow to rest. Observe lathering and scum formation.

Note:

When calcium carbonate is reacted with dilute hydrochloric acid, carbon dioxide gas is produced.

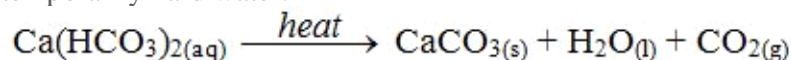


When carbon dioxide gas is bubbled through a suspension of calcium carbonate in water for a long time, the insoluble calcium carbonate dissolves to give the soluble bicarbonate, the presence of which makes the water hard.



The purpose of heating solutions in test tubes M and P was to try to remove water hardness.

However, only the hardness in test tube M was merely removed by boiling because it contains the temporarily hard water.



The hardness in test tube P could not be removed by just boiling because it contained the hard water. Calcium chloride cannot be decomposed by heat. So, no change is expected after heating.

Results:

- Scum was formed in test tubes N, P and Q but P and Q contained more scum than N.
- Lather was formed in test tube M only.
- Test tube M contained temporarily hard water and test tube P contained permanently hard water. The hardness in test tube M was removed by boiling while that in test tube P was not.
- Test tubes P and Q contained permanently hard water. The hardness in this water could not be removed by mere boiling.

Treatment and Purification of Hard Water

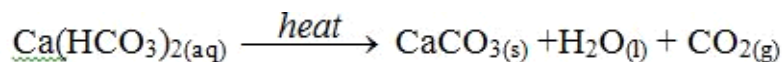
Process of Hard Water Treatment and Purification

Examine process of hard water treatment and purification

Because of the problem it causes, hard water is often softened for use in factories, industries and homes. That means removing the dissolved calcium and magnesium ions. Described below are the methods of treating and purifying hard water.

Boiling

Boiling removes temporary hardness in water, as you saw early. Boiling causes calcium carbonate to precipitate. The hydrogencarbonate in water are decomposed to carbonates, which are insoluble in water



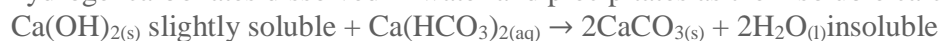
In this way, the calcium is removed, since the calcium carbonates being insoluble, takes no further part in the reaction. An insoluble calcium salt cannot cause hardness. However, this method uses a lot of fuel, which makes it expensive to do on a large scale.

Distillation

Distillation removes all impurities from water. This gets rid of both temporary and permanent hardness. In distillation, the water is boiled and the steam collected, cooled and condensed. Distilled water is pure and softest water. All the dissolved substances have been removed. Like boiling, it is an expensive option in terms of fuel used. But it is essential for some purposes, for example for laboratory experiments and for making drugs.

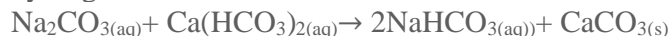
Addition of calcium hydroxide

Addition of calculated amounts of calcium hydroxide can remove temporary hardness. The quantity to be added should be properly calculated because excess would cause hardness on its own account. The amount of calcium hydroxide to be added is calculated based on knowledge of the hardness of water and the capacity of the reservoir (Clark's method). The calcium hydroxide reacts with the hydrogencarbonates dissolved in water and precipitates as the insoluble calcium carbonates.



Addition of sodium carbonate (washing soda)

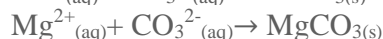
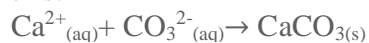
Washing soda removes both temporary and permanent hardness by precipitating calcium carbonate. It reacts with calcium hydrogencarbonate (which causes temporary hardness) to form sodium hydrogencarbonate like this:



It also reacts with calcium sulphate (which causes permanent hardness) to form sodium sulphate thus:

$$\text{Na}_2\text{CO}_3(\text{aq}) + \text{CaSO}_4(\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + \text{Na}_2\text{SO}_4(\text{aq})$$

These sodium salts are soluble, but do not cause the water to be hard. The calcium and magnesium ions are precipitated as insoluble calcium and magnesium carbonates. Ionically, the situation is like this:



Ion Exchange

Another method that removes both temporary and permanent hardness in water is the use of *ion exchange resin*. A typical *ion exchanger* is a container full of small beads. These beads are made of special plastic called ion exchange resin. The resin beads are porous and contain sodium ions. When hard water flows through the resin, the calcium and magnesium ions in the water are exchanged for the sodium ions and attach themselves to the resin. This process, therefore, removes calcium and magnesium ions from the water. They are replaced by sodium ions, which do not make the water hard.



An ion exchange column removes Ca^{2+} and Mg^{2+} ions from the water and replaces them with Na^+ ions

When all sodium ions have been removed from the resin, it is regenerated by pouring a concentrated solution of sodium chloride through it. The sodium ions remove the calcium and/or magnesium ions off the resin and the ion exchanger is ready for the use again. Other ions could also be used instead of sodium for the resin. But sodium chloride is normally used to supply the sodium ions because salt is cheap.

Use of softeners

Many modern washing powders now have softeners added to them. The softeners are often phosphates. The phosphates ions react with calcium ions to form calcium phosphate and remove the hardness. $3\text{Ca}^{2+}_{(\text{aq})} + 2\text{PO}_4^{3-}_{(\text{aq})} \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s})$

The Importance of Hard Water Treatment and Purification

Describe the importance of hard water treatment and purification

The significance of water in daily life is well known to everyone. The water we obtain from natural sources is never pure. It contains dissolved minerals which render the water unfit for direct uses. The water from some sources contains calcium and magnesium compounds dissolved in it. These compounds are responsible for water hardness. To make the water fit for various uses, it is imperative to remove the hardness. The following points state why it is important to treat and purify hard water:

Hard water wastes soap. To get enough lather with hard water, it requires more soap than it does with soft water. So it is important to soften the water in order to save the soap and hence reduce the cost of washing. Laundry uses less soap and can be done at lower temperatures.

Treating and purifying hard water eliminates the possibility of forming limescale deposits in water boilers, kettles, washing machines, water heaters, shower heads and dish washers. The scale formed around the heating elements can cause the element to overheat and fail.

Treated and purified water leaves no scum on clothes during washing. Scum spoils the finishing of some fabrics. It forms nasty deposits (marks) on clothing that has been washed.

Softened water has the advantage of not blocking the water pipes. In industry, deposits of scales can block the pipes in boilers. This is a safety hazard as it could cause pressure to build up until there is an explosion. A similar coating can occur in hot water pipes at home and in central heating systems.

The Importance of Hard Water in Daily Life

State the importance of hard water in daily life

Hard water is not always disadvantageous. The following points explain the importance of hard water:

- The dissolved calcium and magnesium salts improve the taste of water. Distilled water is tasteless and quite unpleasant to drink. This is why water-processing plants add some salts in the distilled water to make it tasteful.
- Calcium dissolved in hard water is an essential mineral for growth of bones and teeth. It makes our teeth and bones hard, strong and resistant to shear and pressure.
- In some places, old lead pipes are used for water supply. Lead is very poisonous, and a little of it can dissolve in soft water. But the carbonate (CO_3^{2-}) or sulphate (SO_4^{2-}) ions present in hard water reacts with lead to form a coating of lead carbonate or lead sulphate that prevents lead from dissolving. This prevents lead poisoning.
- A coating of calcium carbonate inside pipes, boilers and radiators helps to prevent corrosion.

- In recent years, it has been suggested that drinking hard water helps to prevent heart diseases. 6. It has also been found that hard water is good for brewing beer.

TOPIC 3: ACIDS, BASES, AND SALTS

Acids and Bases

The Natural Sources of Acids and Bases

Investigate the natural sources of acids and bases

In everyday life, we deal with many substances that chemists classify as acids. For example, orange juice and grapefruit juice contain citric acid. These juices, and others of the like, contain ascorbic acid, a substance more commonly known as vitamin C. Examples of natural sources of acids and the type of acids they contain are shown in table below.

Some natural sources acids

Source	Type of acid present
Mineral acids (HCl, H ₂ SO ₄ , HNO ₃ , etc.)	Minerals
Tobacco	Salicylic acid
Tea	Tannic acid
Coffee	Chlorogenic acid
Sugar beet	Glutaric and adipic acids
Blackberry	Isocitric acid
Spinach, tomato	Oxalic acid
Sour (fermented milk)	Lactic acid
Bee, ant and nettle stings	Methanoic acid (formic acid)
Grapes, bananas, tamarinds	Tartaric acid
Citrus fruits	Citric acid (lemons and limes have particularly high concentrations of citric acid; it can constitute as much as 8% of the dry weight of these fruits)

Acids have a sour taste. Vinegar, lemon juice, grapefruit juice and spoilt or fermented milk are all sour tasting because of the presence of acids. The acids present in animal and plant materials are known as **organic acids**.

Salads are often flavoured with vinegar, which contains dilute acetic acid. Boric acid is a substance that is sometimes used to wash the eyes.

In any chemistry laboratory, we find acids such as hydrochloric acid (HCl), sulphuric acid (H₂SO₄), and nitric acid (HNO₃). These acids are called mineral acids because they can be prepared from naturally occurring compounds called minerals. Mineral acids are generally stronger and should be

handled with great care, especially the concentrated acids, for they are very corrosive. They can eat away metals, skin and clothing. Nevertheless, some acids are not corrosive even when they are concentrated. They are called weak acids. Ethanoic acid is one example. It is found in vinegar. In general, organic acids are weaker than natural acids.

You can tell if a substance is acid or not by its effect on litmus. Litmus is a purple dye. It can be used as a solution, or on paper, called litmus paper. Litmus solution is purple. Litmus paper for testing acids is blue while that for testing bases is red in colour. Acids will turn litmus solution **red**. They will also turn blue litmus paper **red**.

Bases do not usually occur naturally. So they are not normally obtained from natural sources.

However, they are prepared in the laboratory or in industry. Bases can be classified into oxides, hydroxides or carbonates. Therefore, bases can be defined as the oxides, hydroxides or carbonates of metals. Bases taste bitter. A bitter taste is a characteristic of all bases.

Most bases are insoluble in water. The bases which dissolve in water are known as **alkalis**. The most common alkalis are potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium hydroxide, $\text{Ca}(\text{OH})_2$, and ammonium hydroxide (NH_4OH), also known as ammonia solution.

Alkalis turn litmus solution **blue** and red litmus paper **blue**. A substance, such as litmus, which changes from one colour to another when mixed with an acid or base, is called an **indicator**. Table 3.2 shows how acids and bases (alkalis) affect the colours of different indicators. We can use this clue of colour changes to tell whether an unknown substance is an acid or base (alkali).

Some common indicator colour changes

Indicator	Colour in acid	Colour in alkali (base)
Methyl orange	orange	yellow
Phenolphthalein	colourless	Pink
Litmus	red	blue
Bromothymol blue	yellow	blue

The Reactions of Acids with Various Materials

Determine the reactions of acids with various materials

Acids react with different substances to produce different products. These reactions are best carried out by using dilute acid solutions. The following are some reactions of dilute acids with various substances.

Reaction with metals

Acids react with *quite* reactive metals (not very reactive ones) to produce salt and liberate a hydrogen gas.

metal + acid → salt + hydrogen

It is unsafe to try this reaction with *very* reactive metals such as sodium or calcium. The reaction with such metals is so violent. Metals less reactive than lead, such as silver and gold have no reaction with dilute acids. Even with lead, it is difficult to see any reaction in a short time.

The salt produced when a dilute acid reacts with a metal depends on the acid and a metal used:

- $\text{Mg}_{(\text{s})} + 2\text{HNO}_{3(\text{aq})} \rightarrow \text{Mg}(\text{NO}_3)_{2(\text{aq})} + \text{H}_{2(\text{g})}$
- $\text{Zn}_{(\text{s})} + 2\text{HCl}_{(\text{aq})} \rightarrow \text{ZnCl}_{2(\text{aq})} + \text{H}_{2(\text{g})}$

Reaction with carbonates

Acids react with carbonates to give salt, water and carbon dioxide. In general, all carbonates give off carbon dioxide when they react with acids.

acid + metal carbonate → salt + water + carbon dioxide

The normal methods of preparing carbon dioxide in the laboratory are based on this reaction. Dilute hydrochloric acid is reacted with marble chips (calcium carbonates):

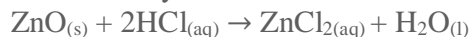


Reaction with oxides and hydroxides (alkalis)

Hydroxides: acids react with alkalis, forming salt and water:



Oxides: They also react with metals oxides, forming salt and water:

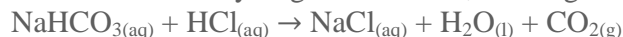


The bases (oxides, hydroxides) all react in the same way with acids, and in the process, salts are formed. This type of reaction is known as **neutralization reaction**. It can be summarized up in a general equation:

acid + base → salt + water

Reaction with hydrogencarbonates (bicarbonates)

Acids react with hydrogencarbonates, forming salt, water and liberating carbon dioxide gas:



The Reactions of Alkalis with Various Materials

Determine the reactions of alkalis with various materials

Alkalis react with acids to produce salt and water. All alkalis, except ammonia solution, will react with ammonium compounds liberating ammonia gas. Aqueous solutions of alkalis will precipitate the insoluble hydroxides of other metals from the solutions of metal salts. Caustic alkalis attack aluminium, zinc and lead to form salts. They react with carbon dioxide to form carbonates.

The Reactions of Bases with Various Substances

Determine the reactions of bases with various substances

Characteristic reactions of bases

Dissolution in water

Most bases are insoluble in water. Some are soluble in water. Soluble bases are known as *alkalis*.

The commonest alkalis are sodium hydroxide, (NaOH), calcium hydroxide, Ca(OH)₂, potassium hydroxide, (KOH), and ammonium hydroxide or ammonia solution, (NH₄OH). All alkaline solutions contain hydroxyl ions, OH⁻. In sodium hydroxide solution, the ions are produced like this:



Like acids, alkalis can also be classified as strong or weak. Ammonia solution is a weak base because it ionizes just partially:

The rest of the bases are strong bases because they ionize fully into ions in solution.

Reaction with acids

Bases react with acids to produce salt and water. Refer to the reactions of acids with oxides and hydroxides discussed early.

Reaction with ammonium compounds

Alkalis turn litmus solution **blue** and red litmus paper **blue**. A substance, such as litmus, which changes from one colour to another when mixed with an acid or base, is called an **indicator**. Table 3.2 shows how acids and bases (alkalis) affect the colours of different indicators. We can use this clue of colour changes to tell whether an unknown substance is an acid or base (alkali).

Reaction with aqueous salts of metals

Aqueous solutions of alkalis will precipitate the insoluble hydroxides of other metals from the solutions of metal salts. Only NH_4OH , KOH and NaOH are soluble enough in water. All other hydroxides are insoluble and can be precipitated from aqueous solution by these three alkalis.

- When sodium hydroxide solution is added to copper (II) sulphate solution, a pale blue precipitate of copper (II) hydroxide is formed. $\text{CuSO}_{4(\text{aq})} + 2\text{NaOH}_{(\text{aq})} \rightarrow \text{Cu}(\text{OH})_{2(\text{s})} + \text{Na}_2\text{SO}_{4(\text{aq})}$
- Another example is the reaction between potassium hydroxide and iron (II) chloride, which precipitates iron (II) hydroxide. $\text{FeCl}_{3(\text{aq})} + 3\text{KOH}_{(\text{aq})} \rightarrow \text{Fe}(\text{OH})_{3(\text{s})} + 3\text{KCl}_{(\text{aq})}$

Reaction with metals

Caustic alkalis attack very few metals. The metals known to be attacked by the alkalis are aluminum, zinc and lead, where the aluminate, zincate and plumbate (II) are formed respectively. The aluminum will react thus: $2\text{Al}_{(\text{s})} + 6\text{NaOH}_{(\text{aq})} + 6\text{H}_2\text{O}_{(\text{l})} \rightarrow 2\text{Na}_3\text{Al}(\text{OH})_{6(\text{aq})} + 3\text{H}_{2(\text{g})}$ (*sodium aluminate*)

Reaction with carbon dioxide

When carbon dioxide gas is bubbled through aqueous solutions of the caustic alkalis, the carbonates are formed.

$2\text{NaOH}_{(\text{aq})} + \text{CO}_{2(\text{g})} \rightarrow \text{Na}_2\text{CO}_{3(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$. With excess of the gas, the hydrogencarbonates are formed. $\text{Na}_2\text{CO}_{3(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} + \text{CO}_{2(\text{g})} \rightarrow 2\text{NaHCO}_{3(\text{aq})}$

Reaction with chlorine

Chlorine reacts with excess of cold dilute caustic alkalis to form the hypochlorite, (NaClO or KClO). $2\text{NaOH}_{(\text{aq})} + \text{Cl}_{2(\text{g})} \rightarrow \text{NaCl}_{(\text{aq})} + \text{NaClO}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$. $2\text{KOH}_{(\text{aq})} + \text{Cl}_{2(\text{g})} \rightarrow \text{KCl}_{(\text{aq})} + \text{KClO}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$

If excess chlorine is bubbled through hot concentrated solutions of caustic alkalis, the chlorates are formed, (NaClO_3 or KClO_3).

$6\text{NaOH}_{(\text{aq})} + 3\text{Cl}_{2(\text{g})} \rightarrow 5\text{NaCl}_{(\text{aq})} + \text{NaClO}_{3(\text{aq})} + 3\text{H}_2\text{O}_{(\text{l})}$. $6\text{KOH}_{(\text{aq})} + 3\text{Cl}_{2(\text{g})} \rightarrow 5\text{KCl}_{(\text{aq})} + \text{KClO}_{3(\text{aq})} + 3\text{H}_2\text{O}_{(\text{l})}$

Applications of acid-base neutralization in everyday life

Applications of acid-base neutralization in everyday life

Acid-base neutralization has many applications in everyday life. The following are some of these applications:

Indigestion and pain relief

The dilute hydrochloric acid produced in your stomach is used for digestion and killing bacteria that might have been swallowed together with food or taken with water. However, excess acid causes indigestion, which can be painful. To ease the pain, we take an anti-acid treatment. Anti-acids are a broad group of compounds with no toxic effects on the body. They are used to neutralize the effects of acid indigestion.

Some of these anti-acids such as milk of magnesia [insoluble magnesium hydroxide, $\text{Mg}(\text{OH})_2$] help to neutralize and hence counteract the excess acid in the stomach. This treatment, therefore, prevents indigestion and pains. The neutralization reaction equation is:

$\text{Mg}(\text{OH})_{2(\text{aq})} + 2\text{HCl}_{(\text{aq})} \rightarrow \text{MgCl}_{2(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})}$

Other anti-acids such as “Alka-Seltzer” contain soluble materials, including sodium hydrogencarbonate. These tablets also contain some citric acid (a solid acid). On adding water, the acid and some of the sodium hydrogencarbonate react, producing carbon dioxide gas. This helps to

spread and dissolve the other less soluble material. When taken, more sodium hydrogencarbonate neutralizes the excess hydrochloric acid in the stomach, thus easing digestion. Some anti-acid tablets also contain painkiller to relieve pain. “Soluble aspirin” tablets dissolve and work in a similar way to “Alker-Seltzer” tablets. Vitamin C (ascorbic acid) can be added to the tablets. Note that it is important to add water to start the action of the acid.

Descaling kettles

The limescale (CaCO_3) is formed inside boilers, kettles and water heaters when hard water is boiled. The limescale can be removed by treatment with an acid that is strong enough to react with CaCO_3 , but not strong enough to damage the metal. Vinegar can be used to descale kettles. Commercial “discalers” use other acid solutions such as methanoic acid

Prevention of tooth decay

Food remnants sticking onto teeth (plaque), after eating especially sugary food is acted upon by bacteria in your mouth. The pH of a sugar solution is 7. However, bacteria in your mouth break down the sugar in plaque to form acids, for example lactic acid. These acids lower the pH. Tooth decay begins when the pH falls below 5.8. The acid attacks the tooth enamel.

To help prevent tooth decay many types of toothpaste contain basic substances to neutralize the acids produced by these bacteria in your mouth. The pH of these basic substances is alkaline (higher than 7). The pH of saliva is slightly alkaline (pH 7.4), so it can also help to counteract the acid, particularly after a meal. After eating a meal, for example, it takes about 15 minutes for saliva to raise the pH above 5.8, and stop further decay.

Soil treatment

Most plants grow best when pH of the soil is close to 7. They prefer the pH of between 6.5 and 7.0. If the soil pH is below 6.0, the soil is too acidic. Above the pH of 8.0, the soil is too alkaline. If the soil is too acidic or too alkaline, the plants grow poorly or not at all.

Chemicals can be added to the soil to adjust its pH. Most often, if the soil is too acidic, it is usually treated by liming. In this context, liming means addition of quicklime (calcium oxide), slaked lime (calcium hydroxide) or powdered chalk or limestone (calcium carbonate) to an acidic soil. These compounds (bases) have the effect of neutralizing the acidity of the soil.

If the soil is too alkaline, acids such as sulphuric acid, nitric acid or hydrochloric acid may be added to the soil to neutralize excessive alkalinity. However, these compounds are very expensive and hence uneconomical to apply on large-scale basis.

Insect stings treatment

When a bee stings someone, it injects an acid liquid into the skin. The bee sting, which is acidic in nature, can be neutralized by rubbing on *calamine solution*, which contains zinc carbonate or baking soda, which is sodium hydrogencarbonate. These compounds are basic in nature and so have the effect of neutralizing the acid in the sting.

Wasp stings are alkaline in nature, and can be neutralized with vinegar, which contains ethanoic acid. Ant and nettle stings contain methanoic acid. These may be neutralized by rubbing an extract squeezed from crushed onion leaves (which contain basic compounds) on the affected skin. The acid in the sting can also be neutralized by applying weak alkalis such as ammonia solution, ash extract, baking powder, etc.

Factory wastes treatment

Liquid wastes from factories often contain acid. If it reaches a river, lake or ocean, the acid will kill fish and other aquatic life. This can be prevented by adding slaked lime (calcium hydroxide) to the waste, to neutralize the acid before being dumped into water bodies.

Indicators

An Indicator from Locally Available Materials

Explain an indicator from locally available materials

Certain coloured substances (many extracted from plants) have been found to change colour if added to an acid or alkaline solution. The colour change is reversed if the acid or alkali is neutralized.

Substances that behave like this are known as indicators.

Coloured extracts can be made from red cabbage or blackberries, but probably the most used indicator is *litmus*. This is extracted from lichens.

Litmus is *purple* in a neutral solution. When added to an acid solution, it turns *red*. Changing this red colour of litmus needs a chemical reaction. The molecules of the indicator are usually changed in the presence of the acid. Substances with the opposite chemical effect to acids are needed to reverse the change, and these are called alkalis. They turn litmus solution to *blue*. Litmus can also be used in paper form, in which case it is called *litmus paper*. Here it comes in the blue and red forms. Litmus is a single chemical compound. It gives a single colour change.

Litmus is not the only single indicator that chemists find useful. Others that are used frequently are *phenolphthalein* and *methyl orange*. These indicators give different colour changes when in acidic and alkaline solutions (see table 3.2). Another commonly used indicator is the *universal indicator* (or full-range indicator). This is made from a mixture of dyes. Such an indicator is useful because it gives a range of colours (“spectrum”) depending on the strength of the acid or alkali added (see table 3.3)

With a universal indicator, different acids produce a range of different colours. Indeed, solutions of the same acid with different concentrations (pH) give different colours.

The more acidic solutions (for example battery acid) turn the universal indicator *bright red*. A less acidic solution (for example vinegar) will only turn it *orange-yellow*. There are also colour differences produced with different alkali solutions. The most alkaline solutions give a *violet* colour while the less alkaline solutions give a *blue* colour.

We learned that many indicators are extracted from plants. Flowers and leaves of different plants have different colours. These plant organs may be used to prepare indicators locally.

Activity 1

To prepare indicators from local plant materials

Procedure:

- Collect flowers from different plants in your local area. You may use coloured leaves if the coloured flowers are not available.
- Crush the flowers/leaves in a motor and pestle to make a fine paste.
- Add ethanol to the paste to wash out chlorophyll. Add about 10cm³ of ethanol per gram of pestle used.
- Grind the mixture to a very fine paste so that the ethanol can penetrate the broken plant cells fully.
- Place the mixture in the sun or heat gently to evaporate off ethanol. Make sure most of the ethanol has evaporated.

- Filter the mixture to obtain a clear but coloured filtrate. To obtain as much extract as possible, squeeze the paste in a clean piece of cloth and collect the juice in a beaker. The liquid you obtain is your indicator.
- Arrange test tubes in a rack and label them A, B, C D and E.
- Pour sodium hydroxide, dilute hydrochloric acid, limewater, lemon juice, vinegar and washing soda in test tubes A, B, C, D and E respectively.
- Add two to three drops of the prepared indicator in each of the test tubes. Observe and record the colour changes.

Questions from the experiment

- What was the colour of your indicator?
- Write down the colour changes in each of the test tubes A to E.
- Which substance showed a sharp colour change?
- Perform a similar experiment using a ready-made universal indicator and observe whether there is any difference in colour changes between this commercial indicator and that one prepared from local plants.

The Acidity and Alkalinity of Substance Using Indicators

Test the acidity and alkalinity of substance using indicators

The Strengths of Acids and Bases

There is a big difference between the strength of an acid or base and its concentration. An acid or alkaline solution is said to be concentrated if it contains a large amount of it in a small amount of water. A dilute acid or base (alkali) has a small amount of it in a lot of water. The concentration of an acid or base tells us how much of it is dissolved in a certain volume of solution. The concentration is normally expressed in grams per litre (g dm^{-3}) or moles per litre (mol dm^{-3}).

The strength of an acid or alkali expresses its dissociation in water. Strong acids or alkalis will dissociate completely in water to form ions. Examples of strong acids are sulphuric acid, hydrochloric acid, nitric acid and phosphoric acid. Weak acids include ethanoic acid, carbonic acid and methanoic acid. Examples of strong alkalis include potassium hydroxide, sodium hydroxide, calcium hydroxide and ammonium hydroxide. Weak bases include ammonia solution and sodium hydrogencarbonate.

