

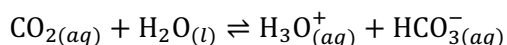
Module 6 Section 1: Properties of Acids and Bases

- Explore the changes in definitions and models of an acid and a base over time to explain the limitations of each model, including but not limited to:
 - Arrhenius' theory
 - Brønsted–Lowry theory (ACSCH064, ACSCH067)
- Investigate the correct IUPAC nomenclature and properties of common inorganic acids and bases (ACSCH067)
- Predict the products of acid reactions and write balanced equations to represent:
 - acids and bases (neutralisation)
 - acids and carbonates
 - acids and metals (ACSCH067)
- Investigate applications of neutralisation reactions in everyday life and industrial processes

Definitions of Acids and Bases

Oxygen Theory of Acids (1776)

- French chemist Antoine Lavoisier showed that many non-metal compounds containing oxygen produced acidic solutions when dissolved in water. For example, oxides of carbon, sulfur and phosphorus.



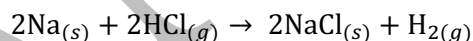
- Lavoisier hypothesised that the presence of oxygen atoms in these compounds gave them their acidic properties.
- Limitation:** many experiments showed acidic properties in substances which do not contain oxygen e.g. HCl

Hydrogen Theory of Acids (1810)

- Davy electrolysed samples of hydrochloric acid and showed that it produced hydrogen gas and chlorine gas, but not oxygen gas → disproves Lavoisier's oxygen theory of acids.
- Later experiments by other chemists showed that other acids e.g. hydrocyanic acid (HCN), also contained no oxygen but did contain hydrogen. As a result, Davy proposed that the presence of hydrogen in acids gave them their acidic properties.
- Limitation:** Davy's theory did not explain why many compounds with hydrogen atoms were not acidic e.g. methane (CH₄).

Extension of Davy's Hydrogen Theory of Acids (1838)

- German chemist Justus von Liebig stated that acids were substances that contained **replaceable hydrogens**. He reasoned this by saying that when acids react with metals, the metals replace the hydrogen atoms in the acid to form a salt.

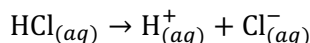


- Limitation:** Von Liebig's ideas failed to account for the production of gases such as nitrogen dioxide (rather than hydrogen gas) when nitric acid reacts with metals.

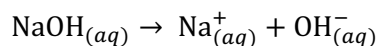
Arrhenius' Hydrogen & Hydroxide Ions Theory (1887)

Swedish scientist Svante Arrhenius describes:

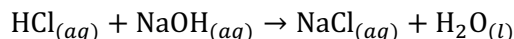
- Acids as hydrogen ion (more correctly hydronium ion) producers. This includes any compounds that can dissociate to form H⁺ in aqueous solution.



- Bases as hydroxide ion producers. This includes any compounds that can dissociate to form OH⁻ in aqueous solution.

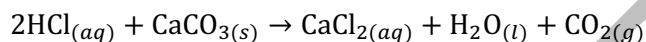


- Arrhenius' theory explains neutralisation between acids and bases. He proposed that when neutralisation occurs, the hydrogen ions (produced by acids), reacts with hydroxide ions (produced by bases), to form **neutral** water.



- **Limitations:**

- Arrhenius could not explain why certain compounds do not contain hydroxide ions, despite displaying basic properties. For example, oxides of metals and carbonates:

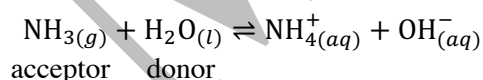
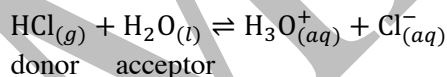


Calcium carbonate (CaCO_3) is basic in nature but it does not contain OH^- .

- Arrhenius could not explain why some neutrally-charged salts e.g. ZnCl_2 are acidic in solution whilst others are basic e.g. Na_2S .

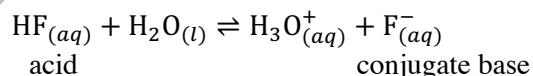
Brønsted-Lowry Theory (1923)

- The Brønsted-Lowry definition describes acids and bases by their **structures**. For example, the theory describes:
 - Acids as protons donors, any compound that can donate protons regardless of its state of matter or the nature of the solvent.
 - Bases as protons acceptors, any compound that can accept protons regardless of its state of matter or nature of the solvent.
- Brønsted-Lowry assigned a role to the solvent. The theory outlines the important role of water as an ionising solvent. Water can act as both an acid (proton donors) and a base (proton acceptors).
- Proton transfer between acids and/or bases can occur in non-aqueous solutions.



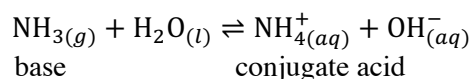
- **Acid-base pairs, conjugate acid and bases**

Consequently, the Brønsted-Lowry theory introduces the concept of acid-base pairs. When a Brønsted-Lowry acid donates its proton to the base, the resultant anion of the acid is deprotonated. This species can act as a Brønsted-Lowry base (conjugate base) by accepting a proton to reform the original acid molecule.