A strong acid or alkali forms many ions in water. The number of hydrogen ions, H^+ , formed when it dissociates in water, determines the strength of an acid. The strength of an alkali depends on the number of hydroxyl ions, OH^- , formed when it dissociates in water. Strong acids and alkalis will form many H^+ and OH^- ions respectively. Weak acids or bases will form very few of the respective ions.

Likewise, the term **weak** acid or base should not be confused with the term **dilute** acid or base. A weak acid dissociates in water only very slightly to form very few protons, H^+ . A weak alkali also dissociates very slightly to form very few hydroxyl ions, OH^- .

The Concept of an Indicator

Describe the concept of an indicator

You have seen that single indicators change their colours only once when put in different acid and alkaline solutions. The single indicators most commonly used include litmus, phenolphthalein and methyl orange.

On the other hand, universal indicators show a range of colour changes depending on the strength of an acid or base.

Single indicators can only tell us whether a certain solution is an acid or an alkali. These types of indicators cannot be used to compare two acids or two alkalis with different strengths. Litmus paper, for example, cannot be used to compare the strengths of sulphuric acid and ethanoic acid. Both acids will change the **blue** litmus paper to **red**. Likewise, you cannot compare the strengths of aqueous ammonia solution (NH_4OH) and sodium hydroxide by just using a litmus paper. They will both turn to **red** litmus paper to **blue**.

A universal indicator can be used to measure strengths of different acids and alkalis. This indicator is a mixture of simple indicators. Instead of changing colour just once, it changes colour a number of times depending on the degree of acidity or alkalinity of the substances tested.

The pH scale is a convenient means of expressing the acidity and alkalinity in liquids. The pH scale is a numerical scale used to indicate the relative strengths of acidic or basic solutions in terms of relative amount of hydrogen ions (protons) or hydroxyl ions in solutions. The scale ranges from 0 to 14.

Acidic solutions will have pH values less than 7.0 and alkaline solutions will have pH values greater than 7.0. All neutral liquids e.g. pure water have pH of 7.0. Table 3.3 shows the pH and strengths of acidic and alkaline solutions and the associated indicator colour changes.

Colours of the universal indicator in different acidic and alkaline solutions

pH range	Colour	Strength
1, 2, 3	Red	Strongly acidic
4	Orange	
5, 6	Yellow	Weakly acidic
7	Green	Neutral
8, 9	Blue Indigo	Weakly alkaline
10, 11, 12, 13, 14	Purple/violet	Strongly alkaline

Remember that there is no clear dividing line between the pH ranges as apparently shown in the above table. This means that you may have substances with, for example, pH 1.2, 1.5, 3.5, 4.4, 5.6, 8.4, etc. The table just tries to simplify the concept of acidity and alkalinity of acid and alkaline solutions.

Salts

The Natural Source of Salts in Daily Life

Investigate the natural source of salts in daily life

A salt is a substance formed when some or all of the hydrogen atoms of an acid are replaced by a metal or ammonium ion. A salt, therefore, may be defined as *a compound in which the replaceable hydrogen of an acid has been wholly or partially replaced by a metal*.

In sodium chloride (NaCl), for example, the hydrogen atom of hydrochloric acid (HCl) has been wholly replaced by an atom of sodium. In magnesium sulphate (MgSO_4) and sodium sulphate (Na_2SO_4), both hydrogen atoms of sulphuric acid (H_2SO_4) have been replaced by one atom of magnesium and two atoms of sodium respectively. In sodium hydrogen sulphate (NaHSO_4), only one out of two hydrogen atoms has been replaced by an atom of sodium. This type of a salt is called an acid salt, because it still contains a replaceable hydrogen atom.

Many chemical compounds may be classified as salts. The salt most familiar to every body is table salt (sodium chloride). Baking soda is the salt, sodium bicarbonate (NaHCO_3). Magnesium sulphate (also called Epsom salt) is often found in the home.

In general, salts are ionic compounds that are composed of metal and non metal ions. For example, sodium chloride is composed of metallic sodium ions (Na^+) and non-metallic chloride ions (Cl^-).

Some salts are made of metallic and non-metallic radicals e.g ammonium nitrate (NH_4NO_3) is composed of ammonium radical (NH_4^+) and nitrate radical (NO_3^-).

There is a wide range of types and natural sources of salts. Common salt is mined from underground deposits. The salt obtained from such a source contains sodium chloride mixed with rock impurities. The other source of sodium chloride is seawater. The salty taste of seawater is due to the presence of salts such as sodium chloride and magnesium bromide. However, there are many different types of salts present in seawater, though in small proportions, as shown in the table below (table 3.5)

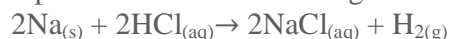
<i>Salt</i>	<i>Formula</i>	<i>Percentage composition</i>
Sodium chloride	NaCl	2.72
Magnesium chloride	MgCl_2	0.38
Magnesium sulphate	MgSO_4	0.17
Calcium sulphate	CaSO_4	0.13
Potassium chloride	KCl	0.09
Calcium chloride	CaCO_3	0.01
Magnesium bromide	MgBr_2	0.01

Sodium nitrate (Chile saltpetre), NaNO_3 and calcium carbonate, CaCO_3 are found in underground deposits. Calcium carbonate occurs naturally as marble, limestone or chalk in the ground from which it can be mined mechanically. What other natural sources of salts do you know?

Types of Salts

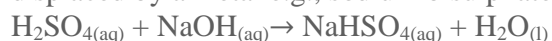
Salts may be classified according to their mode of formation. The following are types of salts grouped according to their mode of formation:

Normal salt:- This is a salt formed when all of the replaceable hydrogen atoms of an acid have been replaced by a metal atom e.g. sodium chloride is a normal salt because all hydrogen atoms are replaced from an acid during its formation.



Other normal salts include magnesium chloride (MgCl_2), potassium chloride (KCl), copper (II) sulphate (CuSO_4), sodium sulphate (Na_2SO_4), sodium carbonate (Na_2CO_3), trisodium phosphate (Na_3PO_4), etc.

Acid salt:- An acid salt is a salt formed when part of the replaceable hydrogen atoms of an acid are displaced by a metal e.g., sodium bisulphate (NaHSO_4) is an acid salt.



Other examples of acid salts include sodium hydrogensulphate, (NaHSO_4), sodium hydrogensulphide, (NaHS) and sodium hydrogencarbonate (NaHCO_3). Since acid salts contain hydrogen ions, they exhibit some acidic properties. Hence, they behave like acids, for example:

- they react with bases to form salts and water only. $\text{NaHSO}_{4(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{Na}_2\text{SO}_{4(aq)} + \text{H}_2\text{O}_{(l)}$
- they react with carbonates to yield carbon dioxide. $2\text{NaHSO}_{4(aq)} + \text{Na}_2\text{CO}_{3(aq)} \rightarrow 2\text{Na}_2\text{SO}_{4(aq)} + \text{H}_2\text{O}_{(l)} + \text{CO}_{2(g)}$

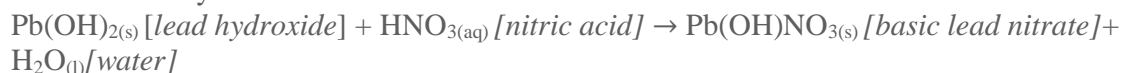
Basic salt:- A basic salt is formed by the action of an acid with higher proportions of the base, than is necessary for the formation of a normal salt.

Examples of basic salts are:

- Basic copper carbonate, $\text{CuCO}_3.\text{Cu}(\text{OH})_2$
- Basic lead carbonate (white lead), $\text{PbCO}_3.\text{Pb}(\text{OH})_2$

- Basic magnesium chloride, $\text{MgCl}_2 \cdot \text{Mg}(\text{OH})_2$
- Basic zinc chloride, $\text{ZnCl}_2 \cdot \text{Zn}(\text{OH})_2$

A basic salt may also be formed by the partial replacement of the hydroxyl groups of a diacidic or triacidic base by an acid radical.



Basic salts are usually insoluble in water. Such salts are formed by the close association of two simple salts, when crystallized from a solution of a mixture of the two.

The Solubility of Different Salts in the Laboratory

Analyse the solubility of different salts in the laboratory

Some salts are more soluble in water than others are. However, other salts are insoluble in water. The knowledge of solubility of different salts in water is very important because it can help us prepare different salts in the laboratory by such methods as precipitation, direct combination (synthesis), crystallization and so forth.

As regards to solubilities, salts can be classified into two groups: salts which are soluble in water (soluble salts) and salts which do not dissolve in water (insoluble salts). Table 3.6 summarizes the solubility of different salts in water.

The patterns of solubility for various types of salts

<i>Soluble salts</i>	<i>Insoluble salts</i>
1. All sodium, potassium and ammonium salts.	silver, mercury(I) and lead chlorides barium, lead (II) and calcium sulphates but other common carbonates are insoluble. but other common hydroxides are insoluble.
2. All nitrates of metals	
3. All chlorides except	
4. All sulphates except.....	
5. Sodium, potassium, and ammonium carbonates.....	
hydroxides.....	
6. Sodium, potassium and ammonium	

Salts in the Laboratory

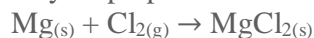
Prepare salts in the laboratory

Several methods are available for the preparation of salts. The solubilities of the prepared salts determine their methods of preparation. Hence, in the choice of a method of preparation of a particular salt, one has to be acquainted with its solubility properties.

Soluble salts are usually prepared by methods which involve **crystallization**. In this method, as the name suggests, resultant salts are in the form of crystals.

Insoluble salts are usually prepared by methods which involve **precipitation**. These methods are sometimes referred to as double decomposition. To precipitate an insoluble salt, you must mix a solution that contains its positive ions with the one that contains its negative ions.

Salts may also be prepared by **direct combination** (or synthesis). For example, magnesium chloride may be prepared in the laboratory by heating magnesium in a stream of chlorine.



Preparation of soluble salts

Soluble salts may be prepared by any of the following methods:

- **Reaction between an acid and an alkali:** In this method, a dilute acid is added to an alkali in the appropriate volume ratio. The reaction between an acid and an alkali is termed as neutralization. For example, sodium chloride may be prepared by the following neutralization reaction: $\text{NaOH}_{(\text{aq})} + \text{HCl}_{(\text{aq})} \rightarrow \text{NaCl}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$. Both reactants are soluble, and no gas is given off during the reaction. So, it is difficult to know when the reaction is over. In this case, you have to use an indicator. A universal indicator or litmus could be used, but even better is phenolphthalein. This is pink in alkaline solution, but colourless in neutral or acidic solutions.
- **Reaction of a metal with an acid:** This is another general method for preparing salts. For example, zinc sulphate can be made by reacting dilute sulphuric acid with zinc: $\text{Zn}_{(\text{s})} + \text{H}_2\text{SO}_{4(\text{aq})} \rightarrow \text{ZnSO}_{4(\text{aq})} + \text{H}_{2(\text{g})}$. However, this method is not suitable for all metals or all acids. It is good for preparing salts of fairly reactive metals such as magnesium, aluminium, zinc and iron. However, the reactions of highly reactive metals like sodium, potassium and calcium with acids are very violent and dangerous. The reaction with lead is too slow. Copper, silver and gold do not react at all.
- **Reaction of a metal oxide with an acid:** Metal oxides, as you studied early, react with dilute acids to produce salts. Copper oxide is an insoluble base. Although copper will not react with dilute sulphuric acid, copper (II) oxide will. The salt that forms is copper (II) sulphate. $\text{CuO}_{(\text{s})} + \text{H}_2\text{SO}_{4(\text{aq})} \rightarrow \text{CuSO}_{4(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$
- **Reaction of a metal carbonate with an acid:** The reaction between metal carbonates and dilute acids are accompanied with evolution of carbon dioxide gas. The evolution of a gas can be used to indicate when the reaction is over. An example of such reactions is the reaction between calcium carbonate and dilute hydrochloric acid. $\text{CaCO}_{3(\text{s})} + 2\text{HCl}_{(\text{aq})} \rightarrow \text{CaCl}_{2(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} + \text{CO}_{2(\text{g})}$

General methods of preparing soluble salts

The above methods for preparing soluble salts are specific for each method mentioned. Generally, soluble salts may be prepared by two broad methods.

Method 1: This route is essentially the same whether starting with a solid metal, a solid base (oxide) or a solid carbonate. The route can be divided into four stages:

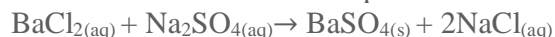
- **Stage 1:** An excess (more than enough) of the solid is added to the acid and allowed to react. Using an excess of the solid makes sure that all the acid is used up. If it is not used up at this stage, the acid would become more concentrated when the water is evaporated later (stage 3).
- **Stage 2:** The excess solid is filtered out after the reaction is completed.
- **Stage 3:** The filtrate is gently evaporated to concentrate the solution. This can be done on a heated water bath. Do not heat so strongly or “spitting” might take place.
- **Stage 4:** The concentrated solution is cooled down to let the crystals form. Filter off the crystals. Wash them with a little distilled water. Dry the crystals carefully between the filter papers.

Method 2: This method (titration method) involves the neutralization of an acid with an alkali (for example sodium hydroxide) or a soluble carbonate (for example sodium carbonate). Since both the reactants and the products are colourless, an indicator is used to find the neutralization point or *end point* (when all the acid has *just* been neutralized). Once the end point is reached, the resulting salt solution is evaporated and cooled to form crystals as described in method 1.

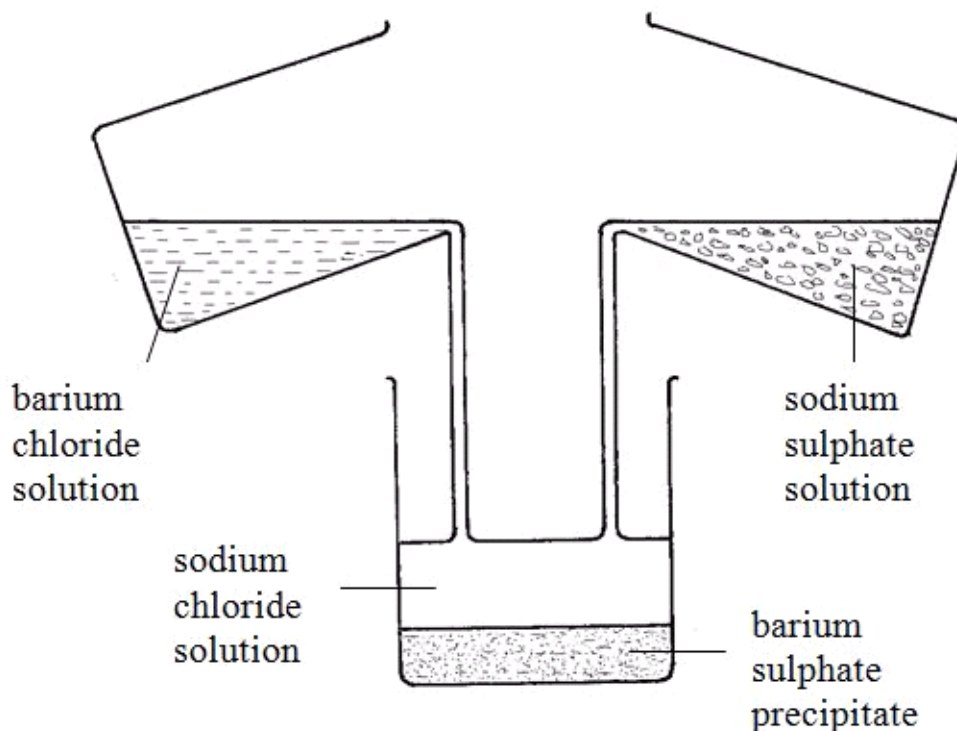
General methods for preparing insoluble salts

Some salts are insoluble in water (for example silver chloride and barium sulphate – see table 3.6). Such salts are generally prepared by ionic precipitation. Precipitation is the sudden formation of a solid either: when two solutions are mixed; or when a gas is bubbled into a solution.

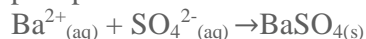
For example, barium sulphate can be prepared by adding a solution of a soluble sulphate (for example sodium sulphate) to a solution of a soluble barium salt (for example barium chloride). The insoluble barium sulphate is formed immediately. This solid falls to the bottom of the container as a precipitate (figure 3.2). The precipitate can be filtered off. It is then washed with distilled water and dried in a warm oven. The equation for the reaction is:



This shows how important the state symbols can be - it is only through state symbols that we can tell this equation shows a precipitation.



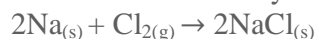
Barium sulphate could also be made from barium nitrate and sodium sulphate, for example, since these salts are both soluble. As long as barium and sulphate ions are present, barium sulphate will be precipitated.



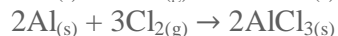
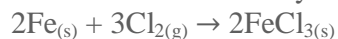
Precipitation reactions are often used in a qualitative analysis to identify salts such as chlorides, iodides and sulphates.

Preparation of salts by direct combination (synthesis)

Some soluble and insoluble salts can be made directly by reacting two elements together. This is called combination (or synthesis). This type of reaction is mainly possible for metal chlorides, bromides and iodides. For instance, if a piece of burning sodium is lowered into a gas jar of chlorine, the two react violently to produce a white powder of sodium chloride:



Other chlorides can also be prepared by combination, for example, iron (III) chloride and aluminium chloride can be made by heating iron and aluminium metals in stream of chlorine:



The reaction between ammonia gas and hydrogen chloride gas to produce ammonium chloride is also a synthesis reaction.



Direct combination reactions do not produce crystals of the salt, but only a powder.

The Effects of Heat on Salts

Examine the effects of heat on salts

When different salts are heated, they behave in different manners. The crystals of some salts contain water of crystallization. When these hydrated salts are heated, their water of crystallization is driven off as steam. The crystals then lose their shape and become a powder.

The following are few examples of hydrated salts:

Salt formula	Chemical name
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Copper (II) sulphate five water
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	Sodium carbonate ten water
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Magnesium chloride six water
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Iron (III) chloride six water
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Iron (II) sulphate seven water
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	Cobalt (II) chloride six water
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Magnesium sulphate seven water
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Calcium sulphate two water

Sulphates

Sulphates of potassium, sodium, calcium, lithium and magnesium are stable to heat and do not decompose when heated. Other sulphates decompose to give the oxide and sulphur trioxide gas except iron (III) sulphate which decomposes to give sulphur dioxide and sulphur trioxide.

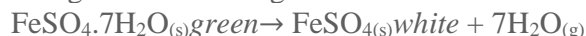
Copper (II) sulphate five water crystals are blue in colour, but when heated, they are dehydrated to form a white powder:



Crystals that have lost their water of crystallization are called anhydrous. If water is added back to the anhydrous copper (II) sulphate powder, the powder turns into blue crystals again and heat is evolved. This can be used as a qualitative test for water. If the white, anhydrous powder is further heated strongly, it decomposes to black copper (II) oxide:



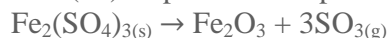
Hydrated iron (II) sulphate is green in colour. When heated, it loses all its water of crystallization and changes colour from green to white:



When heated even more strongly, the white powder decomposes to form a black oxide:



Iron (III) sulphate decomposes on heating to form slightly different products:



Chlorides

The chlorides of most metals are hydrated except those of potassium, lead, mercury and silver.

Hydrated chlorides do not usually give the anhydrous salt when heated. Instead, a chemical change termed as hydrolysis normally occurs. The reaction is accompanied by the evolution of steam and hydrogen chloride gas, and the formation of the basic chloride or oxide. When, for example, hydrated magnesium chloride is heated, its basic chloride is formed:



The same case applies when hydrated calcium chloride is heated. However, when hydrated aluminum chloride is heated, it does not produce the anhydrous salt. Instead, the oxide is formed thus:



Ammonium chloride sublimes when heated. The reaction is reversible and the products may recombine on cooling to form the salt back.



Carbonates and hydrogencarbonates

The carbonates of potassium and sodium are very stable to heat. They do not decompose even when heated to very high temperatures. All other carbonates decompose when heated to give the oxide and carbon dioxide:



However, there are very few and exceptional carbonates that do not behave like this. Ammonium carbonate, for example, decomposes readily when heated to give ammonia gas, water vapour and carbon dioxide gas:



All *hydrogencarbonates* decompose on heating to give the carbonates, water vapour and carbon dioxide:



Nitrates

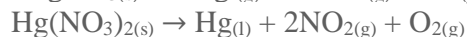
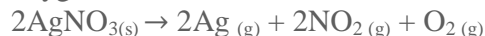
When heated, potassium and sodium nitrates decompose to give the nitrite and oxygen:



The nitrates of common heavy metals (such as Pb, Al, Ca, Mg, Zn and Cu) decompose on heating to give the oxide, nitrogen dioxide and oxygen:



The nitrates of silver and mercury are completely decomposed to the metal, nitrogen dioxide and oxygen:



Ammonium nitrate is decomposed by heat into dinitrogen oxide and water:



Hydroxides

Potassium and sodium hydroxides are very stable to heat. They do not decompose even when heated strongly. All other hydroxides decompose to give the oxide and water vapour, e.g.:



DELIQUESCENT, EFFLORESCENCE AND HYGROSCOPY

Deliquescence

Deliquescence is the absorbing of moisture from the atmosphere by a solid to form a solution. If calcium chloride (CaCl_2) is exposed to air, it absorbs water vapour from the atmosphere and eventually dissolves. Its tendency to absorb water vapour explains why it is used as a drying agent for gases (not ammonia, because it combines with the gas).

Solid sodium hydroxide is also deliquescent. On exposure to air, pellets of sodium hydroxide quickly become shiny and then sticky as they absorb water vapour from the atmosphere. Eventually the sodium hydroxide pellets absorb moisture from the atmosphere so much that they dissolve to form a solution of sodium hydroxide.

Copper (II) nitrate and zinc chloride are the other deliquescent salts. Pure table salt (NaCl) is not deliquescent. However, if the salt is directly obtained from the sea, it is deliquescent. The salt from the sea contains magnesium chloride as one of the impurities. It is this magnesium chloride salt that deliquesces and not sodium chloride.

Hygroscopy

Some substances tend to absorb water vapour from the air but do not change their physical states.

Copper (II) oxide and calcium oxide are both hygroscopic solids because they can absorb moisture from the atmosphere and yet retain their solid states. Because of this behaviour, calcium oxide is used as a drying agent, which absorbs moisture from gases prepared in the laboratory.

Concentrated sulphuric acid is a hygroscopic liquid. When exposed to air, the acid absorbs water vapour from the atmosphere diluting itself to absorb 3 times its original volume.

Therefore, *hygroscopy* may be defined as the tendency of a substance to absorb water vapour from the atmosphere without changing its physical states. The word hygroscopy is a general term applied to all substances that absorb water vapour from the air. Any substance that can take up moisture from the atmosphere is said to be hygroscopic in nature.

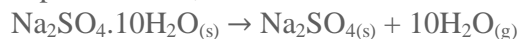
Efflorescence

Efflorescence is the tendency of a hydrated substance to lose the water of crystallization to the atmosphere. Some salt crystals give out some or all of their water of crystallization to the atmosphere when exposed to air. Such substances are said to be *efflorescent* and the process of water loss is known as *efflorescence*. Sodium carbonate ten water (washing soda) is a good example of an efflorescent substance. If washing soda crystals are exposed to open air at room temperature, they lose some of the water of crystallization. The solid loses nine of its ten molecules of water of crystallization to the air. One molecule of water, which remains fixed, can be removed only by strong heating.



The crystal lattice is broken down as the salt loses its water after crystallization. Thus, transparent crystals of hydrated sodium carbonates become white and powdery on the surface.

Another efflorescent compound is Glauber's salt, sodium sulphate ten water ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). On exposure to air, it loses the whole of its water of crystallization to the air.



Iron (II) sulphate seven water ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is also efflorescent.

The Uses of Different Types of Salts in Everyday Life

Explain the uses of different types of salts in everyday life

There is a wide range of salts. A great number of them play an important role in our everyday life.

The following are the uses of some salts:

Sodium chloride (common salt)

Sodium chloride often called common salt or table salt, is essential for life and is an important raw material for industries. At home, it is used for cooking, that is, flavouring different foods. Biologically, it has a number of functions: it is involved in muscle contraction; it enables the conduction of nerve impulses in the nervous system; it regulates osmosis (the passage of solvent

molecules through membranes); and it is converted into the hydrochloric acid that aids digestions in the stomach.

Some industrial uses of sodium chloride include curing bacon, flavouring foods, and in the manufacture of margarine, butter and cheese. It is also used to tan leather in the leather industry. Rock salt is used as a fertilizer for sugar beet, and is spread on roads to melt the ice during winter. The salt is the starting point for many important chemicals, for example, the electrolysis of brine (concentrated solution of sodium chloride) gives sodium hydroxide, chlorine and hydrogen. What other uses of sodium chloride do you know? Mention them.

Calcium carbonate (marble, limestone, chalk)

Calcium carbonate finds a wide range of uses:

- An important use of calcium carbonate is in the building industry. It is widely used in making cement, lime, mortar and making steel from iron.
- Powdered limestone is used as a liming material to neutralize soil acidity. When used in this way, it is termed as agricultural lime. When added in the soil, agricultural lime acts as a calcium source for plants as well as increasing the pH and water retaining capacity of acidic soils.
- It is also used in making paint, plastic, rubber, ceramic and glass; and in oil refining, and iron ore purification.
- Calcium carbonate is the most preferred mineral in the paper industry. It helps in the production of the best quality papers.
- Since calcium is essential for healthy bones and teeth, it is used as a dietary calcium supplement.
- Limestone can also be well shaped, painted, and then used as decorative stones.

Ammonium salts

Most ammonium salts such as $(\text{NH}_4)_3\text{PO}_4$, NH_4Cl , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, CAN, urea, etc are used as nitrogenous fertilizers which are applied to the soil to improve soil fertility and hence enhance plant growth and production. Millions of tonnes of fertilizers are produced every year. Without these chemicals, world food production would probably be halved.

Calcium sulphate (anhydride, CaSO_4 ; gypsum, $\text{CaSO}_4 \cdot \text{H}_2\text{O}$)

Gypsum is chiefly used for the manufacture of Plaster of Paris (P.O.P). The Plaster of Paris is used for making casts for statuary (the expansion during setting ensures a fine impression), in surgery to maintain joints in a fixed position and in cement and wall plasters.

Among the many other uses of calcium sulphate are as a pigment in white paints, as a soil conditioner, in Portland cement, as a sizer, filler, and coating agent in papers, in the manufacture of sulphuric acid and sulphur, in the metallurgy of zinc ores and as a drying agent in many laboratory and commercial processes.

Sodium carbonate (washing soda)

Sodium carbonate is widely used as one of the raw materials for making glass. Glass is made by heating a mixture of limestone, sand, sodium carbonate, and recycled glass in a furnace. The cosmetic industry uses it for manufacturing soap. The chemical industry uses it as a precursor to numerous sodium-containing reagents

It is also important in photography and in the textile industry. In addition to these industrial applications, sodium carbonate is used in medicine as an anti-acid

Sodium carbonate has various environmental applications. Large quantities of the carbonate are used in sewage treatment; in water softening as washing soda crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, and in desulphurisation of flue gas.

Magnesium sulphate (Epsom salt)

Magnesium sulphate is mainly employed for making health salts (laxative, mild purgative). The health salt is used as a medicine (laxative) which aids to empty the bowels following constipation or other health problems.

Copper (II) sulphate

Copper (II) sulphate is used in fungicides, which are sprayed on crops, especially vines and potatoes, to kill moulds which would injure plants and hence curtail crop yield. It is also used in the manufacture of certain green pigments which are used for painting.

Calcium phosphate

It is largely used in making phosphoric acid and fertilizers. Calcium phosphate is used in baking. It is also used in cheese products.

TOPIC 4: THE MOLE CONCEPT AND RELATED CALCULATIONS.

The Mole as a Unit of Measurement

The Mole with Other Units of Measurements

Compare the mole with other units of measurements

When carrying out an experiment, a chemist cannot weigh out a single atom, ion, electron, proton or molecule of a substance. These particles are simply very small. A counting unit that is useful in practical chemistry must be used.

The standard unit is called one **mole** of the substance. One mole of each of these different substances contains the same number of the particles (atoms, molecules, ions, electrons, protons, neutrons, etc).

That number per mole has been worked by several different experimental methods and is found to be 6.0×10^{23} . The value 6.0×10^{23} is called **Avogadro's constant** or Avogadro's number and is abbreviated as L. It is named after the nineteenth-century Italian chemist, Amedeo Avogadro.

The value 6.0×10^{23} is obtained through the following relationship. The mass of one atom of carbon-12 is $1.993 \times 10^{-23}\text{g}$. Then, the number of atoms present in 12g of carbon-12 is derived as follows:

$$1 \text{ atom} = 1.993 \times 10^{-23}\text{g}$$

$$X \text{ atoms} = 12\text{g}$$

$$X \text{ atoms} = \frac{12\text{g} \times 1}{1.993 \times 10^{-23}} = 6.02 \times 10^{23}$$

$$\therefore X = 6.0 \times 10^{23} \text{ atoms.}$$

Therefore, the number of atoms in 12g of carbon-12 and hence the number of particles in a mole are 6.02×10^{23} atoms.

Hence, Avogadro's number is the number of atoms in exactly 12g of carbon-12 isotope. One mole of any substance contains as many as many elementary particles as the Avogadro's number (constant).

So, from the above explanation, **the mole can be defined as the amount of a substance that contains as many elementary particles as the number of atoms present in 12g of carbon-12 isotope.**

Substance	Formula	Relative formula mass, M_r	Mass of one mole (molar mass)	This mass (1 mole) contains
Carbon	C	12	12g	6.0×10^{23} carbon atoms
Iron	Fe	56	56g	6.0×10^{23} iron atoms
Hydrogen	H ₂	$2 \times 1 = 2$	2g	6.0×10^{23} molecules
Oxygen	O ₂	$2 \times 16 = 32$	32	6.0×10^{23} molecules
Water	H ₂ O	$(2 \times 1) + 16 = 18$	18g	6.0×10^{23} formula units
Magnesium oxide	MgO	$24 + 16 = 40$	40g	6.0×10^{23} formula units
Calcium carbonate	CaCO ₃	$40 + 12 + (3 \times 16) = 100$	100g	6.0×10^{23} formula units
Silicon oxide	SiO ₂	$28 + (2 \times 16) = 60$	60g	6.0×10^{23} formula units
Fe ³⁺	Fe ³⁺	56	56g	6.0×10^{23} iron(III) ions
Cl ⁻	Cl ⁻	35.5	35.5g	6.0×10^{23} chloride ions
e ⁻	e ⁻	-	-	6.0×10^{23} electrons

The other substances, which also exist as molecules, include ozone molecule (gas), O₃; phosphorus molecule (solid), P₄; sulphur molecule, S₈, etc.

In real life, when dealing with large numbers of small objects, it is usual to count them in groups.

The objects are grouped and counted in unit amounts. For example, we buy a carton of soap, a gallon of kerosene, a crate of soda, a dozen of pencils, a ream of papers, etc.

Some units of measurement

Unit	Number of objects per unit
Pair	1 pair = 2 objects, e.g. gloves, shoes, socks, scissors, etc are always sold in pairs.
Dozen	1 dozen = 12 objects e.g. a dozen of cups, plates, spoons, etc.
Gross	1 gross = 144 objects, e.g. a box of blackboard chalk contains 144 pieces of chalk.
Ream	1 ream = 500 objects, e.g. papers are sold in reams of 500 sheets.
Mole	1 mole = 6.02×10^{23} particles. In chemistry, extremely small particles are expressed in moles. For example: 1 mole of atoms = 6.02×10^{23} atoms 1 mole of electrons = 6.02×10^{23} electrons 1 mole of protons = 6.02×10^{23} protons 1 mole of ions = 6.02×10^{23} ions 1 mole of molecules = 6.02×10^{23} molecules

Molar Quantities of Different Substances

Measure molar quantities of different substances

The mass of one mole of any substance (its molecular mass) is the atomic mass or molecular mass expressed in grams (or kilograms). For convenience, chemists prefer to express mass in grams, although the SI unit of mass is the kilogram. This is because the amount of substances which chemists usually work with in science laboratories, is quite small and if their masses are expressed in kilograms, the numbers used would be extremely small.

You can calculate the molar mass (M) of any substance by summing up the relative atomic weights of its constituents atoms. For example, ethanol, C₂H₅OH, contains two carbon atoms, six hydrogen atoms and one oxygen atom. So, the molar mass of ethanol can be calculated thus: Molar mass of C₂H₅OH = (2 × 12) + (6×1) + 16 = 46g.

In a similar way, molar masses of other compounds can be calculated. For example, the molar mass of sodium chloride, NaCl, is calculated by adding together the relative atomic masses of the constituents elements (Na = 23 and Cl = 35.5) = 23 + 35 = 58.5g (g mol⁻¹).

It is important to note that *relative atomic mass* or *relative molecular mass* has *no unit* while molar masses are always expressed in grams or kilograms.

The *molar mass of a compound* is the same as the *relative molecular mass* and the **molar mass of an element** is the same as the **relative atomic mass** (A_r) of that element. The only difference lies in the units.

Example 1

- M(CO₂) = 44g (or g mol⁻¹) = molar mass of carbon dioxide
- M_r(CO₂) = 44 = relative molecular mass of carbon dioxide
- M(Fe) = 56g (or g mol⁻¹) molar mass of iron
- M_r(Fe) = 56 = Relative atomic mass of iron

Similarly, the molar masses of each of the following substances can be calculated using values for the relative atomic masses of the elements.

Molar masses of different substances

Substance	Formula	Molar mass
Ammonia	NH ₃	14 + 1×3 = 17g
Ammonium chloride	NH ₄ Cl	14 + (1×4) + 35.5 = 53.5g
Lead (II) nitrate	Pb(NO ₃) ₂	207 + (14×2) + (16×6) = 331g
Sulphuric acid	H ₂ SO ₄	(1×2) + 32 + (16×4) = 98g
Calcium carbonate	CaCO ₃	40 + 12 + (16×3) = 100g
Potassium dichromate	K ₂ Cr ₂ O ₇	(39×2) + (52 ×2) + (16×7) = 294g

Application of the Mole Concept

Known Masses of Elements, Molecules or Ions to Moles

Convert known masses of elements, molecules or ions to moles

In experimental work, chemists work with varying masses. They cannot always use one mole of a substance. The equation that links the mass of a substance to the number of moles present is:

$$\text{Number of moles (n)} = \frac{\text{Mass}}{\text{Molar mass}}$$

Example 2

Convert 49g of sulphuric acid, H₂SO₄, into moles. *Given:* Mass = 49g; molar mass = 98g

Formula:

$$\text{Number of moles (n)} = \frac{\text{Mass}}{\text{Molar mass}}$$

Solution: 49g of H₂SO₄ = 49/98 = 0.5 mol.

Known Volumes of Gases at S.T.P to Moles

Convert known volumes of gases at S.T.P to moles

The volume occupied by one mole of a gas at standard condition of temperature and pressure has been scientifically determined, and it is found to be 22.4 dm^3 . This volume is called the molar volume of a gas. The molar volume of a gas, therefore, has the value of 22.4 dm^3 at s.t.p. Remember that 1 dm^3 (1 litre) = 1000 cm^3 . One important thing about this value is that it applies to all gases. Therefore, at s.t.p. 32g of oxygen (O_2) or 17g of ammonia (NH_3) or 44g of carbon dioxide (CO_2) or 40g of argon (Ar) will occupy a volume of 22.4 dm^3 . This makes it easy to convert the volume of any gas at s.t.p. into moles, or moles into volume. However, it is important to note that as the conditions of temperature and pressure change the molar volume will also change.

The number of moles of a given sample of gas is obtained by dividing the volume of the gas by molar volume (22.4 dm^3).

$$\text{Number of moles} = \frac{\text{Volume}}{\text{Molar volume}}$$

For example, 4.4 dm^3 of carbon dioxide gas at s.t.p. = $4.4/22.4 = 0.196 \text{ mol}$. Similarly, 2.24 dm^3 of neon gas at s.t.p. = $2.24/22.4 = 0.1 \text{ mol}$.

If the volume of the gas is given in cm^3 , then it should be divided by the molar volume of a gas expressed in cm^3 . For example, 560 cm^3 of nitrogen gas = $560 \text{ cm}^3 / 22400 \text{ cm}^3 \text{ mol}^{-1} = 0.025 \text{ mol}$.

Alternatively, the volume may, first, be converted to dm^3 and then divided by the molar volume, expressed in dm^3 , that is, $0.46 \text{ dm}^3 / 22.4 \text{ dm}^3 = 0.025 \text{ mol}$

Masses of Solids or Volumes of Known Gases to Actual Number of Particles

Change masses of solids or volumes of known gases to actual number of particles

The number of particles in one mole of any substance is 6.02×10^{23} . To find the number of particles in a substance, we use the expression:

- $N = n.L$, where
- N = the number of particles in that substance;
- n = the amount of substance (moles); and
- L = the Avogadro's constant (6.02×10^{23}).

This conversion requires two steps: first convert the mass of solid or volume of gas to moles, and then multiply the number of moles by the Avogadro's constant. For example, to convert 5.6 dm^3 of ammonia gas to the actual number of ammonia (NH_3) molecules, change 5.6 dm^3 of ammonia to moles = $0.46 \text{ dm}^3 / 22.4 \text{ dm}^3 = 0.025 \text{ mol}$. Then multiply by the Avogadro's constant to get the total number of molecules $0.025 \times 6.02 \times 10^{23} = 1.5 \times 10^{22}$ molecules

Similarly, 1.12 dm^3 of hydrogen gas = $1.12/22.4 = 0.05 \text{ mol}$. This is equal to $0.05 \times 6.02 \times 10^{23} = 3.0 \times 10^{22}$ molecules

Alternatively, we may find out the number of particles by converting the given volume to the number of molecules straight forward without passing through the number of moles first. We know that one mole (22.4 dm^3) of a gas at s.t.p. = 6.02×10^{23} molecules. So, $5.6 \text{ dm}^3 = 5.6 \times 6.02 \times 10^{23} / 22.4 = 1.5 \times 10^{22}$ molecules

Molar Solutions of Various Soluble Substances

Prepare molar solutions of various soluble substances

A molar solution is a solution which contains one of the compound in one litre (1 dm^3 or 1000 cm^3) of the solution. Let us consider the case of sodium hydroxide, NaOH. The molecular weight of this

compound is 40g. Therefore, a molar solution of sodium hydroxide will contain 40g in 1000 cm³ (1 dm³) of the solution.

Also, consider anhydrous sodium carbonate, Na₂CO₃. 1 mole of this carbonate weighs 106g. Hence, its molar solution will contain 106g of the anhydrous salt in 1000 cm³ of solution. If, however, 0.1 moles (10.6g) of the solute is dissolved in 1.0 dm³, the solution is 0.1 molar. But if 0.1 moles is dissolved in 0.1 dm³ of the solution, the solution is still 1.0 molar (since 1 dm³ of solution would contain 1.0 mole of the solute).

The molecular weights of some common substances are shown below:

Compound	Molecular weight (1 mole)
Potassium hydroxide, NaOH	56g
Hydrochloric acid, HCl	36.5g
Sulphuric acid, H ₂ SO ₄	98g
Sodium chloride, NaCl	58.5g
Sodium bicarbonate, NaHCO ₃	84g
Calcium hydroxide, Ca(OH) ₂	74g

The molar solution of each of these substances can be prepared by dissolving one mole of each substance in 1000 cm³ (1 dm³) of distilled water. We see, therefore, that 40g of sodium hydroxide in 1000 cm³ of solution will give a 1.0M solution. Hence, 20g of the hydroxide should give a 0.5M solution. In a similar way, we can make derivative solution concentrations ranging as follows: 0.1M, 0.2M, 0.3M, 0.4M...1M, 2M, etc.

However, in each case the amount of solution should always be 1000 cm³. The concentration ranges like these are known as *molarities* of solutions. Hence, 0.5M sodium carbonate can also be read as “a sodium carbonate solution with a molarity of 0.5M.”

The Concentration of Solutions

When a chemical substance (the solute) is dissolved in a given volume of solvent, we can measure the “quantity” of solute in two ways; we can measure either its **mass** (in grams) or its **amount** (in moles). The final volume of the solution is usually measured in dm³.

When we measure the **mass** of the solute in **grams**, we obtain the **mass concentration** in g/dm³

$$\text{Concentration (g/dm}^3\text{)} = \frac{\text{Mass of solute(g)}}{\text{Volume of solution(dm}^3\text{)}}$$

Example 3

Calculate the concentration (g/dm³) of sodium chloride solution (NaCl) that contains 20g of sodium chloride in a final solution of 100 cm³

Solution

First, convert the given volume to dm³

$$\text{Volume (dm}^3\text{)} = 100/1000 = 0.1 \text{ dm}^3$$

Then, work out the concentration of the solution by dividing the mass (weight) of solute (g) by the volume (dm³).

$$\text{Concentration (g/dm}^3\text{)} = \frac{\text{Mass of solute(g)}}{\text{Volume of solution(dm}^3\text{)}}$$

$$= 20\text{g}/0.1\text{dm}^3$$

$$= 200\text{g/dm}^3$$

Alternatively, we could calculate the concentration straightforward without having to convert the given volume into dm^3 , e.g.: If 20g of the solution are contained in 100 cm^3 of the solution, then the amount of solute in 1000 cm^3 (1 dm^3) of the solution would be
 $1000 \times 20 / 100 = 200 \text{g/dm}^3$

Calculations Based on the Mole Concept

Perform calculations based on the mole concept

A chemist always wants to know how much of one substance would react with a given amount of another substance. This is achieved by use of balanced chemical equations. Such equations are called stoichiometric equations.

A stoichiometric equation is the one in which the reactants and the products are correctly balanced; all the atoms, ions and electrons are conserved. Such an equation gives correct mole ratios of reactants and products in chemical reactions. This quantitative relationship is called stoichiometry.

Consider an equation for the reaction between hydrogen and nitrogen to produce ammonia:



This can be read as follows:

three moles of hydrogen reacts with one mole of nitrogen to yield two moles of ammonia.

The numbers 3, 1 and 2 are called stoichiometric coefficients. They tell us the proportions in which the substances react and in which the products are formed.

Example 4

What volume of carbon dioxide (CO_2) measured at s.t.p. will be produced when 21.0g of sodium hydrogencarbonate (NaHCO_3) is completely decomposed according to the equation.
 $2\text{NaHCO}_{3(\text{s})} \rightarrow \text{Na}_2\text{CO}_{3(\text{s})} + \text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$

Solution

First, find the weight of carbon dioxide that will be produced by the hydrogencarbonate.

- Mass of $2\text{NaHCO}_3 = 2 \times 84 = 168\text{g}$
- Mass of $\text{CO}_2 = 44\text{g}$

The weight of carbon dioxide produced can be obtained from the following relation:

$$168\text{g} \equiv 44\text{g}$$

$$21\text{g} \equiv X$$

$$X = 21 \times 44 / 168 = 5.5\text{g}$$

The weight of carbon dioxide produced = 5.5g

Then, convert this weight of CO_2 to volume at s.t.p. We know that one mole (44g) of carbon dioxide at s.t.p. occupies 22.4 dm^3

$$\text{That is, } 44\text{g} \equiv 22.4\text{dm}^3$$

$$5.5\text{g} \equiv X \text{ dm}^3$$

$$X = 5.5 \times 22.4 / 44 = 2.8\text{dm}^3$$

TOPIC 5: VOLUMETRIC ANALYSIS

Standard Volumetric Apparatus

The Concept of Volumetric Analysis

Explain the concept of volumetric analysis

Volumetric analysis is a quantitative analysis involving the measurement of different solutions.

These solutions are made to react completely and the completion of the reaction is indicated by certain substances called *indicators*. The quantitative composition of the solution is then determined.

Important steps of volumetric analysis include:

- Weighing;
- Preparation of the solution;
- Titration; and
- Calculation

In volumetric analysis, we deal with volumes of solutions. That is why this quantitative determination of solutions of substances is called **volumetric analysis**.

The amount of a substance present in a solution is given in terms of its volume and its concentration. The volume of a solution is usually given in litres (dm^3). The concentration of a solution is given in moles per litre (mol/dm^3) or grams per litre (g/dm^3).

Volumetric analysis is a means of finding the concentration of an unknown solution. For example, the concentration of an unknown solution of an acid can be found if it is reacted with a standard solution of an alkali. A **standard solution** is one whose concentration is well known and does not change with time.

In volumetric analysis, the reaction is carried out in a carefully controlled way. The volumes are measured accurately using a pipette and burette. The method is to add a solution of one reactant to the solution of another reactant until the reaction is complete. When the reaction is complete, we say the **end-point** has been reached. If the reactants are acids and bases, completion (end-point) is determined by the change in colour of an acid-base indicator. The method is called **titration**. In other reactions, completion is determined by a colour change of reactant(s). The concentration of one of the reactant solutions must be known in order to be able to find the concentration of unknown solution.

Significance of Volumetric Analysis

- Volumetric analysis is used to quantify the amount of substances present in solutions by analytical procedure, which involves precise measurements of volumes of solutions and masses of solids.
- Volumetric analysis helps in the determination of the accurate volumes and concentrations of the reacting substances, often solutions.
- Volumetric analysis (titration) helps in the preparations of standard solutions.
- Volumetric analysis knowledge helps in the standardization of acids and bases.

Volumetric Apparatus

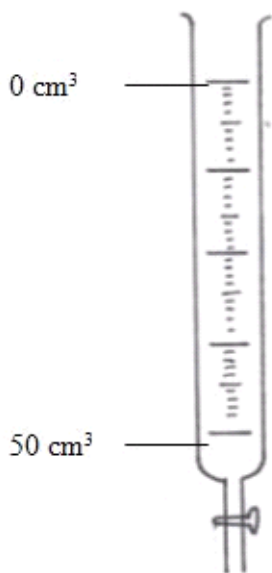
Use volumetric apparatus

We have seen that volumetric analysis involves determinations of quantities of substances, usually acids and alkalis, present in volumes of solutions. This is usually done by using measuring apparatus. Apparatus used in volumetric analysis is based on volume measurements and since the analysis demands high accuracy, the apparatus has to be calibrated with the highest possible accuracy. It is for this reason that all apparatus for volumetric analysis are specifically for this and not other purposes. Apparatus used for volumetric analysis include, burette, pipette, burette stand, white tile, conical flask, filter funnel, reagent bottle, watch glass, beaker, measuring cylinder and measuring flask (or volumetric flask). For approximate measurements, measuring cylinders may be used. For accurate measurements of volumes, volumetric flasks are used.

Burette

This is a long glass tube with a narrow lower part, which is fitted with a tap that controls the amount of solution let out of the burette. This instrument is calibrated from 0 to 50 cm^3 . Before measuring the solution, rinse the burette with distilled water, then with the solution it is going to hold. It has to be

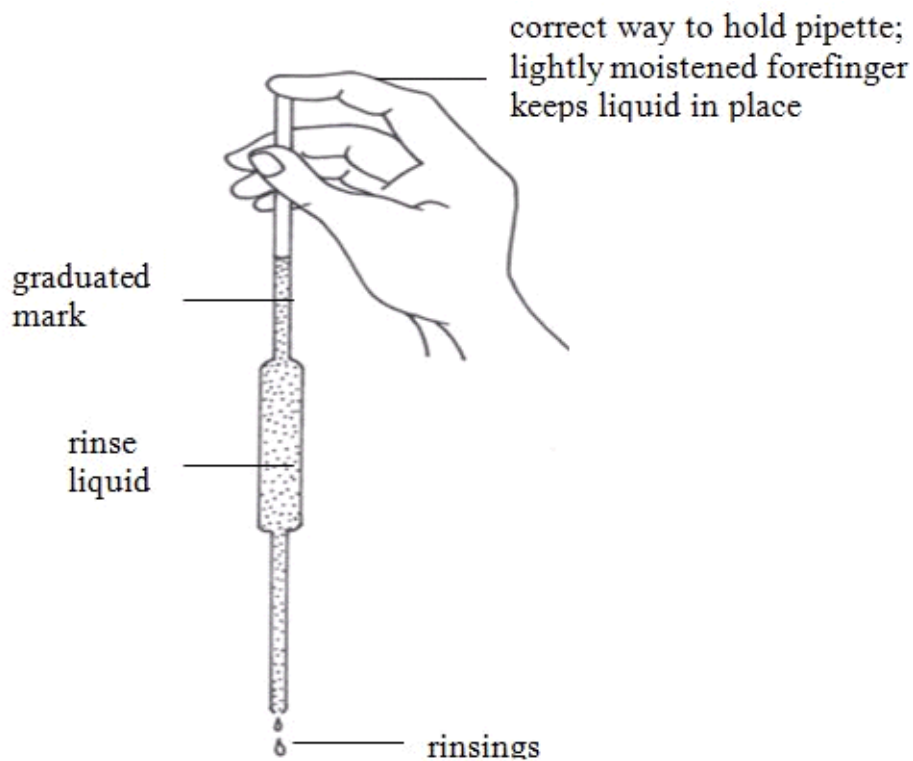
filled to the tip and all gas bubbles removed. Thus, the burette is an apparatus used for transferring the solution to the titration vessel (normally a flask).



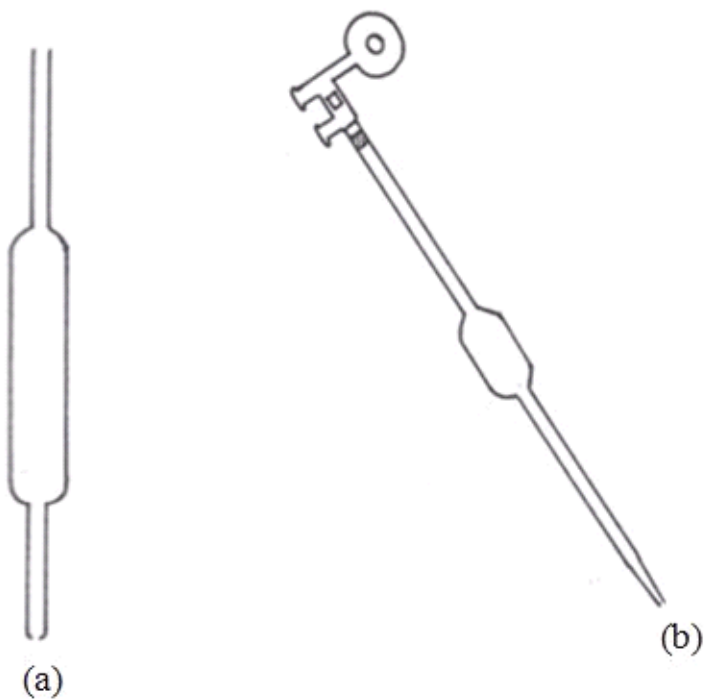
Pipette

This apparatus has a wider middle part with narrow parts at either ends. The upper narrow part has a mark which marks the volume of all the space below it. If, say, the pipette is one that is marked 25 cm³, we can say that a solution, when filled in the pipette up to this mark, will have a volume of 25 cm³.

The pipette is used in transferring a standard solution to the titration flask. There are many types of pipettes depending on their volume capacity. The common ones are the 25-cm³ and 20-cm³ capacity pipettes. Less common ones are the 10-cm³ capacity. Before measuring the solution, rinse the pipette several times with distilled water and then with the solution to be measured; suck the rinsing solution above the graduated mark, then discard the rinsing.



The pipette is commonly filled by mouth suction but the use of pipette fillers is highly recommended. When using a pipette, never blow out the last drop.

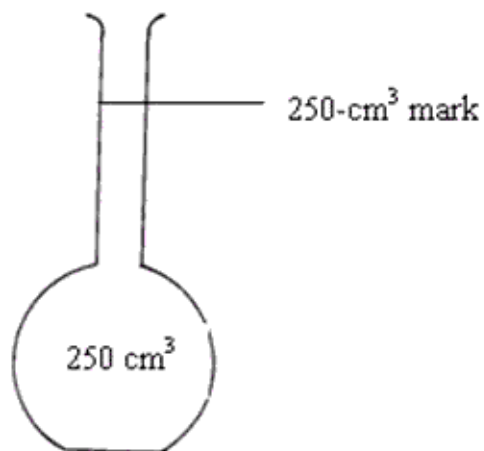


(a) A pipette (b) A pipette and pipette filler (used to fill and empty pipettes)

Measuring (Volumetric) flask

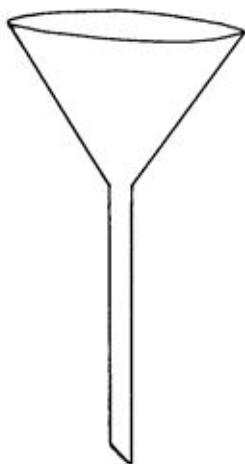
The flask is made of glass and has a mark at the upper part of the narrow tube. The space in the flask up to this mark represents a certain volume. If a solution is filled up to this mark, the volume of the

solution is equal to the volume indicated by inscriptions on the flask e.g. 50 cm^3 , 100 cm^3 , 150 cm^3 , 250 cm^3 , 500 cm^3 , etc.



Filter funnel

A filter funnel is required for effective transfer of the weighed solid, liquid or solution into the volumetric flask or burette.



A filter funnel

Wash bottle

Wash bottle contains water and when squeezed, water squirts out. This is used in washing down the remains of the weighed solid into the volumetric flask.



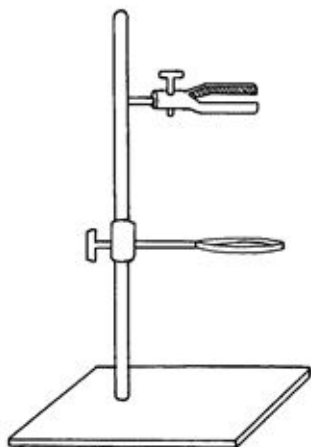
A wash bottle

A weighing bottle

This is used in weighing the solute. It is a stoppered bottle. A watch glass can also be used to serve the same purpose.

Retort stand

A burette stand is used for holding the burette in place while carrying out volumetric analysis experiments.



A burette stand

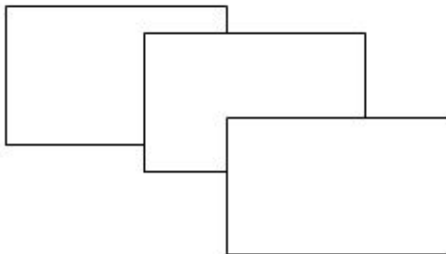
Dropper

A dropper is used to add the indicator dropwise into the solution.



White tile or paper

A white tile or piece of paper is placed under the flask to give a clear background for accurate observation of the colour change at the end of the reaction (end point).



Standard Solutions

The Steps for Preparation of Standard Solutions of Common Acids

Explain the steps for preparation of standard solutions of common acids

A *standard solution* is a solution of known concentration. For example, a solution containing 15g of sulphuric acid in 1 dm³ of solution is a standard solution.

It has now been approved that volumetric work should be based upon the *molar* (M) solution. A *1 molar* (1M) *solution of a compound is a solution which contains one mole of that compound in 1 dm³ of the solution.* For example, 58.5g of sodium chloride (NaCl) dissolved in 1 dm³ of the solution makes a molar solution of sodium chloride (1M NaCl). Likewise, 106g of sodium carbonate (Na₂CO₃) in 1 dm³ of the solution gives a molar solution of sodium carbonate. Therefore, a 1 molar sodium carbonate solution contains 106g of the salt in 1 dm³ of the solution.

1 molar solution of some compounds commonly used in titration contain the following masses of the compounds in 1 dm³ of solution:

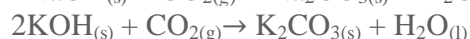
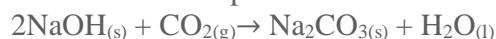
Compound	Relative molecular weight (1 mole)
Sodium hydroxide, NaOH	40g
Potassium hydroxide, KOH	56g
Sulphuric acid, H ₂ SO ₄	98g
Hydrochloric acid, HCl	36.5g
Sodium carbonate, Na ₂ CO ₃	106g
Sodium bicarbonate, NaHCO ₃	84g

Derivative concentrations are also used e.g. 0.1M, 0.5M, 2M, etc.

Preparation of standard solutions

A standard solution is required as a starting point for volumetric analysis. We learned early that in order to find the unknown concentration of a substance in volumetric analysis, the concentration of one of the solutions must be known.

A small range of substances are suitable for direct preparation of accurately standard solutions. Substances that cannot be used for direct preparation of standard solutions include sodium hydroxide, potassium hydroxide and concentrated sulphuric acid. These substances absorb water vapour from the air and hence cannot be weighed out precisely without taking extra precautions. Apart from absorbing water vapour from the air, sodium and potassium hydroxides react with carbon dioxide of the air to form respective carbonates.



Some solutions are volatile in nature and so are likely to change slowly in concentration during ordinary use. These include concentrated hydrochloric acid and ammonia.

A compound commonly used for preparation of a precisely standard solution is anhydrous sodium carbonate. It is best prepared from highly pure sodium carbonate. This is achieved by heating sodium bicarbonate to constant mass to make sure the compound is fully decomposed.



The sodium carbonate so formed is suitable for preparation of a standard solution and can be weighed without undergoing any appreciable change in composition.

Precautions to be observed while preparing a standard solution

- Transference of the substance from the weighing bottle to the beaker or flasks should be done with utmost care so that not a single particle of the substance is lost.
- Undissolved substance should not be transferred to the measuring flask. Make sure all the solid dissolves into solution before transferring the solution to flask.
- During making up of the volume, the last drop of the water should be added carefully. Do not blow out the final drop.

Standard Solutions of Bases

Prepare standard solutions of bases

Preparation of 0.1M sodium carbonate solution

The molecular mass of sodium carbonate (Na_2CO_3) is 106g. Therefore, a molar (1M) solution of sodium carbonate contains 106g in 1 dm^3 (1000 cm^3) of solution.

In order to prepare 0.1M solution of the carbonate, we have to weigh 10.6g of the carbonate and put it into a volumetric flask, which has a capacity of 1000 cm^3 .

However, normally 250 cm^3 flasks are used. This means, in a 250 cm^3 flask we have to add $10.6/4 = 2.65\text{g}$ of sodium carbonate.

Thus, $1000 \text{ cm}^3 \equiv 10.6\text{g}$

$250 \text{ cm}^3 \equiv X \text{ g}$

$X = 250/1000 \times 10.6 = 10.6/4 = 2.65\text{g}$

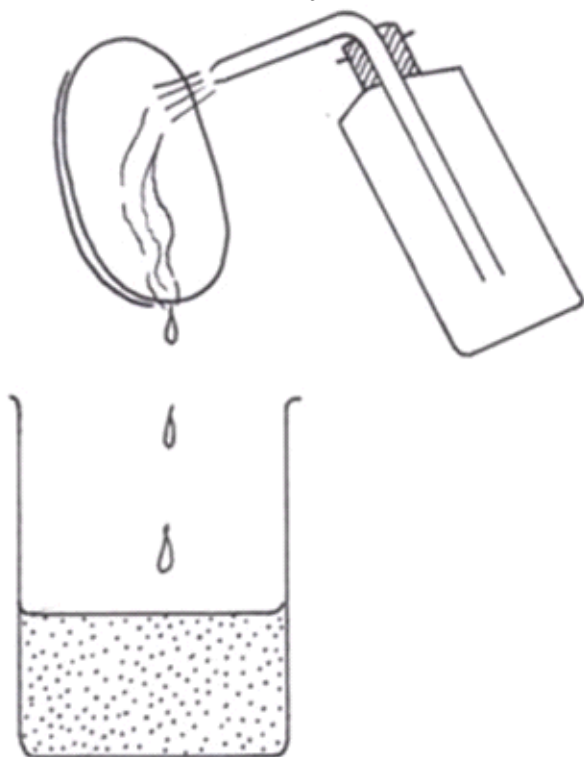
The same procedure can be followed when preparing 0.25M, 0.5M, 2M, etc. of the solutions.

Procedure

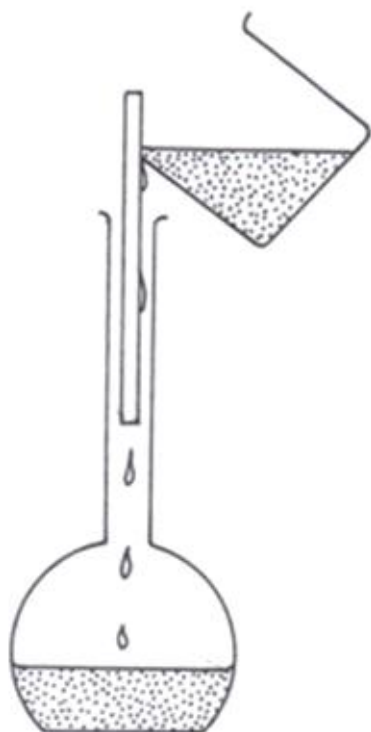
- Weigh exactly 2.65g of sodium carbonate using a common balance and put it onto a watch glass.
- Transfer it slowly into a beaker of 500-cm^3 capacity containing about 50 cm^3 of hot distilled water.
- Wash down the watch glass with a jet of hot distilled water from a wash bottle and allow the washings to fall into the beaker (figure 5.7). Make sure all the sodium carbonate is washed into the beaker.
- Stir with a glass rod until all the solid is completely dissolved, and then cool the solution to room temperature. Leave the rod standing in the solution.
- Pour the solution carefully down the glass rod into a 250 cm^3 measuring flask.
- Wash the beaker out at least twice with jets of cold distilled water directed round the sides and pour the washings down the glass rod into the measuring flask (figure 5.8).
- Shake the flask gently and fill it up with cold distilled water almost to the mark.

- Add more distilled water drop by drop from a pipette until the meniscus is on the graduation mark (figure 5.9).
- Stopper the measuring flask and shake well. The liquid should then be exactly 0.1M sodium carbonate solution.

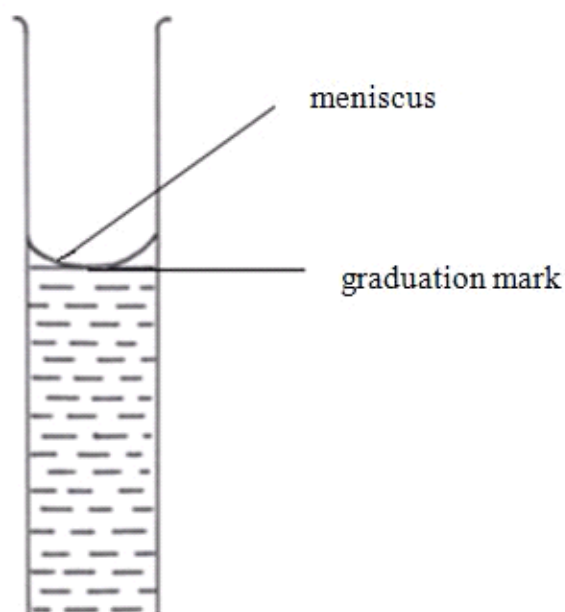
Preparation of standard solutions of other bases of different molarities e.g. 0.2M, 0.5M, 1.0M, 2.0M, etc. can be achieved by using the above procedures. The only variable will be the weight of the solids and volume of water as stated early.



Washing the watch glass



Filling the washings into the flask



Correct reading of the liquid volume

Acid-base Titration Experiments

Carry out acid-base titration experiments

Preparation of 0.1M sulphuric acid solution

A standard solution of sulphuric acid cannot be prepared directly because concentrated sulphuric acid is hygroscopic in nature (it tends to absorb water vapour from the air diluting itself) and is never reliably pure. A solution a little above 0.1M is prepared and then standardized and diluted with

distilled water to exactly 0.1M. A molar solution of H_2SO_4 contains 98g of pure acid in 1 dm^3 . Therefore, the 0.1M acid contains 9.8g of the acid in 1 dm^3 of the solution. The pure concentrated acid has a density (concentration) of about 1.8 g/cm^3 . So, 9.8g of it occupy about $9.8/1.8 = 5.5 \text{ cm}^3$. The preparation of a standard solution of sulphuric acid involves two stages:

- Diluting a concentrated solution of the acid to an approximate molarity.
- Finding the exact concentration of the acid (standardizing it) by titrating it against a standard solution of a base (previously prepared).

Dilution of concentrated sulphuric acid

Caution: Make sure you wear safety goggles and gloves before carrying out this experiment.

Procedure

- Cautiously, because the acid is very corrosive, take $5.5 - 6.0 \text{ cm}^3$ of concentrated sulphuric acid in a small measuring cylinder.
- Pour the acid carefully, with stirring, into a 250-cm^3 volumetric flask containing about 100 cm^3 of cold distilled water.
- Pour this solution into, say, 700 cm^3 of cold distilled water in a measuring flask of capacity 1000 cm^3 .
- Wash out the acid solution remaining in the measuring cylinder with cold distilled water twice and add the washings into the measuring flask.
- Then add distilled water approximately to the mark on the measuring flask, stopper it, and shake well.

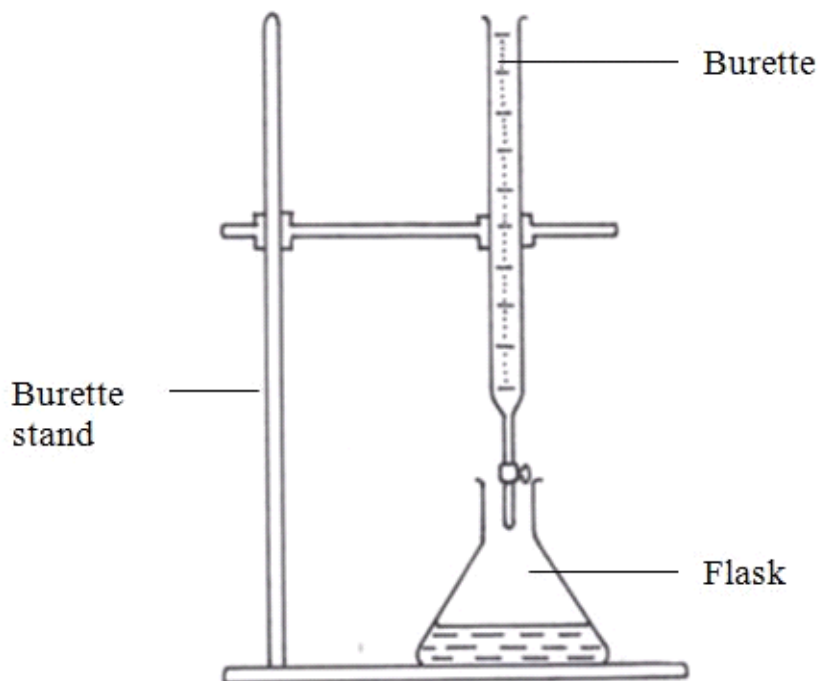
This should give sulphuric acid of concentration a little above 0.1M. The diluted acid is now standardized with the 0.1M sodium carbonate solution prepared above.

Determination of the molarity (standardization) of sulphuric acid solution by titrating it against 0.1M sodium carbonate solution

The estimation of the concentration of a solution of an acid by reacting the acid with a standard alkali solution is known as **titration**. The end-point of an acid-base reaction is commonly determined by using a substance known as an **indicator**.

Procedure

- Measure 25 cm^3 of 0.1M sodium carbonate solution and transfer it into a conical flask, using a pipette. Add a few drops of *methyl orange* indicator. This will turn the sodium carbonate solution yellow.
- Set up the apparatus as shown in figure 5.10
- Pour the acid into a 50-cm^3 burette. Read and note the level of the acid in the burette.



Titration setup

- By means of a tap at the base of the burette, drip the acid slowly into the conical flask, swirling the flask continuously until the colour of the liquid in the flask turns *orange*. This is the *end-point* of titration. Record the new level of acid in the burette.
- Repeat the titration three to four times, noting the initial and final reading of the burette each time.
- Find the volume of the acid as shown below:

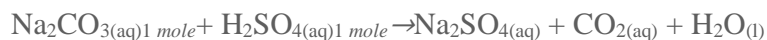
Specimen readings

Titration	Rough titration (Pilot)	Titre 1	Titre 2
Final burette reading	24.20	23.65	23.55
Initial burette reading	0.00	0.00	0.00
Volume of acid added	24.20	23.65	23.55

Neglecting the first (rough) trial run, the average titration is 23.60 cm^3

Calculation

The first step in calculating the molarity of any solution from the results of an acid-base titration is to write the equation for the reaction. From the equation, find the number of reacting moles of the acid and base.



Now we have the following data.

- Volume of acid, $V_a = 23.60 \text{ cm}^3$
- Volume of base, $V_b = 25.00 \text{ cm}^3$ (this is the average amount of the base that was added to the flask in titration)
- Molarity of acid, $M_a = ?$
- Molarity of base, $M_b = 0.1\text{M}$
- Number of moles of acid, $N_a = 1$

- Number of moles of base, $N_b = 1$

The molarity of the acid can be calculated from the following general formula:

$$\frac{V_a M_a}{N_a} = \frac{V_b M_b}{N_b}$$

$$M_a = \frac{N_a \times V_b \times M_b}{V_a \times N_b}$$

$$= \frac{1 \times 25 \times 0.1}{23.6 \times 1}$$

$$= 0.106M$$

The concentration of sulphuric acid is 0.106M.

To make the molar concentration of the sulphuric acid solution exactly equal to that of the sodium carbonate solution (0.1M), 23.6 cm³ of the acid must be diluted to 25 cm³, that is, 1.4 cm³ of distilled water must be added to 23.6 cm³ of the acid.

Remember it was stated early that in order to prepare 0.1M sulphuric acid solution, you need to dissolve 9.8g of the acid in 1000 cm³ (1 dm³) of distilled water. Assume that some of the acid was wasted through spillage and mishandling and that only 920 cm³ of the acid was left. If, say, 920 cm³ of the acid was left, it can be made exactly 0.1M by the addition of $920 \times 1.4 / 23.6 = 55 \text{ cm}^3$ of distilled water. This gives exactly 0.1M of the acid. This is the same as saying that, if 23.6 cm³ of the acid were diluted with 1.4 cm³ of distilled water, then 920 cm³ of the acid would be diluted with

$$920 \times \frac{1.4}{23.6} = 55 \text{ cm}^3, \text{ i.e.}$$

$$23.6 \text{ cm}^3 \equiv 1.4 \text{ cm}^3$$

$$920 \text{ cm}^3 \equiv X \text{ cm}^3$$

$$X = 920 \times \frac{1.4}{23.6}$$

$$= 55 \text{ cm}^3$$

If, for instance, the volume of acid left was, say, 850 cm³, the amount of distilled water to be added would be $= 850 \times 1.4 / 23.6 = 50.4 \text{ cm}^3$. This, also, would give exactly 0.1M of the acid.

In principle, the amount of distilled water to be added is always calculated based on the amount of the acid left as exemplified above.

These two standard alkaline and acidic solutions can be used to standardize other solutions, e.g. sodium hydroxide, potassium hydroxide, hydrochloric acid, nitric acid, etc. You may dilute any base or commercial acid to some required concentration e.g. 0.2M, 0.5M, 0.25M, etc and then standardize it by similar procedures.

Choice of indicators in acid-base titration

We learned early that the estimation of the concentration of a solution of an acid or base by reaction with a standard alkali or acid solution respectively, is known as titration. The end-point of an acid-base titration is commonly determined using substances known as indicators, which usually portray certain characteristic colours when in alkaline or acid solutions.

The indicators in acid-base titrations must be chosen carefully because the choice of an inappropriate indicator would lead to an incorrect result. The choice of an indicator is based on the strength of an acid or base involved in the reaction.

There are three common indicators which are used in titration experiments involving acids and bases namely, methyl orange, litmus and phenolphthalein. The other indicators in less common use are as included in the table below. The table shows the colours which each of these indicators take up in acid or alkaline solution.

Colour of indicators in acid and alkaline solutions

Indicator	Colour of indicator
acid solution	alkaline solution
Methyl orange	pink yellow
Litmus	red blue
Phenolphthalein	colourless pink
Malachite green	yellow blue/green
Thymol blue	red yellow
Bromocresol green	yellow blue
Bromothymol blue	yellow blue

Indicators suitable for particular types of acid-base reactions are as given in the table below:

Indicators suitable for different acid-base reactions

Acid-base titration	Example	Choice of indicator
Strong acid/strong base	H ₂ SO ₄ and NaOH	Any indicator
Weak acid/strong base	CH ₃ COOH (ethanoic acid) and KOH	Phenolphthalein
Strong acid/weak base	HCl and NH ₃	Methyl orange
Weak acid/weak base	CH ₃ COOH and NH ₃	No satisfactory indicator available

Volumetric Calculations

Common Mineral Acids

Standardize common mineral acids

Data for calculations of volumetric analysis problems are obtained from volumetric analysis experiments. For any volumetric analysis problem, at least one standard solution is required. A correctly balanced reaction equation (from which moles ratios can be derived) is a prerequisite for all these calculations. This is because the mole ratio is an integral part of the general expression used for all volumetric analysis calculations. The general expression is given by:

$$\frac{V_A M_A}{V_B M_B} = \frac{N_A}{N_B} \text{ or } \frac{V_A M_A}{N_A} = \frac{V_B M_B}{N_B} ,$$

where;

- V_A = Volume of acid
- M_A = Molarity of acid
- V_B = Volume of base
- M_B = Molarity of base
- N_A = Number of moles of acid

- N_B = Number of moles of base

The Relative Atomic Mass of Unknown Element in an Acid or Alkali

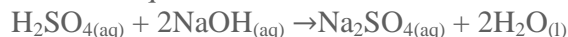
Find the relative atomic mass of unknown element in an acid or alkali

Example 1

12.5 cm³ of 0.5M sulphuric acid neutralized 50 cm³ of a given solution of sodium hydroxide. What is the molarity of the alkali?

Solution

Reaction equation is:



From the equation, 1 mole of sulphuric acid solution reacts with 2 moles of sodium hydroxide solution. So, the number of moles of the acid, $N_A = 1$ and the number of moles of base, $N_B = 2$. The other data are as follows:

$V_A = 12.5 \text{ cm}^3$, $M_A = 0.5\text{M}$ and $V_B = 50 \text{ cm}^3$

Substituting titre values in the expression $\frac{V_A M_A}{V_B M_B} = \frac{N_A}{N_B}$, we have

$$\frac{12.5 \times 0.5}{50 \times M_B} = \frac{1}{2}, \text{ and } M_B = \frac{2 \times 12.5 \times 0.5}{50} = 0.25$$

So, the molarity of the acid = 0.25M

Example 2

20 cm³ of a solution containing 7g/dm³ of a metal hydroxide, XOH, were exactly neutralized with 25 cm³ of 0.10M hydrochloric acid.

- Write a balanced chemical equation for the neutralization of the metal hydroxide, XOH, with hydrochloric acid.
- Calculate the concentration of the metal hydroxide in moles per dm³.
- (i) Calculate the molar mass of XOH (ii) Identify element X

Solution



From the reaction equation, $N_A = 1$ and $N_B = 1$.

$V_A = 25 \text{ cm}^3$, $V_B = 20 \text{ cm}^3$, $M_A = 0.1\text{M}$, $M_B = ?$

$$\frac{V_A M_A}{V_B M_B} = \frac{N_A}{N_B}$$

$$\frac{25 \times 0.1}{20 \times M_B} = \frac{1}{1}$$

$$M_B = \frac{25 \times 0.1}{20}$$

$$= 0.125\text{M}$$

$$\text{Molar mass of XOH} = \frac{\text{Concentration (g / dm}^3\text{)}}{\text{Molarity (mol / dm}^3\text{)}}$$

$$= \frac{7\text{g dm}^{-3}}{0.125\text{mol / dm}^3}$$

$$= \underline{56\text{g mol}^{-1}}$$

$$\text{Molar mass of XOH} = 56\text{g mol}^{-1}$$

$$\text{I.e. X} + 16 + 1 = 56$$

$$\text{X} + 17 = 56$$

$$\text{X} = 56 - 17$$

$$\text{X} = 39\text{g}$$

Therefore, element X is potassium (K)

The Percentage Purity of an Acid or an Alkali

Calculate the percentage purity of an acid or an alkali

Example 3

5.1g of impure sodium carbonate solution was dissolved in water to make 500 cm³ of solution. 20 cm³ of this solution was titrated against 20.45 cm³ of 0.04M hydrochloric acid. Calculate the percentage purity of the sodium carbonate solid.

Solution

To calculate the concentration of *impure* Na₂CO₃ solution: 5.1g per 500 cm³ = 10.2g dm⁻³ Reaction equation is:



From the equation, N_A = 2 and N_B = 1.

Given:

$$V_A = 20.45 \text{ cm}^3, V_B = 20 \text{ cm}^3, M_A = 0.04M, M_B = ?$$

$$\frac{V_A M_A}{V_B M_B} = \frac{N_A}{N_B} = \frac{20.45 \times 0.04}{20 \times M_B} = \frac{2}{1}$$

$$M_B = \frac{20.45 \times 0.04 \times 1}{20 \times 2}$$

$$= 0.02045M$$

Therefore, molarity of the base = 0.02045M

To calculate the concentration of *pure* base (Na_2CO_3 solution) in g dm^{-3} :

Concentration = *Molarity* \times *Molar mass*

But molar mass of $\text{Na}_2\text{CO}_3 = 106$.

So, concentration (g/dm^3) = $0.02045 \times 106 = 2.1677 \text{ g dm}^{-3}$

$$\begin{aligned}\text{Percentage purity} &= \frac{\text{Concentration of pure sample}}{\text{Concentration of impure sample}} \times 100 \\ &= \frac{2.1677}{10.2} \times 100 \\ &= 21.25\%\end{aligned}$$

The percentage purity of sodium carbonate = 21.25%

The Number of Molecules of Water of Crystallization of a Substance

Find the number of molecules of water of crystallization of a substance

Example 4

0.465g of a hydrated form of sodium carbonate exactly reacts with 75 cm^3 of 0.10M hydrochloric acid. Calculate the number of molecules of water of crystallization present in one mole of the hydrated salt.

Solution

The balanced reaction equation for the anhydrous salt is:



Number of moles of HCl present in $75 \text{ cm}^3 = 75/1000 \times 0.1 = 0.0075M$

$$\text{But } \frac{\text{Moles of acid}}{\text{Moles of base}} = \frac{N_A}{N_B} = \frac{2}{1}$$

$$\frac{0.0075}{\text{Moles of base}} = \frac{2}{1}$$

$$\text{Moles of base} = \frac{0.0075}{2} = 0.00375M$$

Mass of 0.00375 moles of $\text{Na}_2\text{CO}_3 = 0.00375 \times 106 = \mathbf{0.3975g}$ (= mass of anhydrous salt)

Molar mass of anhydrous salt = 106g

Mass of water contained in the hydrated salt = mass of hydrated salt - mass of anhydrous salt
 = 0.465 – 0.3975
 = 0.0675g

Therefore, the mass of water of crystallization = **0.0675g**

But, remember that mass of the anhydrous salt = 0.3975g

Now, let the formula of the hydrated salt be $\text{Na}_2\text{CO}_3 \cdot X\text{H}_2\text{O}$, where X is the number of moles of water crystallization

$$\text{Then } \frac{XH_2O}{Na_2CO_3} = \frac{\text{Mass of water of crystalization}}{\text{Mass of anhydrous salt}}$$

$$\frac{18x}{106} = \frac{0.0675}{0.3975}$$

$$X = \frac{106 \times 0.0675}{18 \times 0.3975}$$

$$= 1$$

Therefore, the formula of the salt is $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$

Application of Volumetric Analysis

The Application of Volumetric Analysis in Real Life Situations

Explain the application of volumetric analysis in real life situations

Volumetric analysis has a variety of laboratory and industrial applications in everyday life. The following are just a few of the applications (uses) of volumetric analysis in daily life:

- **Use in preparation of standard solutions:** Standard solutions are prepared by applying the knowledge of volumetric analysis. Volumetric analysis is used in school, college and university chemistry laboratories to determine concentrations of unknown substances. The titrant (the known solution) is added to a known quantity of analyte (unknown solution) and a reaction takes place. Knowing the volume of the titrant allows one to determine the concentration of the unknown substance.

- **Use in environmental and water safety:** Titration is important in environmental chemistry, where scientists can use it to analyze acid rain or contaminants in surface water samples. Environmental studies usually involve an analysis of precipitation and its response to pollution. To quantify the degree of contamination in natural rainwater or snow, titration is used. The process is quick and results are reliable. Since most titration processes do not require expensive or specialized equipment, the test can be performed often and in different areas with relatively little effort. The safety of water is based on its chemical ingredients. By analyzing wastewater, the extent of contamination and the requirements for filtering and cleaning can be determined. Titration is a key mechanism in this analysis. Often, more specialized titration equipment is used in this application, which measures ammonia levels in combination with other reactants to quantify other chemicals present.

- **Use in food and beverage industry:** In the food and beverage industry, manufacturers must ensure their products meet certain quality criteria or contain standard concentrations of specific additives, so titration is often used to analyze the products before sale. Wine is often affected by its

degree of acidity. It is possible to improve wine production by measuring acidity using titration. Simple, inexpensive titration kits are available to winemakers for this purpose. The results of a titration test on wine can suggest if additional ingredients are necessary to maintain its quality. In general, all brewing industries and distilleries apply the knowledge of volumetric analysis (titration) to determine the acidity and alcohol contents of their beers and other alcoholic beverages. The process also finds ample use in food industry. The compounds which make up food products help determine their nutritional implications. Titration is one technique that assists in these studies. The acidity of orange juice, for example, is easily determined using a standard titration process. In this process, an electrode is added to a solution made up of orange juice and deionized water. The titrant catalyst then measures the acidity of the juice. Manufacturers can use the technique to vary this quality to satisfy customers or those with special nutritional needs.

- **Use in agriculture:** Volumetric analysis technique is used to determine the soil pH. This is important because, if the pH of a certain soil is found to be extremely low or high, corrective measures are taken by adding the correct quantity of agricultural limes or other chemicals to make the soil suitable for plant growth. The method is also used by agronomists and farmers to analyse the kind and amount of plant nutrient elements present in a particular sample of soil, the knowledge of which helps determine soil fertility.

Industrial and Laboratory Skills of Volumetric Analysis

Compare industrial and laboratory skills of volumetric analysis

The knowledge of volumetric analysis (titration) is used in hospitals and medical laboratories to carry out such duties as preparation of solutions and suspensions, blood analysis, and diagnosis of certain diseases and health problems. For example, when dissolving a solid drug to make a solution for injection, utmost precision is required to measure the correct volume of liquid to be used to dissolve a correct amount of solid drug to prepare the solution of a given concentration to inject to a patient. Also titration is very important in the pharmaceutical industry, where precise measurements of quantities and concentrations are essential throughout the manufacturing process. Titration is thus an important part of the pharmaceutical industry to ensure quality control. Many variations of the titration technique are used, and specialized equipment for pharmaceutical titration is often developed to make the process more efficient.

TOPIC 6: IONIC THEORY AND ELECTROLYSIS

Ionic Theory

To account for the phenomena of electrolysis the Ionic Theory was put forward by Arrhenius in 1880. The theory states that electrolytes are made up of ions, which are built up in certain patterns called crystal lattice. When these substances dissolve in water, the structure is destroyed and the ions are set free to move. Concentrated mineral acids such as sulphuric acid, hydrochloric acid and nitric acid do not contain ions but they consist of molecules. However, when they are diluted, the molecular structure is destroyed and ions are formed.

Electrolytes and Non-electrolytes

Distinguish electrolytes from non-electrolytes

The main purpose of this chapter is to investigate the effects which electricity has on a range of substances, and to develop a thorough explanation of those effects in terms of our present knowledge

of atomic structure. Before we begin, it is important that we familiarize ourselves with different terms that we are going to use to explain different phenomena. It is crucial that the definitions and meanings of these terms be understood at the outset in order that concepts defined in this chapter are easily and clearly apprehended. These terms are given hereunder:

- **Electrolysis:** decomposition of a compound in solution or molten state by passing electricity through it.
- **Conductor:** a solid substance that allows electricity to pass through it. All metals are included in this class.
- **Non-conductor or insulator:** a solid substance that does not allow electricity to flow through it. All non-metals fall in this class.
- **Electrolyte:** a substance which, when dissolved or molten, conducts electricity and is decomposed by it.
- **Non-electrolyte:** a compound which cannot conduct electricity, be it in molten or solution state.
- **Electrode:** a graphite or metal pole (rod) or plate through which the electric current enters or leaves the electrolyte.
- **Cathode:** a negative electrode which leads electrons into the electrolyte.
- **Anode:** a positive electrode which leads electrons out of the electrolyte.
- **Ion:** a positively or negatively charged atom or radical (group of atoms).
- **Cation:** a positive ion which moves to the cathode during electrolysis.
- **Anion:** a negative ion which moves to the anode during electrolysis.

Electrolytes and non-electrolytes

Liquids such as ethanol, paraffin, petrol and methylbenzene do not conduct electricity. The bonding in these compounds is covalent. These substances consist of molecules. There are no free electrons or charged particles to flow through them. Solutions of covalent compounds, for example sugar solution, do not conduct electricity.

These compounds are **non-electrolytes**. Non-electrolytes exist only in the form of molecules and are incapable of ionization.

Ionic compounds contain charged particles (ions), but in solid state, the ions are firmly held in place and they are not free to move. An ionic solid does not conduct electricity. However, the ions present can become free to move if the solid is melted or dissolved in water. Then they can conduct electricity. For example, solid sodium chloride cannot conduct electricity but when melted or dissolved in water, the ions, Na^+ and Cl^- are set free. Then these ions are free to move in solution and hence conduct electricity. These compounds are called **electrolytes**.

Weak and Strong Electrolytes

Categorize weak and strong electrolytes

Weak electrolytes are compounds that are only partially or slightly ionized in aqueous solutions.

Some substances, for example, ethanoic acid solution ionize partially.



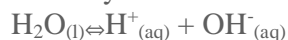
Most of the electrolytes exist in solution in the form of unionized molecules. For example, in ordinary dilute (2M) ethanoic acid, out of every 1000 molecules present, only 4 are ionized and 996 are unionized.

A solution of ammonia water is also a weak electrolyte, containing a relatively small proportion of ammonium and hydroxyl ions.



Most of the organic acids are weak electrolytes, e.g. tartaric, citric and carbonic acids.

However, there is no sharp dividing line between weak and strong electrolytes. Water is also a weak electrolyte. It ionizes only slightly.



Study shows that for every molecule of water ionized, there are 6 million molecules of water not ionized. *Strong electrolytes* are compounds that are completely ionized in aqueous solutions. When sodium chloride is dissolved in adequate water it ionizes completely into Na^+ and Cl^- ions. There are no NaCl solid particles left unionized. All strong electrolytes (salts, the mineral acids and caustic alkalis) ionize completely in solutions.

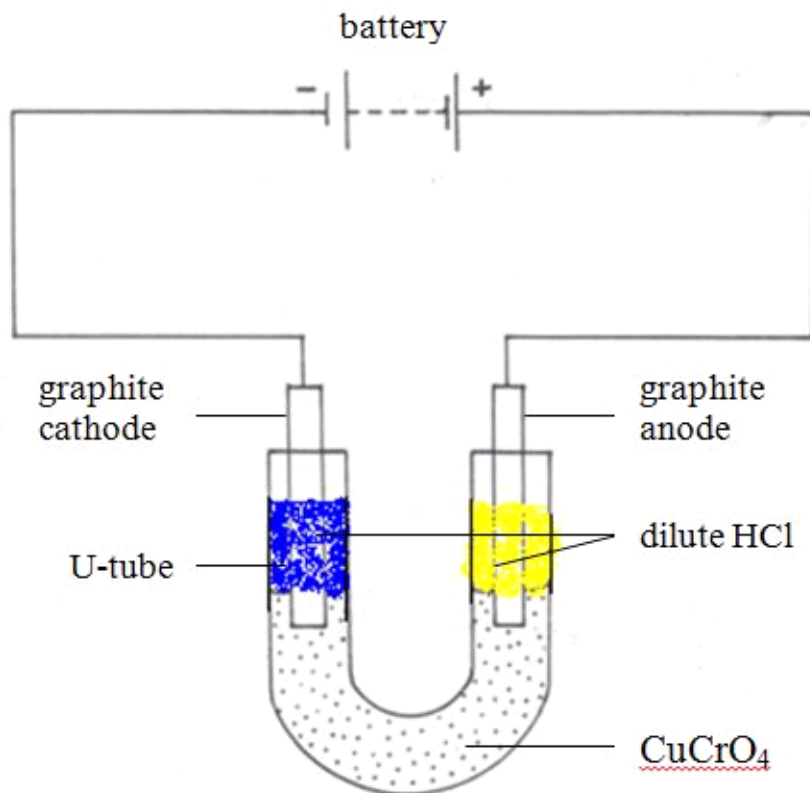
The Mechanisms of Electrolysis

Electrolytic Cells of Different Electrolytes in the Molten and Aqueous States

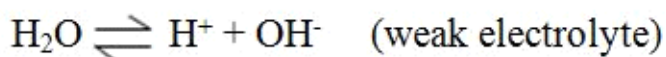
Set up electrolytic cells of different electrolytes in the molten and aqueous states

The conductivity of ionic compounds is explained by the fact that ions move in a particular direction in an electric field. This can be shown in experiments with coloured salts. For example, copper (II) chromate (VI) (CuCrO_4) dissolves in water to give a **green** solution. This solution is placed in a U-tube. A colourless solution of dilute hydrochloric acid (HCl) is then layered on top of the salt solution in each arm. Graphite rods are fitted as shown in figure 13.3. These rods (electrodes) carry the current into and out of the solution.

After passing the current for a short time, the solution around the cathode becomes **blue**. Around the anode, the solution becomes **yellow**. These colours are produced by the movement (migration) of the ions in the salt. The positive copper ions (Cu^{2+}) are blue in solution. They are attracted to the cathode (negative electrode). The negative chromate ions (CrO_4^{2-}) are yellow in solution. They are attracted to the anode (the positive electrode). The use of coloured ions in solution has shown the direction that positive and negative ions move in an electric field. Always positive ions (cations) move to the cathode and negative ions (anions) move to the anode.



Ionic Migrations During Electrolysis and the Preferential Discharge of Ions at the Electrodes
 Explain ionic migrations during electrolysis and the preferential discharge of ions at the electrodes
 When a salt such as sodium chloride is dissolved in water, its ions are set free to move. So the solution can be electrolysed. Since the salts, alkalis and acids are dissolved in water, most of the solutions are aqueous. There is then a complication in electrolysis of such substances in aqueous form. This is because the water used to dissolve them also do ionize partially (it is a weak electrolyte) Then at each electrode, we get more than one ion for discharge, but only one is supposed to be discharged. Take an example of electrolysis of copper (II) sulphate solution using platinum electrodes. By ionic theory, the solution ionizes thus: $\text{CuSO}_4(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ (strong electrolyte)



During electrolysis, Cu^{2+} and H^+ ions move to the cathode while SO_4^{2-} and OH^- ions move to the anode.

Cathode	Anode
Cu^{2+}	SO_4^{2-}
H^+	OH^-

In situations like this, the order of discharge of the ions at the electrode will depend on:

- the position of the metal ion or radical in the electrochemical series;
- the concentration or nature of the ions (or electrolyte) to be discharged; and
- the nature of the electrodes used.

The position of ion or radical in the electrochemical series

Cations		Anions	
K ⁺	ease of discharge increases	SO ₄ ²⁻	ease of discharge increases
Ca ²⁺		NO ₃ ⁻	
Na ⁺		Cl ⁻	
Mg ²⁺		Br ⁻	
Al ³⁺		I ⁻	
Zn ²⁺		OH ⁻	
Fe ²⁺			
Pb ²⁺			
H ⁺			
Cu ²⁺			
Ag ⁺			

The arrangement of ions above is the same as that of the electrochemical series. If all other factors are constant, any ion will be discharged from solution in preference to those above it.

Cathode	Anode
Cu ²⁺	SO ₄ ²⁻
H ⁺	OH ⁻
Cu ²⁺ + 2e ⁻ → Cu _(s) <i>copper is discharged (loses its charge)</i>	4OH ⁻ → 2H ₂ O _(l) + O _{2(g)} + 4e ⁻ <i>hydroxyl ion is discharged</i>

In other words, we can say that the reaction that occurs at the **cathode** is *reduction* (electron gain) and that which occurs at the **anode** is *oxidation* (electron loss).

Result

- At cathode, copper is deposited
- At anode, oxygen is given out (liberated)
- The solution at the end of electrolysis is colourless and acidic because in the electrolyte there are left H⁺ and SO₄²⁻ ions, which remain moving freely in the solution as ionic sulphuric acid.

The concentration or nature of electrolyte

Take an example of electrolysis of sodium chloride using platinum electrodes when in:

- aqueous solution;
- concentrated aqueous solution; or
- fused or molten state.

aqueous solution



During electrolysis:

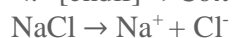
Cathode	Anode
Na ⁺ and H ⁺	Cl ⁻ and OH ⁻
H ⁺ ions are discharged in preference to Na ⁺ ions: 2H ⁺ + 2e ⁻ → H _{2(g)}	OH ⁻ ions are discharged in preference to Cl ⁻ ions: 4OH ⁻ → 2H ₂ O _(l) + O _{2(g)} + 4e ⁻

Result

- At cathode, hydrogen is given out
- At anode, oxygen is out

- The concentration of the solution remains constant since all Na^+ and Cl^- ions remain undisturbed in the solution. This means that the Na^+ and Cl^- ions that are left in the solution are equivalent to sodium chloride solution.

Concentrated aqueous solution

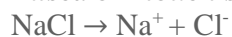


Cathode	Anode
Na^+ and H^+ ions are discharged in preference to Na^+ ions since Na^+ and H^+ are very far from each other in e. c. s $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})}$	Cl^- and OH^- ions are discharged in preference to OH^- ions since Cl^- and OH^- ions are very close to each other in the e. c. s (and because there are more Cl^- ions in the solution) $2\text{Cl}^- \rightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$

Results

- At cathode $\text{H}_{2(\text{g})}$ is given off
- At anode $\text{Cl}_{2(\text{g})}$ is given off
- The solution becomes progressively more alkaline as the electrolysis goes on because Na^+ and OH^- ions remain in solution as caustic soda (sodium hydroxide) solution. This is the main method used in the manufacture of sodium hydroxide in industry. $\text{Na}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{NaOH}_{(\text{aq})}$

Fused or molten sodium chloride



During electrolysis:

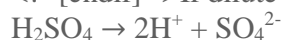
Cathode	Anode
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}_{(\text{l})}$	$2\text{Cl}^- \rightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$

Result

- At cathode sodium is liberated (deposited)
- At anode chlorine is given off

The nature of electrodes (inert vs active electrodes)

If dilute sulphuric acid is electrolysed using platinum electrodes:



Cathode	Anode
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})}$	SO_4^{2-} and OH^- $4\text{OH}^- \rightarrow 2\text{H}_2\text{O}_{(\text{l})} + \text{O}_{2(\text{g})} + 4\text{e}^-$

Result

- At cathode $\text{H}_{2(\text{g})}$ is given out
- At anode $\text{O}_{2(\text{g})}$ is given out
- The solution becomes acidic at the end of electrolysis because of the acidic ions (SO_4^{2-}) left in the final solution.

Charge flow during electrolysis

The coulomb is the electrolytic unit of charge. A current of one ampere is the rate of flow of charge equal to one coulomb per second. The charge is calculated from the knowledge of the number of seconds for which a steady current is passed.

Current in circuit	Time taken	Total charge
1 ampere	1 second	1 coulomb
1 ampere	10 seconds	10 coulombs
20 amperes	10 seconds	200 coulombs

A amperes	t seconds	At coulombs
-----------	-----------	-------------

Therefore charge = quantity of electricity (Q) = I × t

Flow of charge required to liberate 1 mole of element during electrolysis

Electrolysis always produces chemical reactions. Consider a reaction (at cathode) in which one mole of silver Ag^+ ions is discharged and deposited. $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}_{(\text{s})}$

In this case, 1 mole of electrons (e^-) is required to discharge 1 mole of Ag^+ ions to produce 1 mole of silver atoms ($\text{Ag}_{(\text{s})}$). 1 mole of electrons is a large charge and experiments show that it is equal to 96500 coulombs. Therefore 1 mole of electrons = 96500 coulombs. This is called the faraday.

The number of faradays (moles of electrons) required to liberate 1 mole of an element during electrolysis is deduced from the equation for the electrode reaction.

Example 1

Element	Electrode reaction	Faradays
• Sodium	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}_{(\text{s})}$	1
• Copper	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}_{(\text{s})}$	2
• Aluminium	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}_{(\text{s})}$	3
• Chlorine	$2\text{Cl}^- \rightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$	2

That is, 1 faraday is needed to deposit 1 mole of sodium atoms (23g), 3 faradays to deposit 1 mole of aluminium atoms (27g) and 2 faradays to liberate 1 mole of chlorine gas (71g).

- The mass of an element liberated by 1 coulomb of electricity during electrolysis is called *electrochemical* equivalent of that element.
- The mass of an element deposited or liberated by 1 faraday during electrolysis is called *chemical* equivalent of that element.

Experiments to Identify the Products of Electrolysis when Different Electrolytes are Used

Perform experiments to identify the products of electrolysis when different electrolytes are used

Activity 1

Perform experiments to identify the products of electrolysis when different electrolytes are used

Experiments to Identify the Products of Electrolysis when Different Electrodes are Used

Perform experiments to identify the products of electrolysis when different electrodes are used

Activity 2

Perform experiments to identify the products of electrolysis when different electrodes are used

Laws of Electrolysis

Experiments to Relate Masses Liberated and Quantity of Electricity Passed

Carry out experiments to relate masses liberated and quantity of electricity passed

The laws expressing the quantitative results of electrolysis were first stated by a British chemist called Michael Faraday. The laws assert that the amount (expressed in moles) of an element liberated during electrolysis depends on:

- the time of passing the steady current;
- the magnitude of the steady current passed; and
- the charge on the ion of the element.

An Experiment to Verify Faraday's First Law of Electrolysis

Carry out an experiment to verify Faraday's First Law of Electrolysis

The fact that the amount of a substance liberated during electrolysis depends upon these factors can be proved by conducting experiments. The product of time (measured in seconds) and the current passed (measured in amperes) gives a measure of electricity known as the quantity of electricity.

Quantity of electricity (Q) [coulombs]= current (I) [amperes]×time (t) [seconds]

$$Q = I \times t$$

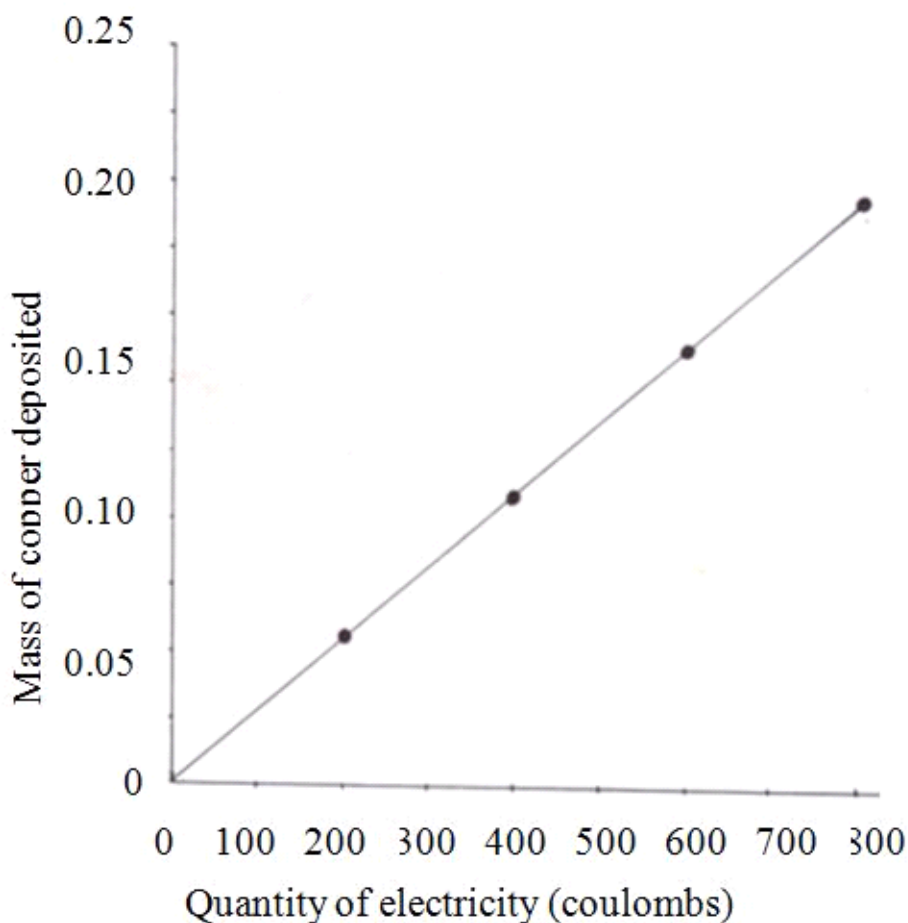
Because of this relationship, factors (1) and (2) may be included in the same experiment. The experiment to determine the effect of time on the amount of element deposited or liberated is carried out by passing a steady current through a solution of the compound of that element for different lengths of time.

The following table summarises the specimen results obtained by passing a steady current (0.21 amps) through a solution of copper (II) sulphate for 15, 30, 45 and 60 minutes. The last column shows the mass of copper deposited.

Specimen results for electrolysis of copper (II) sulphate

Current (amps)	Time(s)	Quantity of electricity (coulombs)	Mass of copper deposited (grams)
0.21	15 × 60=900	900 × 0.21=189	0.063
0.21	30 × 60=1800	1800 × 0.21=378	0.129
0.21	45 × 60=2700	2700 × 0.21=576	0.187
0.21	60 × 60=3600	3600 × 0.21=756	0.250

The relationship between the amount of copper deposited and the quantity of electricity passed can be assessed by considering the values in the last two columns in the table. This data may be represented in a graph illustrated in figure 6.4. The shape of the graph shows a straight line passing through the origin. From this fact, it is clear that the mass of copper deposited is directly proportional to the quantity of electricity passed. This is in accordance to what Faraday formulated in his First Law.



Graph of mass deposited versus amount of electricity passed

Faraday's First Law of Electrolysis states that *the mass of a substance liberated at (or dissolved from) an electrode during electrolysis is directly proportional to the quantity of electricity passing through the electrolyte.*

The quantity of electricity is measured in coulombs where a coulomb is the passage of an electric current of one ampere for one second. Let

- m be the mass of the substance liberated;
- I be the current passed in amperes; and
- t be the time in seconds.

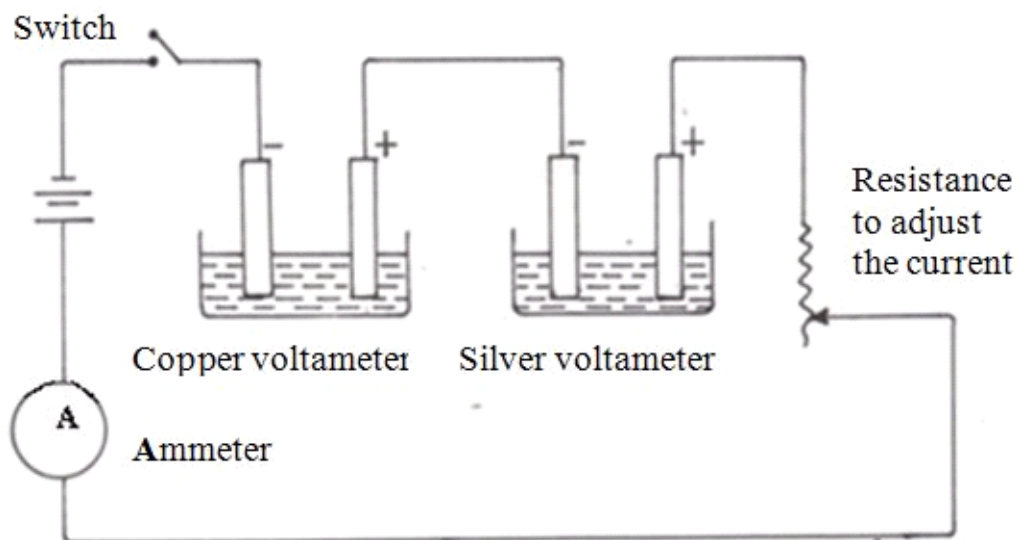
We can therefore represent the first law mathematically as: $m \propto I \times t$ or $m = Z \times I \times t$ where Z is the proportionality constant referred to as electrochemical equivalent of the substance liberated.

Electrochemical equivalent is the mass of a substance (element) liberated by 1 coulomb of electricity during electrolysis.

An Experiment to Verify Faraday's Second Law of Electrolysis

Carry out an experiment to verify Faraday's Second Law of Electrolysis

The third (3) factor mentioned previously as affecting the amount of substance liberated during electrolysis may also be investigated experimentally. Because our interest is the effect of the charge on the ions present in solution, we need to keep the quantity of electricity fixed whilst varying the types of the ions in solution. This may be achieved by passing the same quantity of electricity through two cells, with ions of different charges in each cell.



Apparatus for confirmation of Faraday's Second Law

The experiment is conducted using two voltameters. The two voltameters are connected in series as shown. The first one is a copper voltameter and the second is a silver voltameter. The copper voltameter has **copper electrodes** in a solution of **copper (II) sulphate**. Hence, in this voltameter, copper ions are discharged and deposited at the cathode.

The silver voltammeter has **silver electrodes** in a solution of **silver nitrate**. The discharged silver ions are deposited at the cathode.

Before the experiment is started, each cathode electrode in the voltameters is cleaned, dried and weighed. The electrodes are then connected to the circuit, after which a suitable current is passed for a measured period of time.

After this, the cathode are removed from the voltameters, cleaned, dried and reweighed. The increase in mass of the two cathode electrodes represents the respective amounts of copper and silver deposited at the cathodes. The quantity of electricity required to deposit one mole of each element is calculated using Faraday's Second Law of Electrolysis.

Specimen results

Current flowing	=	0.45A
Duration of current flow	=	25 minutes
Mass of copper deposited	=	0.221g
Mass of silver deposited	=	0.755g

The results show that the masses of silver and copper deposited are different. A comparison of the amounts of each of the elements deposited can be made simple by calculating the number of moles of atoms of each of the element deposited.

Thus:

Amount of copper deposited = $0.221/63.5 \text{ mole} = 0.0035 \text{ mole}$

Amount of silver deposited = $0.755/107.8 \text{ mole} = 0.0070 \text{ mole}$

It is seen that twice as many atoms of silver are deposited as atoms of copper. The difference in amount of each element deposited arises from the difference in charges on ions of the element concerned.

The change on the copper ion is twice that on the silver ion and therefore twice the quantity of electricity will be required to liberate one mole of copper as for the liberation of one mole of silver.

This relationship is in accordance to Faraday's Second Law of Electrolysis, which describes the relationship between the amount of element deposited and the charge on the ions of that element. Faraday's Second Law of Electrolysis states that *when the same quantity of electricity is passed through solutions of different electrolytes the relative numbers of moles of the elements deposited are inversely proportional to the charges on the ions of each of the elements respectively.*

In order to discharge one mole of monovalent ions such as hydrogen ion, Sodium ion, Silver ion and Chlorine ion, 96500 C of electricity are required. This quantity of electricity has been experimentally determined and is known as the Faraday constant.

It represents one mole of electrons, which is the same as the quantity of electrons required to discharge one mole of Silver ions to give one mole of silver atom. The validity of Faraday's Second Law of Electrolysis is evident from the following observations:

- One faraday (1F) discharges one mole of H^+ , Na^+ , Ag^+ , Cl^- and OH^- ions.
- Two Faradays (2F) discharges one mole of Cu^{2+} , Pb^{2+} , Mg^{2+} , Ca^{2+} , Fe^{2+} , etc ions.
- Three Faradays (3F) discharge one mole of Al^{3+} , Fe^{3+} , etc. ions.

Relationship between the Chemical Equivalents of Elements and Quantity of Electricity Passed
Relate the chemical equivalents of elements and quantity of electricity passed

A steady current of 4 amperes is passed through aqueous copper (II) sulphate solution for 1800 seconds using platinum electrodes. Calculate:

- mass of copper deposited
- mass of oxygen liberated

Given:

- Atomic weight of copper = 63.5
- Atomic weight of oxygen = 16
- 1 Faraday = 96500 C

Solution

Cathode reaction: $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$

In this case, 2 Faradays of electricity are required to deposit one mole of copper atom 63.5g.

This means 2×96500 C liberates 63.5g of copper.

Quantity of electricity passed = $I \times t = 4 \times 1800$ C. So, if 2×96500 C liberates 63.5g, then $I \times t = 4 \times 1800$ C will liberate 2.4g of copper.

Therefore, mass of copper deposited = 2.4g

Anode reaction: $4OH^- \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^-$

The reaction shows that 4 moles of electrons (4 Faradays) are lost during the reaction process.

Therefore, 4×96500 C are needed to liberate one mole (32g) of oxygen.

Quantity of electricity flowing = 4×1800 C

So if 4×96500 C = 32g, then

$$4 \times 1800 \text{ C} = \frac{4 \times 1800 \times 32}{4 \times 96500} = 0.6 \text{g}$$

Therefore, mass of oxygen liberated = 0.6g

Application of Electrolysis

Electrolysis has several uses in industry. Its main application has been in the fields of manufacture of chemicals and in the purification of metals for which other purification methods prove either too difficult or highly expensive to apply. Some applications of electrolysis are as discussed below:

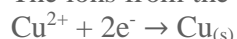
The Industrial Purification of Copper by Electrolysis

Outline the industrial purification of copper by electrolysis

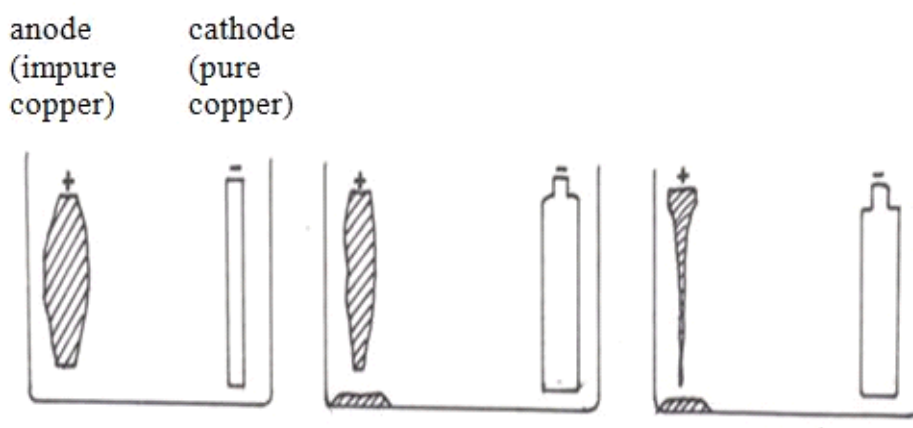
Some metals can be purified by means of electrolysis. This process is used in industry to purify copper, which must be very pure 99.9% for electrical wiring. Copper made by roasting the sulphide ore is about 99.5% pure (so it has an impurity level of 0.5%). This level of impurity cuts down electrical conductivity significantly.

This is how the electrolytic purification (refining) process is carried out: The anode is made of a large block of impure copper. The cathode is a thin sheet of pure copper. The electrolyte is copper (II) sulphate solution. During the refining process, the copper atoms of the impure block become ions (the anode dissolves). $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$

The ions from the solution become atoms.



They stick onto the cathode. A layer of pure copper builds up on the cathode. As electrolysis takes place, the cathode gains mass as copper is deposited on it. As a result, the cathode gets smaller while the anode gets bigger as electrolysis proceeds. Eventually the whole anode dissolves.



Purification of copper by electrolysis

Only pure copper sticks to the cathode. Most impurities fall to the bottom of the electrolytic cell.

They form a solid material (**anode sludge** or **slime**) which contains small quantities of precious metals such as silver, gold and platinum. The precious metals recovered from the slime are purified and sold.

An Experiment on Electroplating of Metallic Materials

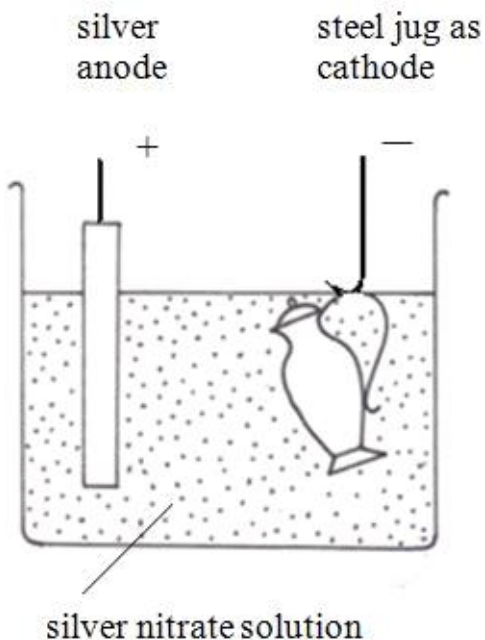
Carry out an experiment on electroplating of metallic materials

Electroplating is the coating of a metal with a layer of another metal by means of electrolysis.

Electrolysis can be used to coat a thin layer of a less reactive metal onto a more reactive metal. The thin layer of less reactive metal will provide protection from corrosion for the more reactive metal underneath. It may also make the product more attractive.

The object to be coated should be made the cathode and the coating material should be the anode. The most commonly used metals for electroplating are copper, chromium, silver and tin. Steel can be electroplated with chromium or tin. This prevents the steel from rusting and gives it a shiny, silver finish. This is also the idea behind chromium-plating articles such as car bumpers, kettles, bath taps, etc. Chromium does not corrode, it is a hard metal that resists scratching and wear, and can also be polished to give an attractive finish.

Nickel can be electroplated with silver. This will make nickel more attractive. The diagram below shows how a steel jug is electroplated with silver. The jug becomes the cathode of an electrolytic cell. The anode is made of silver. The electrolyte is a solution of a silver compound, for example silver nitrate.



Silverplating a steel jug

At the anode: The silver dissolves, forming ions in solution: $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$

At the cathode: The silver ions receive electrons, forming a coat of silver on the jug: $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}_{(\text{s})}$

When the layer of silver is thick enough, the jug is removed. In general, to electroplate any object with metal M, the set up is:

- Cathode – object to be electroplated
- Anode – metal M
- Electrolyte – solution of a soluble compound of M

TOPIC 7: CHEMICAL KINETICS, EQUILIBRIUM AND ENERGETICS

The Rate of Chemical Reactions

Comparison between the Rates of Chemical Reactions

Compare the rates of chemical reactions

Chemical reactions take place at different rates. Some are fast whereas others are very slow. Let us consider the following reactions:

- Addition of sodium metal to water: $2\text{Na}_{(s)} + 2\text{H}_2\text{O}_{(l)} \rightarrow 2\text{NaOH}_{(aq)} + \text{H}_{2(g)}$ The reaction takes place immediately and violently. It is therefore a fast reaction.
- The rusting of iron in the presence of air and water giving hydrated iron (III) oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$: This is an extremely slow reaction.

These two reactions could be taken as representative examples of extremely fast and extremely slow reactions, respectively. There are, however, other reactions which proceed at rates intermediate between these two extremes. Rates of some of these reactions can be measured.

The rate of a chemical reaction can be measured in various ways. Let us consider the reaction between zinc and sulphuric acid to produce zinc sulphate and hydrogen gas:



When zinc is added to dilute sulphuric acid in a flask, they react together. The zinc slowly disappears and the gas (H_2) bubbles off. After sometime, the bubbles of a gas form less quickly. The reaction is slowing down. Finally, no more bubbles appear. The reaction is over, because all the acid has been used up. Some zinc remains behind in a beaker.

In this reaction both zinc and sulphuric acid get used up in the reaction. At the same time, zinc sulphate and hydrogen form. The rate of this reaction could be determined by measuring any of the following:

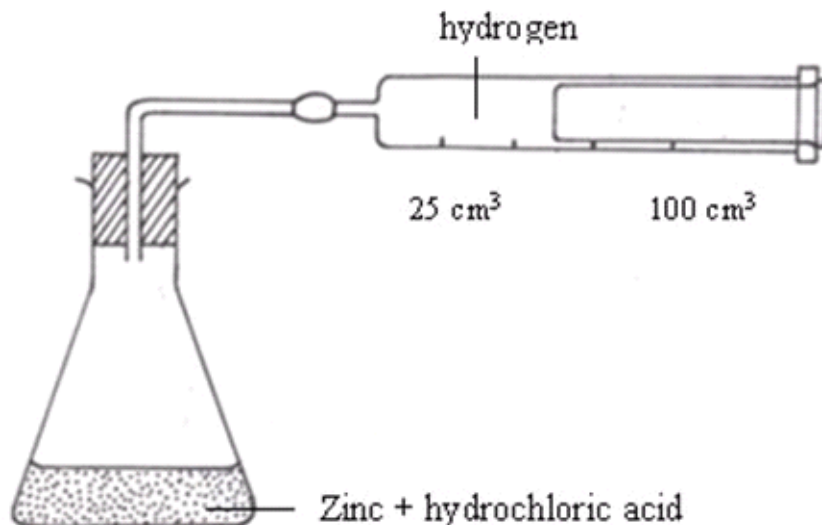
- the amount of zinc used up per unit of time;
- the amount of sulphuric acid used up per unit of time;
- the amount of zinc sulphate produced per unit of time; or
- the amount of hydrogen produced per unit of time.

In general, the rate of a chemical reaction is determined by measuring *the amount of reactant used up* per unit of time or the *amount of product produced* per unit of time. Therefore, the rate of a chemical reaction simply refers to the amount of reaction which occurs in a unit time.

Experiments to Measure the Rates of Chemical Reactions

Perform experiments to measure the rates of chemical reactions

For the reaction described above, it is easiest to measure the amount of hydrogen produced per minute. The hydrogen can be collected as it bubbles off and its volume can then be measured as shown in figure



Apparatus for measuring the production of gas

An experiment may be designed to measure the volume of hydrogen produced after every twenty seconds or so and then recording the data in a notebook. The table below shows sample results from such an experiment.

Time (s)	Volume of hydrogen gas (cm ³)
0	0
20	13
40	22
60	30
80	37
100	41
120	44
140	46
160	47
180	47
200	47

Questions from the experiment

Use these data to draw a graph of time (horizontal axis) against volume of hydrogen (vertical axis).

Note: rate of reaction =
$$\frac{\text{Change in volume}}{\text{Change in time}}$$

There are also other ways by which rates of chemical reactions can be measured. These include measuring the:

- *change in intensity of colour:* Many chemical reactions involve a change in colour. Potassium permanganate, for example, when it reacts with sulphur dioxide it changes from purple to colourless. The rate of such a reaction could be determined by measuring the rate at which the colour changes.

- *formation or disappearance of a precipitate:* The reaction between hydrochloric acid and sodium thiosulphate produce a yellow precipitate of sulphur. The rate at which this precipitate forms is a measure of the rate of a reaction.

Factors Affecting the Rate of Chemical Reactions

The Effect of Concentration on the Rate of a Reaction

Describe the effect of concentration on the rate of a reaction

A chemical reaction will occur only if the particles of the reacting substances are allowed to come in contact. Increasing the concentration means increasing the density of the particles and hence the probability of particles being close together and colliding more often. Thus, a reaction can be made to go faster or slower by changing the concentration of a reactant.

The effect of concentration on the rate of reaction can be determined by mixing dilute hydrochloric acid with sodium thiosulphate solution to produce a precipitate of sulphur. Since this reaction produces a precipitate from two different colourless solutions, the intensity of the precipitate at any given moment in time represents the extent of the reaction.

The experiment to determine this effect is carried out by mixing 2M hydrochloric solution acid with 50 cm³ of the thiosulphate solution (at different concentrations as shown in the table below) and noting the time taken by the cross to disappear using a stopclock. The procedure similar to that used to investigate the effect of temperature above is used except that, in this particular experiment, the concentration of the thiosulphate is altered each time the experiment is repeated. The following table shows the results.

Concentration of thiosulphate (g/dm ³)	10	20	30	40	50
Time(s) for the cross to disappear	250	120	65	32	15

As the results show, a reaction goes faster when the concentration of the thiosulphate (reactant) is increased. According to the above data, the rate of the reaction approximately doubles as the concentration of the thiosulphate is increased is increased by 10g dm⁻³.

The results clearly indicate that, as the concentration of the reaction is *increased* the time for the disappearance of the cross decreases, which chemically means that the rate of the reaction *increases*.

The Effect of Temperature on the Rate of a Reaction

Demonstrate the effect of temperature on the rate of a reaction

Increasing the temperature of the system means increasing the kinetic energy and hence the speed at which the reacting particles of the substance move. Thus, the particles collide more often and combine to form new substances. Temperature also provides the energy required to break the bonds of a substance and hence enhances the decomposition or splitting of a complex substance into more simpler substances. Therefore, an increase in the temperature of the system will result to an increase in the rate of reaction.

The effect of temperature on the rate of reaction can be determined experimentally. When dilute hydrochloric acid is mixed with sodium thiosulphate solution, a fine yellow precipitate of sulphur forms.

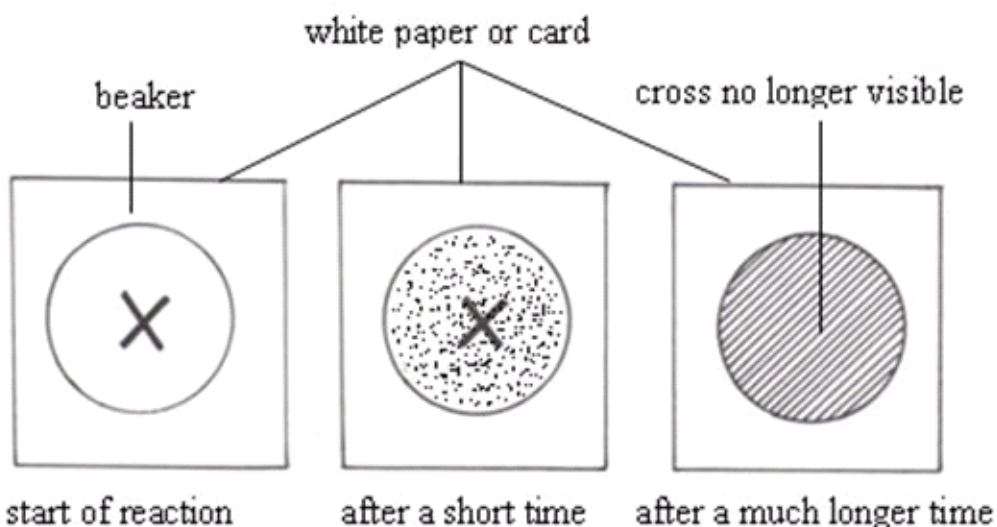


The solid sulphur (S_(s)) produced in this reaction makes the colourless solution go cloudy. The reaction is usually carried out in a flask placed on a piece of white paper, with a black cross marked on it. An experiment is designed such that each time a different temperature is used, while keeping the concentrations of the reactants constant.

At the beginning of the reaction, the cross can be seen easily. As the reaction goes on, more and more sulphur is deposited, the flask becomes more and more cloudy and the cross gradually gets harder to see. At last, the cross can no longer be seen. It is fully covered by the precipitate of sulphur. Time taken by the cross to disappear at a given temperature indicates the rate of reaction at that temperature. The quicker the disappearance of the cross, the faster is the reaction and vice versa.

The reaction rate can be determined by the following procedure:

- 50 cm³ of a solution of sodium thiosulphate (containing 40g per litre of the solution) is measured and put into a 100 cm³ beaker.
- A wire gauze is placed on a tripod stand, then the beaker is put on the gauze, and the solution is gently warmed with a Bunsen burner flame.
- A thick black cross is marked on a white piece of paper or cardboard.
- When the temperature reaches a little above 20°C, the beaker is taken quickly and placed on the cross.
- 10 cm³ of 2M hydrochloric acid solution is added quickly to the beaker and a clock is started at the same time. The temperature of the mixture is noted.
- When the cross is no longer visible, the clock is stopped.
- The experiment is repeated more times at temperatures of 30°C, 40°C, 50°C, 60°C, etc. Each time 10 cm³ of 2M hydrochloric acid and 50 cm³ of the thiosulphate solution are used.



Measuring the effect of temperature on the rate of reaction

The following table shows the specimen results obtained from such an experiment:

Temperature (°C)	20	30	40	50	60
Time (s) for cross to disappear	200	125	50	33	24

The results show that the higher the temperature the faster the cross disappears, which in turn, means that the rate of the reaction increases. Therefore, the data clearly indicate that a reaction goes faster when the temperature is raised. When the temperature is increased by 10°C, the rate approximately doubles.

The Effect of Surface Area of a Solid on the Rate of a Reaction

Show the effect of surface area of a solid on the rate of a reaction

In many reactions, one of the reactants is a solid. The reaction between hydrochloric acid and calcium carbonate (marble chips) is one example. Carbon dioxide gas is produced.



One of the ways by which the rate of such a reaction can be increased is by reducing the particle size of the solid substance (marble chips). If this substance is grinded to fine powder or to small pellets, the surface area of the marble is increased. Therefore, more of the marble is exposed to the acid for efficient reaction. This leads to increase in the rate of reaction. Increased rate of reaction results to increased production of carbon dioxide gas. Hence, the rate of reaction can be determined by measuring the time taken to produce a given volume of carbon dioxide by reacting equal masses of whole marble and crushed (or powdered) marble, and then comparing the two results. The data obtained is recorded in a table as shown below:

Time (s)		0	10	20	30	40	50	60	70	80	90	100
Volume (cm ³)	Whole marble	0	18	24	32	38	45	53	62	72	80	80
	Grinded marble	0	34	52	67	74	76	80	80	80	80	80

The data above shows that it takes 90 seconds for whole marble chips to react to completion while for powdered marble it takes only 60 seconds. Also there is seen a small increase in volume of carbon dioxide gas per unit of time in the case of ungrounded (whole) marble as compared to the powdered sample. This absolutely proves that an increase in the surface area of marble (a solid reactant) increases the rate of reaction and hence the rate of production of carbon dioxide gas.

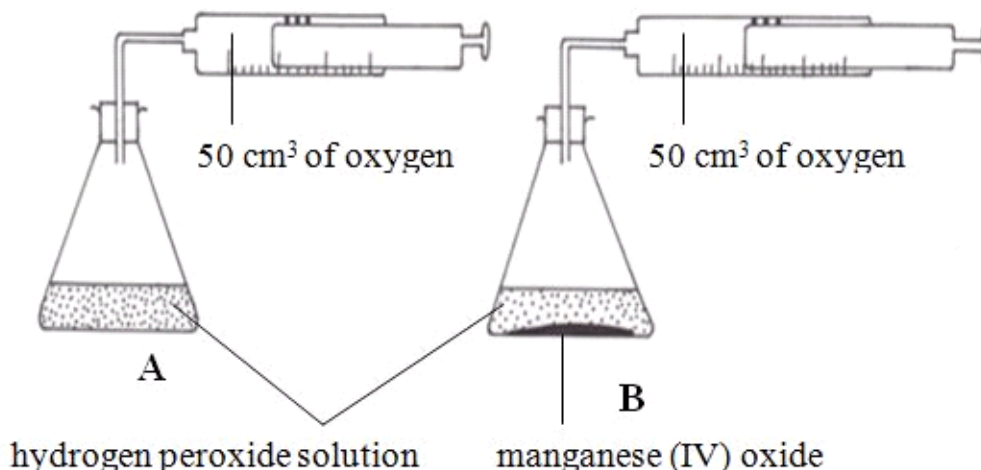
The Effect of Catalyst on the Rate of a Reaction

Demonstrate the effect of catalyst on the rate of a reaction

A catalyst usually increases the rate of a reaction and this is called positive catalysis. In general, a catalyst will function even if present in very small amounts. Hydrogen peroxide is a clear, colourless liquid. It can decompose to water and oxygen:



The rate of decomposition (reaction) of the peroxide can be increased tremendously by adding a very little of manganese (IV) oxide in the reaction vessel.



Investigating the effect of catalyst on rate of reaction

The reaction in flask A above is in fact very slow. It could take several days to produce just 50 cm³ of oxygen. In flask B only 1g of manganese (IV) oxide is added. The reaction goes very faster. 50 cm³ of oxygen is produced in a few minutes.

The manganese (IV) oxide speeds up the reaction without being used up itself. It is called a catalyst for the reaction. A catalyst is a substance that changes the rate of a chemical reaction but remains chemically unchanged at the end of the reaction.

Catalysts for many reactions have been discovered. They are usually transition metals or compounds of transition metals. There are also biological catalysts, called enzymes. For example, the pancreatic juice secreted by the pancreas contains enzymes that speed up digestion process. Examples of catalysts for some common reactions are given in the following table:

Reaction	Catalyst
Heating of potassium chlorate $2\text{KClO}_{3(s)} \rightarrow 2\text{KCl}_{(s)} + 3\text{O}_{2(g)}$	Manganese (IV) oxide (MnO_2)
Synthesis of sulphur trioxide $2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$	Vanadium (IV) oxide (V_2O_5)
• 1. Synthesis of ammonia	Reduced iron powder
• 2. Decomposition of hydrogen peroxide	Manganese (IV) oxide or platinum powder

Reversible and Irreversible Reactions

Comparison between Reversible and Irreversible Reactions

Compare reversible and irreversible reactions

Chemical reactions can be classified into two groups, that is, reversible and irreversible reactions.

Irreversible reactions are those reactions which go to completion. In such reactions, a known product is formed. The product(s) cannot be reversed back to the original reactant(s). Consider the reaction between sodium and chlorine to produce sodium chloride: $2\text{Na}_{(s)} + \text{Cl}_{2(g)} \rightarrow 2\text{NaCl}_{(s)}$

You cannot turn sodium chloride back to chlorine gas and pure sodium metal by ordinary means.

This is a typical irreversible reaction.

Several reactions are known to proceed in both directions, provided certain conditions are maintained. $\text{A} + \text{B} \rightleftharpoons \text{AB}$ Such reactions are said to be reversible. The sign \rightleftharpoons indicates reversibility.

The Concept of Reversible and Irreversible Reactions

Describe the concept of reversible and irreversible reactions

A reversible reaction is a chemical reaction in which the products can react to re-form the reactants. In such reactions, reactants combine to form products. However, under certain conditions, the products may be converted back to reactants. The idea of “reactants” and “products” in such circumstances is really confusing.

Example 1

Examples of reversible reactions

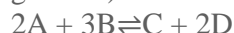
- When you heat blue crystals of copper (II) sulphate, they breakdown into anhydrous copper (II) sulphate, a white powder: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{CuSO}_{4(s)} + 5\text{H}_2\text{O}_{(g)}$ The reaction can be reversed by just adding water to the white powder, which quickly turns to blue crystals again. In fact, this is used as a test for water: $\text{CuSO}_{4(s)} + 5\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)}$
- When you heat ammonium chloride (a solid) in the bottom of a test tube, it breaks down into ammonia and hydrogen chloride (gases). The gases readily combine at the top of the tube where it is cool: $\text{NH}_4\text{Cl}_{(s)} \rightleftharpoons \text{NH}_{3(g)} + \text{HCl}_{(g)}$ This is a reversible reaction.

Equilibrium Reactions

Difference between Equilibrium Reactions and Simple Reversible Reactions

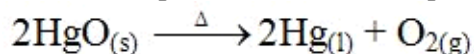
Differentiate equilibrium reactions from simple reversible reactions

Suppose that 2 molecules of substance A reacts with 3 molecules of substance B to produce 1 and 2 molecules of substances C and D respectively in a homogenous system (i.e. entirely liquid or entirely gaseous).

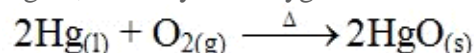


As soon as a little of C and D are formed, a reverse reaction will begin. At first the forward reaction will predominate, but, as C and D accumulate the reverse reaction will build up until an equilibrium position is reached, with forward and reverse reactions proceeding at the same rate. The composition of the mixture will then appear constant, though it is the net result of the two opposing reactions. Since chemical equilibrium involves the balancing of two reactions which are proceeding at the same time in opposite directions, it is said to be a **dynamic equilibrium**, that is, it is an equilibrium involving the constant interchange of particles in motion. Equilibrium is a dynamic condition in which two opposing changes can occur at equal rates in a closed system. In a closed system, matter cannot enter or leave, but energy can. Both matter and energy can escape or enter an open system. For example, sunlight, heat from a burner, or cooling by ice can cause energy to enter or leave a system.

An example of a real equilibrium reaction is the decomposition of mercury (II) oxide. Mercury (II) oxide decomposes when heated to produce mercury and oxygen gas.



Again, mercury and oxygen combine to form mercury (II) oxide when heated gently



Suppose mercury (II) oxide is heated in a closed system. Once the decomposition has begun, the mercury and oxygen released can re-combine to form mercury (II) oxide again. Thus, both reactions can proceed at the same time. Under these conditions, the rate of the composition (re-combination) reaction will eventually equal that of the decomposition reaction. Then the reaction is said to be at equilibrium. At equilibrium, mercury and oxygen will combine to form mercury (II) oxide at the same rate that mercury (II) oxide decomposes into mercury and oxygen. The amounts of mercury (II) oxide, mercury and oxygen can then be expected to remain constant as long as these conditions persist. At this point, a state of dynamic equilibrium has been reached between the two chemical reactions. Both reactions continue, but there is no net change in the composition of the system. *A reversible reaction is in chemical equilibrium when the rate of its forward reaction equals the rate of its reverse reaction, and the concentrations of its reactants and products remain unchanged.*

Two Equilibrium Reactions of Industrial Importance

Describe two equilibrium reactions of industrial importance

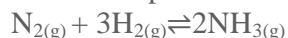
Conditions for the industrial synthesis of different substances have to be carefully chosen if the process is to be efficient and thus economically viable. The considerations are:

- Yield – how much yield is produced?
- Rate – how fast is it produced?
- Energy – how much energy is lost during the process?

The way in which this is achieved in practice is described briefly for three important industrial reactions, namely, the Haber Process for the manufacture of ammonia, the Contact Process for the manufacture of sulphuric acid and the thermal dissociation of calcium carbonate for the industrial manufacture of lime.

THE HABER PROCESS FOR THE INDUSTRIAL MANUFACTURE OF AMMONIA

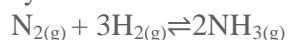
The Haber process involves the reaction between nitrogen and hydrogen to produce ammonia:



A German Chemist, Fritz Haber, was the first to show how this reaction could be controlled to make useful amounts of ammonia. The first industrial plant making ammonia by the Haber process opened in Germany in 1913. Now over 100 million tones of ammonia are produced each year by this process. Because of its importance, the Haber process for making ammonia has been studied over a wide range of conditions of temperature and pressure.

The effect of pressure

Ammonia is produced from its elements by reduction of volume. Therefore, if the system is in equilibrium and the pressure is raised, the equilibrium will shift to the right. This is because the system will shift to favour the side of the equation that has fewer molecules.



Therefore, high pressure will increase the yield of ammonia. Modern industrial plants use a pressure of 200-500 atmospheres. Pressure higher than this range could be used, but high-pressure reaction vessels are expensive to build.

The effect of temperature

The forward reaction producing ammonia is exothermic and the reverse reaction is therefore endothermic. Therefore, *lowering* the temperature will *favour* ammonia production. However, the rate at which the ammonia is produced will be so slow as to be uneconomical. So, it is necessary to include a catalyst which will give sufficient reaction rate in spite of a relatively low pressure. In practice, a compromise or optimum temperature is used to produce enough ammonia at an acceptable rate. Modern plants use temperatures of about 450°C.

The effect of concentration

If the system is in equilibrium and more nitrogen is then added to increase its concentration in the reaction mixture, the equilibrium shifts to the right so as to tend to reduce the concentration of nitrogen. That is, more ammonia will be produced to use up nitrogen. Also, if hydrogen is added the equilibrium will, similarly, shift to the right.

However, in practice, there is no particular advantage in using excess of either material (nitrogen or hydrogen) since the gases, nitrogen and hydrogen, are mixed in a ratio of 3:1 by volume. Hydrogen is manufactured from partial combustion of hydrocarbons, and nitrogen is obtained from the air. They are mixed in the ratio of 3:1 proportion by volume and dried (e.g. by silica gel). They are pre-heated by gases leaving the catalyst chamber over the catalyst at 450°C. The ammonia produced is absorbed in water or liquefied by refrigeration and the remaining nitrogen and hydrogen gases are recycled.

If the system was at equilibrium and then some of the ammonia was removed, more ammonia would be produced to replace that which is removed. The gas is removed from the reaction chamber when the percentage of ammonia in the equilibrium mixture is 15%.

Based on the above discussions, the overall conditions used for the maximum production of ammonia are as follows:

- N_2 and H_2 are mixed in the ration of 3:1
- An optimum temperature of 450°C is chosen.
- A very high pressure (200-500 atm) is applied.
- A catalyst of finely divided reduced iron, usually promoted by alumina (aluminium oxide) is used.
- The ammonia is condensed and removed out of the reaction mixture and the remaining N_2 and H_2 recycled.

THE CONTACT PROCESS FOR THE INDUSTRIAL MANUFACTURE OF SULPHURIC ACID

The first step in the production of sulphuric acid is the conversion of sulphur dioxide to sulphur trioxide. The process involves the reaction between sulphur dioxide and oxygen. The reaction is exothermic and reversible. $2\text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{SO}_{3(\text{g})}$

To make sulphuric acid, the sulphur trioxide gas produced is dissolved in 98% concentrated sulphuric acid, forming “oleum” which is then diluted with the correct amount of water to give ordinary concentrated sulphuric acid.

- **The effect of pressure:** There are fewer gas molecules on the right of the equation. Therefore, *increasing* the pressure would *favour* the production of sulphur trioxide. In fact, the process is run at atmospheric pressure because the conversion of sulphur dioxide to sulphur trioxide is about 96% complete under these conditions. In practice, it is found that use of high pressure produces a very small gain in yield and involves extra cost. It is for this reason that ordinary atmospheric pressure is used.
- **The effect of temperature:** The reaction to produce sulphur trioxide is exothermic so, if the temperature is lowered the equilibrium shifts to the right. Hence, more sulphur trioxide will be produced. This means that sulphur trioxide production would be favoured by low temperatures. However, too low temperatures reduce the rate of reaction so increasing the time required for the production of the sulphur trioxide. This would mean an increase in production cost. For this reason, a catalyst must be introduced. A catalyst of vanadium (V) oxide is used to increase the rate of reaction. An optimum temperature of about 450°C is used. This gives sufficient sulphur trioxide at an economic rate. In general, low temperatures give an equilibrium favourable to an exothermic reaction, but catalysis is needed to give a favourable reaction rate.
- **Effect of concentration of reactants:** Suppose that in the contact process reaction, an equilibrium has been reached in certain conditions and oxygen is added to the system. According to Le Chatelier's principle, the reaction would shift to the right so as to oppose this change, that is, to reduce the concentration of the oxygen added towards its former level. This can only be achieved by combining it with sulphur dioxide to form sulphur trioxide. So, increased concentration of oxygen favours conversion of more sulphur dioxide to trioxide. Likewise, a similar case can occur when sulphur dioxide is added to the system. In a similar manner, increased concentration of sulphur trioxide would favour the conversion of oxygen to sulphur trioxide and hence increased formation of the trioxide. In general, the conditions used in the contact process are as follows: An optimum temperature of about 450°C is chosen; A catalyst, vanadium (V) oxide, is used to speed up the reaction; An operating pressure of 1 atmosphere is applied. A higher pressure, which would theoretically increase the yield of SO_3 , is not used as it is uneconomical; Yield of SO_3 would be increased by increasing either SO_2 or O_2 . The cheaper reactant is O_2 .

Endothermic and Exothermic Reaction

The Concept of Endothermic and Exothermic Reactions

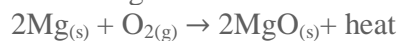
Explain the concept of endothermic and exothermic reactions

You have met many different chemical reactions so far in chemistry. But they all have one thing in common, that is, they involve an energy change. The great majority of chemical reactions are accompanied by a marked heat change.

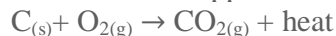
During chemical reactions as reactants form products, there is a change in heat content. This is referred to as the enthalpy change and is always expressed in kilojoules per mole (kJ mol^{-1}). Two types of heat change are distinguished. Those reactions that are accompanied by evolution of heat to the surroundings are termed as *exothermic* reactions while those that are accompanied by absorption of heat from the surroundings are *endothermic* reactions.

- An exothermic reaction is one during which heat is liberated to the surroundings.
- An endothermic reaction is one during which heat is absorbed from the surroundings

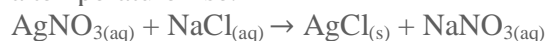
When magnesium is burnt in air heat is evolved.



The same case applies to the burning of coal in air.



Mixing sulphur nitrate and sodium chloride solutions gives a white precipitate of silver chloride and a temperature rise.



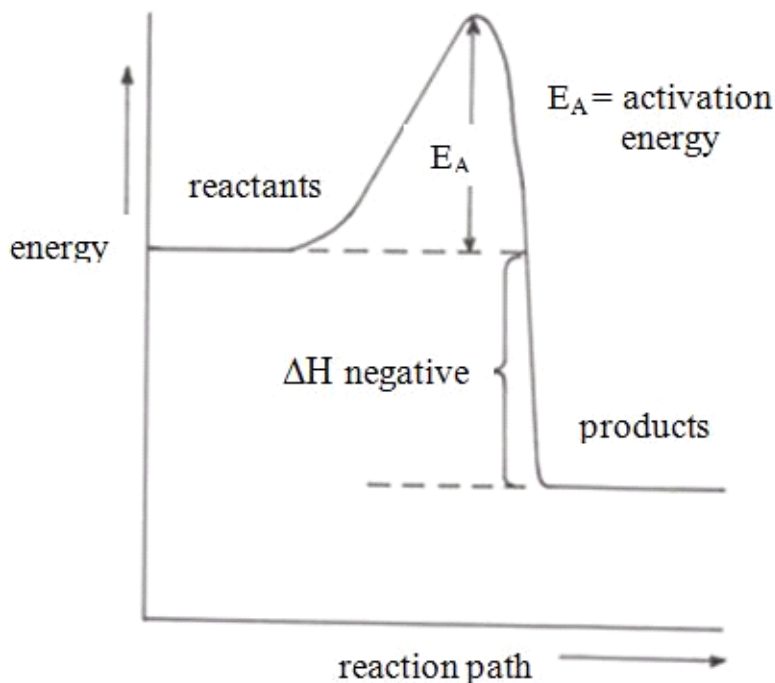
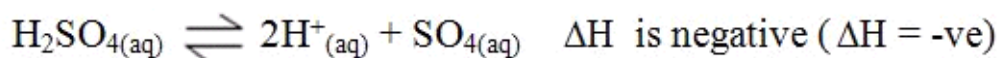
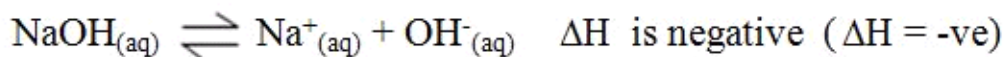
When ammonium nitrate is dissolved in water, there is a fall in temperature. Also adding a mixture of citric acid and sodium bicarbonate to water produces bubbles and a fall in temperature. In both reactions, the temperature of the water falls because the reactions take heat energy from it. These reactions are therefore **endothermic**.

The heat changes that occur during any chemical reaction represent changes in the energy content of the whole system. The energy content may increase or decrease depending upon whether heat is absorbed or evolved.

Energy Level Diagrams for Exothermic and Endothermic Reactions

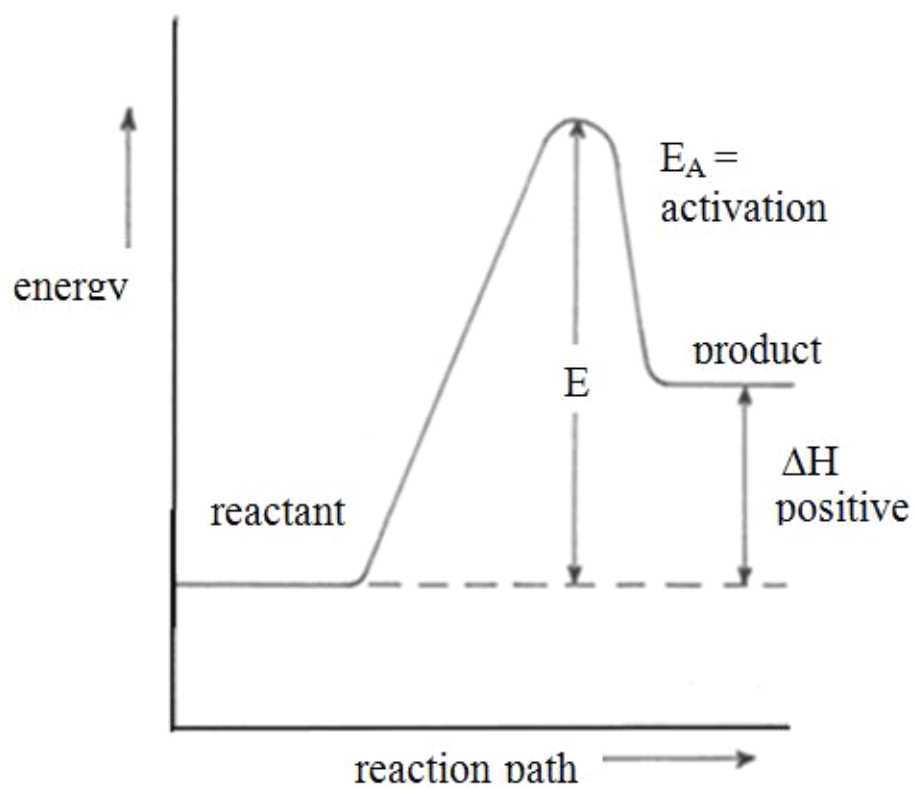
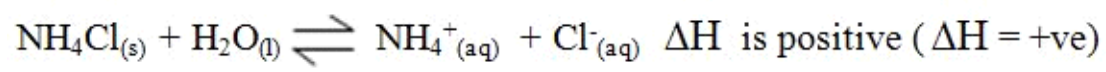
Draw energy level diagrams for exothermic and endothermic reactions

For *exothermic reactions*, the enthalpy change is conventionally assigned a negative value. For example, when pellets of sodium hydroxide or concentrated sulphuric acid dissolve in water, heat is evolved and the system loses heat to the surrounding.



Energy level diagram for exothermic reaction

For *endothermic reactions*, the enthalpy change is assigned a positive value. For example, when potassium iodide or ammonium chloride dissolves in water, heat is absorbed from the surroundings.



TOPIC 8: EXTRACTIONS OF METALS

Occurrence and Location of Metals in Tanzania

Locations of Important Metal Ores in Tanzania

Identify locations of important metal ores in Tanzania

Most metals are found naturally as compounds called **minerals**. Rocks are made up of crystals of metals. An ore is a rock that contains enough of a metal compounds for it to be worth extracting the metal. The most common ores contain oxides. An example is the ore haematite, which contains iron (III) oxide. Some contain other metal compounds. Malachite contains copper (II) carbonate.

Tanzania is blessed with an assortment of minerals. The mineral found in Tanzania include gold, which is found in Geita (Mwanza), Kahama (Shinyanga), Nyamongo, Buhemba and Majimoto (Mara), and Nzega (Tabora). Large deposits of iron occur at Liganga in Ludewa (Iringa). Copper is found in Mpanda (Rukwa). We also have sodium which occurs in the form of sodium chloride, at Uvinza (Kigoma), in the form of soda ash (Na_2CO_3) in lake Natron, as a rock salt in Kilwa and as a dissolved salt (NaCl) in sea water.

The Abundances of Metals in the Earth's Crust

Compare the abundances of metals in the earth's crust

Metals occur in the sea and in the earth. The form in which they occur depends on their reactivity.

The most reactive metals are extracted from the sea. Calcium is extracted from limestone, chalk and marble in the sea. Metals of medium reactivity are found in the earth in form of oxides and sulphides. Examples of these metals include aluminium, zinc, iron and tin. Least reactive metals such as silver and gold occur as free uncombined elements.

We obtain most of the metals we use from the earth's crust. The majority of metals are too reactive to exist as natural elements. They are found as compounds in ores. The chief ores in order of their economic importance are oxides, sulphides, chlorides and carbonates.

The most common metal is aluminium, which makes about 7.8% of the earth's crust, followed by iron, which accounts to approximately 4.5%. Others include calcium (3.5%), sodium (2.5%), potassium (2.5%) and magnesium (2.8%). The remaining metals make about 3% of the earth's crust.

Chemical Properties of Metals

The Difference between Physical and Chemical Strengths of Metals

Differentiate the physical and chemical strengths of metals

Metals are known to have a greater tendency to lose **electrons** in the course of which they go into solution as **ions**. A metal, therefore, may be defined as an *element which can ionize by electron loss*. The number of electrons lost per atom is the valency of the metal and the ion carries an equal number of positive charges, as:

- $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$ (univalent)
- $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$ (divalent)

- $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$ (trivalent)

The following are important chemical properties of metals:

- They react with oxygen to form oxides. For example, magnesium burns in air to form magnesium oxide. Metal oxides are bases, which mean they react with water to form an alkaline solution and with acids to form salts.
- Metals form positive ions when they ionize. Consider the ionization of sodium, magnesium and aluminium in the above equations in which case ionization resulted into Na^+ , Mg^{2+} , and Al^{3+} ions respectively. However, there are some exceptions. For example, *hydrogen* is a non-metal which forms positive ions in solution, H^+ . This is the only exception in this case.

Physical strength is different from chemical strength. Physical strength is tensile strength of the metal. There are metals with high tensile strengths like iron, copper and aluminium. Other metals like sodium and potassium have low tensile strengths. Chemical strength is the reactivity of the metal. Sodium and potassium have very low tensile strengths but they are the strongest metals chemically. Sodium and potassium are very weak physically. Sodium is very soft metal and can be cut easily with a knife. It melts at 98°C . It is so light that it floats on water, but it reacts immediately with the water forming an alkaline solution. When freshly cut, it has a silvery lustre but rapidly furnishes due to its reaction with atmospheric carbon dioxide and moisture.

Potassium is a white metal with lustre. It melts at 63°C . Like sodium, potassium is a very light metal and it can also float on water, with which it reacts to form an alkaline solution.

However, sodium and potassium are among the strongest metals chemically. These metals are very reactive and they are always found combined with other elements. The metals are so reactive that they will combine with any non-metal nearby. They never occur free in nature. Both sodium and potassium are so reactive that they have to be stored under oil to prevent them coming into contact with water or air. The compounds of sodium and potassium are quite abundant in nature.

The reactivity and tensile strengths of some metals

- *Calcium:* Calcium is amongst a group of metals that are too reactive to occur in the free state. It occurs mainly as carbonate, sulphate, fluoride and silicate. It is a soft, greyish metal. In comparison with potassium and sodium, it has a lower tensile strength and high density.
- *Iron:* Iron is a typical metal. Its density is 7.87. It melts at 1530°C . Iron is a moderately reactive metal. The metal reacts with excess steam at red heat to produce triiron tetraoxide.
- *Copper* Copper is a less reactive metal. It is a red-brown metal with a lustre. It can be polished. Its tensile strength is fairly high. When heated in air, copper forms a layer of black copper (II) oxide on the surface: $2\text{Cu}_{(\text{s})} + \text{O}_{2(\text{g})} \rightarrow 2\text{CuO}_{(\text{s})}$. It reacts with hot concentrated sulphuric acid to form copper (II) sulphate and liberate sulphur dioxide. $\text{Cu}_{(\text{s})} + 2\text{H}_2\text{SO}_{4(\text{aq})} \rightarrow \text{CuSO}_{4(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} + \text{SO}_{2(\text{g})}$

The table below compares the tensile strengths of calcium, iron and copper metals.

Tensile strengths, densities and melting points of calcium, iron and copper

	Calcium	Copper	Iron
Tensile strength	Low	Fairly high	High
Melting point ($^\circ\text{C}$)	850	1080	1535
Density (g cm^{-3})	1.55	8.95	7.9

The Reducing Power of Different Metals

Compare the reducing Power of different metals

As we learned early, metals tend to lose electrons during chemical reactions. This process of losing electrons is called *oxidation*. Metals normally lose electrons to non-metals, which accept those electrons. Therefore, metals are said to be electron donors while non-metals are electron acceptors. In

this case, metals can be termed as *reducing agents*, because they donate electrons which, when accepted by non-metals, tend to lower their oxidation numbers. Non-metals are called *oxidizing agents*, because they oxidize or increase the oxidation number of metallic atoms through accepting the electrons donated by metals.

Metals differ in the ease of losing the electrons, depending on their electronic configurations. This is because; it is only the outer electron(s), which take part in a chemical reaction. The nucleus of an atom, being positively charged, normally attracts the electrons towards itself, hence making the electrons difficult to remove from their shells. The further the electrons are from the central nucleus, the easier it is removing them from their shells and vice versa. Therefore, atoms with larger atomic radii donate their electrons more easily than those with small atomic radii.

For example, compare the electronic configuration of sodium (2:8:1) with that of potassium (2:8:8:1). Sodium ionizes by losing one electron from its outer shell to attain the structure of the nearest noble gas (2:8). Likewise, potassium ionizes by losing one electron from its outer shell to attain the noble gas structure, 2:8:8. But, in which of the two cases is it easy to remove electron and why? It is easy to remove the electron from the outer shell of potassium than sodium because the atomic radius of potassium is too large as compared to that of sodium. This is because in potassium the outer electron is more loosely held by the central nucleus and hence easy to remove from its shell. This is true because the ability of the nucleus to hold the electrons firmly depends on the distance of the electrons from the nucleus.

Metals that release the electrons more readily are said to be strong reducing agents compared to those that release their electrons least readily. For example, potassium with an electronic configuration of 2:8:8:1 is a stronger reducing agent than sodium, which has an electronic configuration of 2:8:1. Therefore, it is clear that when atoms of elements lose electrons from their outermost shells, they obtain **octet** or **doublet** structures and hence become chemically stable. It is not easy to remove electron(s), by ordinary chemical means from such stable noble gas structures.

From the context of the above explanations, the reducing power of a metal can be defined as its readiness to release electrons from its outer shell. Metals whose atoms release electrons more readily have high reducing powers than those metals whose atoms do not readily release their electrons.

Reactivity series of metals

Reactivity series refers to arranging or listing the metals in order of reactivity. The reactivity series are obtained by consideration of the action of *air*, *water* and *acids* on the metals, and how easily the oxides of these metals can be reduced. Consider the table of reactivity series below (Table 8.2).

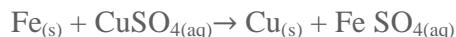
Oxides of the first group of five metals cannot be reduced by carbon. Those of the second group of three metals can react with acids, displacing hydrogen. The third and last group comprises of least reactive metals. In table 8.2, the metals are arranged in order of reactivity series. It indicates the inverse order in which the elements were isolated. Thus, metals low in the series such as gold, silver and lead have been known since early times. Metals high in the series proved very difficult to isolate. It was Davy's work on electrolysis that led to isolation of potassium, sodium, calcium, magnesium and aluminium over a period of years from 1807, when Davy isolated potassium and sodium, to about 1850, when aluminium was isolated.

K	}	Very reactive. Never found as free elements. Extracted by electrolysis.
Na		
Ca		
Mg		
Al		
Zn	}	Moderately reactive. Found as oxides, carbonates, or sulphides. Extracted by reaction with carbon or carbon monoxide
Fe		
Pb		
(Hydrogen)		
Cu	}	Not very reactive. May be found in nature as free elements. Known for a very long time.
Hg		
Ag		
Au		

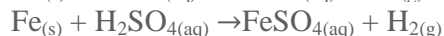
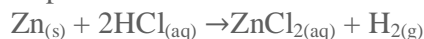
The reactivity series of metals

Metals low down in the series are frequently found as the free elements, although they may also be obtained from ores because the amounts found as the free metal are not sufficient for industrial purposes. Gold, however, the last element of the series is found and mined almost entirely as the free element.

Generally, it is these relatively uncreative metals that we find the most uses for. Iron and copper, for example, can be found in many household and everyday objects. Metals higher up in the series are more reactive than those lower down. A metal higher up in the series will displace a metal lower down from a solution of one of its salts. For example, iron will displace copper from its salt.



Zinc and iron will displace hydrogen from dilute acids such as dilute hydrochloric acid or dilute sulphuric acid.



Copper has no reaction on either dilute sulphuric acid or dilute hydrochloric acid. With hot concentrated sulphuric acid, sulphur dioxide is liberated and copper (II) sulphate is formed.



Useful things to remember about the reactivity series

- The more reactive the metal, the more compounds it forms. So only copper, silver and gold are ever found as free elements in the earth's crust. The other metals are always found as compounds.
- When a metal reacts, it gives up electrons to form ions. The more reactive the metal, the more easily it gives up electrons.

- The more reactive the metal, the more **stable** its compounds are. Stable means difficult to breakdown. For example, when you heat sodium nitrate you get sodium nitrite: $2\text{NaNO}_{3(s)} \rightarrow 2\text{NaNO}_{2(s)} + \text{O}_{2(g)}$ But copper (II) nitrate breaks down further, to oxide, giving off nitrogen dioxide: $2\text{Cu}(\text{NO}_3)_{2(s)} \rightarrow 2\text{CuO}_{(s)} + 4\text{NO}_{2(g)} + \text{O}_{2(g)}$
- The more reactive the metal, the more difficult it is to **extract** from its compounds (since the compounds are stable). For the most reactive metals, you will need the toughest method of extraction: **electrolysis**.
- The less reactive metals have been known and used since ancient times, because they are easiest to extract. 6. If you stand two metals in an electrolyte and join them up with a copper wire, electrons will flow from the more reactive metal to the less reactive one.

Extraction of Metals by Electrolytic Reduction

The Criteria for the Choice of the Best Methods of Extracting a Metal from its Ore

Outline the criteria for the choice of the best methods of extracting a metal from its ore

Most metals are naturally found in compounds called ores. The metals are obtained from the ores by a process called **extraction**. The extraction consists of separating the metal from minerals in the ore

A few metals are found “native”. This means that they are uncombined with other elements, for example, silver and gold. To extract ores containing minerals, a chemical reaction must be used to separate the metal from other elements. The choice of the best method for extraction of a metal from its ore depends on the chemical reactivity of the metal to be extracted. Most ores contain metal oxides. To extract the metal, oxygen must be removed from it. This reaction is called **reduction**.

Because the metal is always the most electropositive part of an ore, and so has a positive oxidation state, the formation of the free metal from its ore is always a reduction.



Very reactive metals like sodium and potassium are strongly bonded in their ores. The more reactive the metal is the more stable its compounds are, and the more energy is needed to break down the bond between the metal and oxygen. Therefore, the extraction of these metals requires a strong method of reduction: *electrolysis* (or electrolytic reduction).

Hence, metals at the top of the reactivity series are obtained from their ores by electrolysis (electrolytic reduction). Electrolysis is a more expensive process than reduction with carbon or carbon monoxide. However, it is the only economic way to obtain metals such as aluminium. For less reactive metals at the middle of the reactivity series, the oxygen can be removed by chemical reduction with carbon or carbon monoxide. This method is used for extraction of metals such as zinc, iron and copper as shown and discussed in table 8.3. Least reactive metals such as copper, silver and gold may be found in uncombined state.

Methods of extraction of different metals from their ores

Metal	Method of extraction from ore
Potassium	Electrolysis
Sodium	
Calcium	
Magnesium	
Aluminium	
Zinc	Chemical reduction with carbon or carbon monoxide
Iron	

Lead	
Copper	Roasting in air
Silver	
Gold	Occur naturally as elements

Stages of the extraction of moderately reactive metals

There are four main stages for the extraction of moderately reactive metals:

- Mining and concentration of the ore
- Roasting in air
- Reduction of oxides to metals
- Purifying the metal

Mining and concentration of the ore

Mining is just the first step. The ore must then be decomposed to give the metal. This is called *extraction*. The unwanted rock material in the ore is called **gangue**. The ore is treated to remove as much gangue as possible. For example:

- It is crushed and washed. In this case, the ore is broken down into small pieces, which are then grinded down to fine powder. Then it is either dropped into water, where the fragments containing the metal sink faster or jets of air are blown at it, where the lighter waste material is carried to one side.
- A method called **froth flotation** is used with sulphide ores (e.g. CuS or ZnS). The ore is powdered, fed into water tanks and made into slurry with water. Then “frothing” chemicals (a suitable oil) are added. Sulphides are attracted to these chemicals. When air is blown through the slurry, froth rises to the top of the tank carrying the metal sulphides with it. They are skimmed off and dried. The gangue sinks.
- Magnetic separation can be used. The iron ore can be separated from other material in the crushed ore by using electromagnet.

Roasting in air

For the ores that occur as sulphides or carbonates of the metal, the concentrated ore is heated (roasted) in air to convert the ore into an oxide, for example:

- $2\text{PbS}_{(s)} + 3\text{O}_{2(g)} \rightarrow 2\text{PbO}_{(s)} + 2\text{SO}_{2(g)}$
- $2\text{ZnS}_{(s)} + 3\text{O}_{2(g)} \rightarrow 2\text{ZnO}_{(s)} + 2\text{SO}_{2(g)}$
- $\text{ZnCO}_{3(s)} \rightarrow \text{ZnO}_{(s)} + \text{CO}_{2(g)}$

It is usual to convert sulphides and carbonates into oxides before reduction because oxides are more easily and efficiently reduced than sulphides. The oxides resulting from roasting (heating) the sulphides or carbonates in air are then reduced chemically with carbon or carbon monoxide. Most copper is extracted from copper pyrites, CuFeS_2 . The ore is roasted in a limited supply of air to produce to produce copper (I) sulphide:

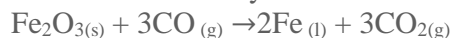


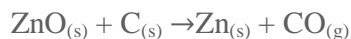
The copper (I) sulphide is then reduced to copper by heating in air: $\text{Cu}_2\text{S}_{(s)} + \text{O}_{2(g)} \rightarrow 2\text{Cu}_{(s)} + \text{SO}_{2(g)}$

The copper produced by this method is never pure. It must be refined (purified) by electrolysis if it has to be used for electrical wiring.

Reduction of oxides to metals

This is another important stage in the extraction of metal. Here, the roasted ore must now be reduced to respective metals. Reduction occurs at a very high temperature. The materials employed for reduction are mainly carbon or carbon monoxide. Thus;





Purification (Refining)

Very often, the product of the reduction process is never pure. The product has to be purified first before being put into use. Purification is normally done through a number of ways, which include:

- **Electrolysis:** Electrolysis is used to produce a pure metal directly from its molten compounds. Examples of metals which are purified by electrolysis are copper and zinc. Copper produced in large scale is purified by electrolysis, a process often called *copper refining*.
- **Oxidation:** The molten crude metal is exposed to hot air in a furnace. The impurities in the crude metal are oxidized with oxygen from the air. They escape as vapour or form a scum over the molten metal, which is then removed by skimming. However, this method is used only when the impurities have a greater affinity for oxygen than the metal. The method is applied in the manufacture of steel from pig iron and in the purification of tin and lead.
- **Distillation:** In distillation, the crude metal is heated in a furnace until the pure metal evaporates, leaving behind the impurities. The vapour is then collected and condensed in a separate chamber. This method forms an integral part in the extraction of zinc, cadmium and mercury. A further distillation, usually in vacuum, gives a very pure product.
- **Formation of carbonyls:** very pure nickel and iron are made by forming their volatile carbonyls, which are then decomposed by heating.
- **Zone refining:** This recently developed method is used to produce silicon and germanium of extreme purity. In this method, a small high-frequency induction furnace is placed round one end of a long rod of the metal and a thin cross-section of the metal is melted. The furnace is then moved slowly along the rod. Pure crystals of the metal separate from the melting metal but impurities remain in the liquid and are carried along to the other end.

The Extraction of Sodium from its Ore

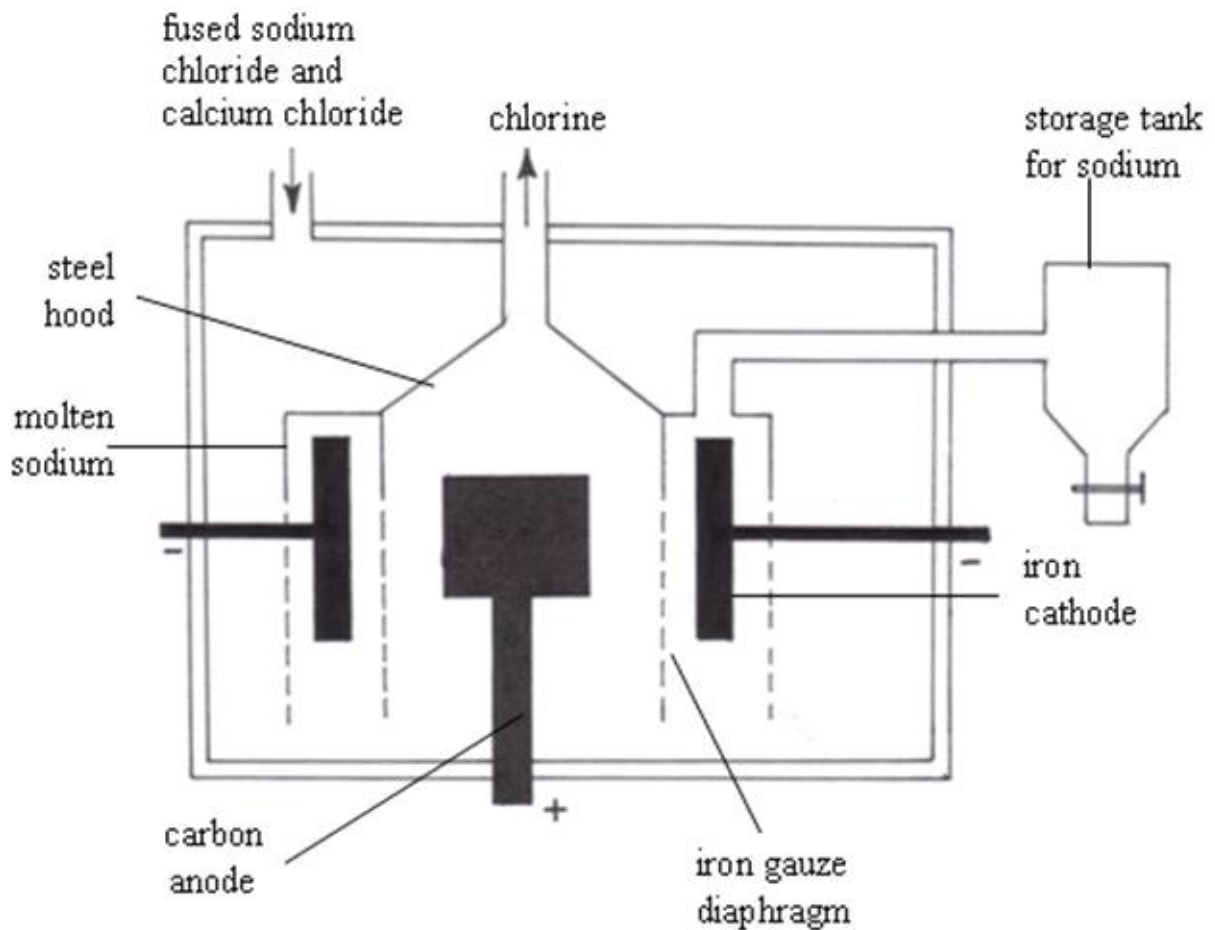
Explain the extraction of sodium from its ore

Alkali metals are strong reducing agents and cannot be extracted by chemical reduction of their oxides or other compounds. The only possible method of their extraction is by electrolysis of their fused chlorides. Sodium is extracted industrially by electrolysis of either fused sodium hydroxide (Castner's process) or fused sodium chloride (Down's process), in which sodium chloride is electrolysed in the molten condition.

Electrolysis of sodium chloride by the down's process

In this case, fused sodium chloride is used. And because the melting point of sodium chloride is high (about 800°C), calcium chloride is added to lower the melting point to about 600°C and thus economize on electrical power. The composition of the electrolyte is 40% sodium chloride and 60% calcium chloride. The Down's cell (figure 8.1) used for the extraction of sodium consists of an iron box through the bottom of which rises a circular carbon anode. A ring-shaped iron cathode surrounds this carbon anode. The cathode is enclosed in iron gauze diaphragm, which also separates the two electrodes. At 600°C, the sodium and chlorine produced would react violently if allowed to come in contact. A diaphragm around the anode, which keeps the two products apart, prevents this. During electrolysis, chlorine is liberated at the anode and escapes via the hood. Sodium is liberated at the cathode, collects in the inverted trough placed over the cathode, rises up the pipe, and overflows into the storage tank, from which it is tapped off through the iron vessel.

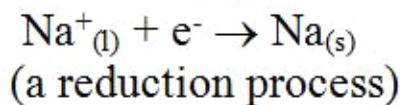
The sodium metal is collected upwards in the Down's cell because of its low density which makes it float over the mixture. The sodium metal from Down's cell contains some calcium, which is also formed through electrolysis. The calcium crystallizes when the mixture cools and a relatively pure sodium metal is obtained.



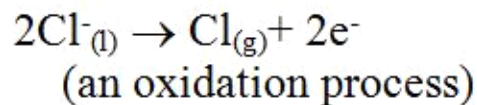
The Down's cell

Fused sodium chloride produces Na^+ and Cl^- ions, where Na^+ moves to the cathode and Cl^- moves to the anode. The reactions taking place at the electrodes are as follows:

At the cathode



At the anode



Chlorine gas is therefore formed at the anode while sodium metal is produced at the cathode.



Chlorine is a valuable by-product of the decomposition process

Extraction of Metals by Chemical Reduction

The Extraction of Iron from its Ore

Describe the extraction of iron from its ore

Iron is only second to aluminium as the most abundant metal in the earth's crust. Its chief ores are haematite, an impure iron (III) oxide, Fe_2O_3 , which contains about 70% of iron; magnetite (or magnetic iron ore), triiron tetraoxide, Fe_3O_4 , which contains 72.4% of iron; and spathic iron ore, iron (II) carbonate, FeCO_3 . It also occurs as limonite, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and as the sulphide in iron pyrites,

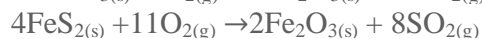
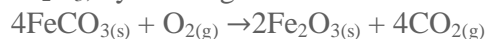
FeS₂. However, though abundant in the earth's crust, iron pyrite is not used as a source of iron. It is mainly used in the production of sulphuric acid.

To extract iron, three substances are needed:

- **Iron ore:** The chief ore is haematite. It is mainly iron (III) oxide, Fe₂O₃ mixed with sand.
- **Limestone:** This is mainly calcium carbonate, CaCO₃.
- **Coke:** This is made from coal and is almost pure carbon.

The extraction of iron in a blast furnace

Before being introduced into the blast furnace, all forms of iron ore must be converted to the oxide, Fe₂O₃, by roasting in air.



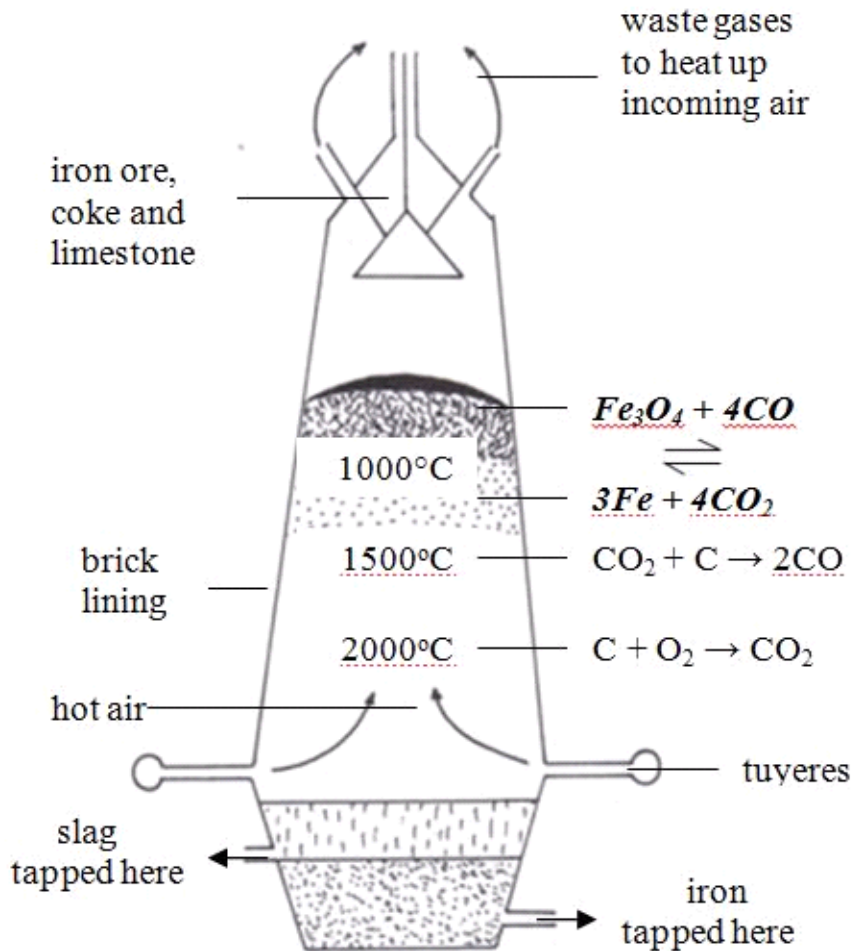
Iron ore, coke and limestone are mixed together to give a mixture called **charge**. The charge is introduced into a tall tower called a **blast furnace** (figure 8.2). At the bottom of the furnace, hot air is blasted in through several pipes known as tuyeres. A well at the bottom of the furnace serves to hold the molten iron and slag until these can be run off. The charge is fed in continuously from the top.

Reactions that occur in the furnace

- At the *bottom* of the furnace where temperature is the highest, air attacks the coke to produce carbon dioxide. $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
- In the *middle* of the furnace, the rising up carbon dioxide gas is reduced by more coke, producing carbon monoxide. $\text{C}_{(s)} + \text{CO}_{2(g)} \rightarrow 2\text{CO}_{(g)}$
- At the *top* of the furnace, carbon monoxide reduces iron (III) oxide to metal. $\text{Fe}_2\text{O}_{3(s)} + 3\text{CO}_{(g)} \rightarrow 2\text{Fe}_{(s)} + 3\text{CO}_{2(g)}$

The molten iron trickles down the furnace and gathers at the bottom. Periodically, this molten iron is tapped off and run into moulds (or containers), where it is allowed to cool in long bars of about 1 metre long and 10 cm in diameter. At this stage, it is called 'cast iron' or 'pig iron'.

The *hot waste gases*, mainly *nitrogen* and *oxides of carbon*, escape from the top of the furnace and are used to heat incoming air. This helps to reduce the energy costs of the process.



The Blast furnace

Action of limestone

The limestone, which is introduced together with the ore, is first decomposed at this high temperature to form calcium oxide. $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

The main impurity in iron ore is sand, made of silicon dioxide (SiO_2). This reacts with calcium oxide to form calcium silicate. $CaO_{(s)} + SiO_{2(s)} \rightarrow CaSiO_{3(l)}$

The calcium silicate, which is in liquid state, falls to the bottom of the furnace. This liquid, called **slag** (because it is less dense than the molten iron) is tapped off separately. Slag is a useful by-product. It is used for making roads, production of cement, and as a fertilizer.

Environmental Consideration

Environmental Destruction caused by Extraction of Metals

Identify environmental destruction caused by extraction of metals

Mining and mineral extraction is important for economic development and general human welfare.

Without mining, we would have no cars, computers, handsets, washing machines or other equipment that we use to simplify our work and hence improve the quality of our lives. However, mining can cause many environment problems. The following are some of the environmental problems caused by mining:

- **Land subsidence (sagging):** Holes created due to underground mining cause land to sink (or subside). This is because the holes underneath the ground cause imbalance in weight of the soil above the ground. This may result to severe damage to buildings and other infrastructures such as roads, railway trucks and so forth.
- **Poisonous substances:** Poisonous compounds (for example of lead, cadmium and arsenic) are found in many ores. These may be washed into the soil and streams because of the mining process. If they happen to reach the water, they can kill fish and plant life, and can end up in your food as well. Gold extraction process makes use of mercury. If untreated effluent from the gold mine is directed to nearby rivers or streams, the metals may end up in fish, which might be someone's food. Consumption of such fish can result to brain damage due to mercury contained in it.
- **Large volume of waste:** Large-scale mining operations inevitably produce a great deal of waste. This waste not only comprises of earth from the soil and gangue but also includes the toxic chemicals added to the ore to aid metal extraction. The waste material gets washed into streams and rivers. The *sediment* that builds up blocks rivers and alters their routes. This serves as a source of pollutants to natural water systems.
- **Noise and dust:** Mining activities produce a lot of noise and dust. Noise and dust can be caused by haulage trucks, rock blasting and crushing, drilling operations and heavy traffic. Everything for miles around the mine may get covered with dust.
- **Big holes in the ground:** Mineral extraction leads to boring of deep holes through the ground in the course of searching for rich ores. Huge amounts of rock are dug up to get a small amount of ore. For example, 1000 tonnes of rock may produce just 5 tonnes of copper. This leaves huge scars on the landscape (if it is opencast method) or huge holes underground (if it is underground mining).
- **Great heaps of earth material:** unwanted rock material, after the metal has been extracted from the ore, gets heaped up in tips. These are unsightly. They can be unstable and therefore dangerous. During heavy rains, a landslide is likely to occur, a catastrophe that often results to loss of life and destruction of property.
- **Soil erosion:** Before mining operation is carried out, the natural vegetation on or around the mining site is usually cleared up in order to give enough room to mining activities. The consequent removal of vegetation cover leaves the soil bare and, therefore, susceptible to erosion.
- **Air pollution:** Large-scale mineral extraction results to production of gases such as sulphur dioxide, carbon dioxide and other bad gases which are emitted to the atmosphere. These gases may bring about a green house effects and even cause acid rains.

Intervention Measures to Rectify Environmental Destruction

Suggest intervention measures to rectify environmental destruction

Different measures are taken to check the environmental degradation (problems) caused by mining activities. The following are some remedy measures taken to prevent such environmental destructions:

- Governments are getting ever tougher with mining companies about damage to the environment. Sadly, in developing countries like Tanzania where much mining takes place, laws may be less strict.
- Stern controls apply to the production of wastes that may be toxic or may cause environmental damage. Safety regulations and practices must be maintained to avoid the risk of accidental release of harmful materials.
- Mine reclamation activities are undertaken gradually with the levelling of the heaps of earth material, replacement of the top soil with a fertile one and planting of trees in the mined out areas.

Care must be taken to relocate streams, wildlife and other valuable resources. Quarries and opencast workings can be reclaimed by the process of filling the holes with solid wastes. The eroded bare soil can be conserved by planting trees and grasses to serve as a soil cover, which would counteract the impacts of wind, running water, rain and animals to the soil. Reclaimed land can have many uses such as agriculture, forestry, wildlife, habitation and recreation.

- Dust levels can be controlled by spraying water on roads, stockpiles and conveyors. Other steps can also be taken including filling of drills with dust collection systems, and purchasing additional land surrounding the mine to act as a buffer zone. Trees planted in these buffer zones can also minimize the visual impact of dust, from the mining operations, to local communities.
- Noise can be controlled through careful selection of equipment and insulation, and enclosures around machinery.
- The poisonous and toxic substances used in metal extraction must be treated properly before being directed into rivers and streams. Alternatively, these materials may be drained into reservoirs where they can gradually percolate deep into the soil and evaporate into the air without causing much harm to the surrounding ecosystems. In some mines, absorbent carpets are spread on the surface of the ground to trap the toxic substances contained in liquid chemicals used for mining, hence preventing these chemicals from finding their way to water bodies.