The acid-conjugate-base concept only applies to **weak acids** because the deprotonated anion of strong acids e.g. Cl^- has very little to no tendency of accepting a proton. In other words, if the K_a of an acid is too high or K_b of its conjugate base is too low, the equilibrium has little reversibility.

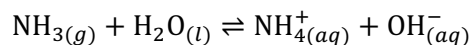
A weak base, after accepting a proton, forms a conjugate acid. For example, protonation of ammonia by water:



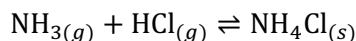
Arrhenius versus Brønsted-Lowry Theory

Overall, the Brønsted-Lowry theory is better than the Arrhenius theory because it can explain the acid and base nature of more species. For example:

- Bases that do not contain hydroxide ions e.g. ammonia, NH_3 . In Arrhenius' theory, ammonia is not considered a base because it does not contain nor dissociate into hydroxide ions (OH^-).



- Acid and base reactions that occur in non-aqueous solution, namely the reaction between ammonia and hydrogen chloride gas. In this reaction, ammonia accepts a proton from hydrogen chloride (base) while hydrochloride donates a proton to ammonia (acid).



The Arrhenius theory does not explain the acid base nature of the two reactants above because they are in gaseous states (non-aqueous).

Major Advantages of the Brønsted-Lowry Definition

The Brønsted-Lowry definition of acids and bases offers many advantages over the Arrhenius and operational definitions.

1. It expands the list of potential acids to include positive and negative ions, as well as neutral molecules. Therefore, it can explain a wider range of acids.
2. It explains the role of water in acid-base reactions: Water accepts H^+ ions from acids to form the H_3O^+ ion.
3. It can be expanded to include solvents other than water and reactions that occur in the gas or solid phases.
4. It links acids and bases into conjugate acid-base pairs. This concept
 - explains the relationship between the strengths of an acid and its conjugate base.
 - explains differences in the relative strengths of a pair of acids or a pair of bases.

Nomenclature – Naming Acids

Acid names apply to the following two different groups of acids:

- binary acids** do not contain oxygen (particularly hydrohalic acids).
- oxoacids** (oxyacids) are inorganic compounds made up of oxygen.

Hydrohalic acids

- Hydrohalic acids are aqueous solutions of binary inorganic compounds in which hydrogen, H, is combined with a halogen (Group 17) element.

molecular formula	prefix	+	modified name of element	+ acid =	"acid" name
HF _(aq)	hydro	+	fluorine + ic	+ acid =	hydrofluoric acid
HCl _(aq)	hydro	+	chlorine + ic	+ acid =	hydrochloric acid
HBr _(aq)	hydro	+	bromine + ic	+ acid =	hydrobromic acid
HI _(aq)	hydro	+	iodine + ic	+ acid =	hydroiodic acid

Oxyacids

- Oxoacids (or oxyacids) are inorganic compounds made up of oxygen (O), hydrogen (H) and one other element (E) called the central atom or central element.
- Examples of molecular formula and their corresponding possible structures showing the **general** relative positions of hydrogen (H), oxygen (O) and the central element (E) are shown below:

possible structure	HO- E =O	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{E}-\text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{E}-\text{OH} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{E}-\text{OH} \\ \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{E}-\text{OH} \\ \\ \text{OH} \end{array}$
molecular formula	HEO ₂	HEO ₃	H ₂ EO ₃	H ₂ EO ₄	H ₃ EO ₄

- Oxoacids are named with the name of the central element first using a modified ending (suffix) to indicate the relative amount of oxygen present, followed by the word "acid".
- Non-halogenic oxyacids**
The **"ic" suffix** indicates more oxygen is present in the compound than for the **"ous" suffix**. The table below includes compounds containing oxygen and hydrogen and one other element that is **not** a halogen (Group 17) element.

Table: naming nomenclature of oxyacids where the central atom is not a halogen.

Central element in oxyacid	Most oxygen (highest oxidation state)	Least oxygen (lowest oxidation state)
Nitrogen	Nitric acid (H <u>N</u> O ₃)	Nitrous acid (H <u>N</u> O ₂)
Phosphorus	Phosphoric acid (H ₃ <u>P</u> O ₄)	Phosphorous acid H ₃ <u>P</u> O ₃
Sulfur	Sulfuric acid (H ₂ <u>S</u> O ₄)	Sulfurous acid (H ₂ <u>S</u> O ₃)

- Halogenic oxyacids**

- perhalic acid has the most oxygen of all with the general molecular formula HXO_4
- halic acid has less oxygen than perhalic acid and has the general molecular formula HXO_3
- halous acid has less oxygen than halic acid has the general molecular formula HXO_2 .
- hypohalous acid has the least oxygen of all and has the general molecular formula HXO

Table: naming nomenclature of oxyacids where the central atom is a halogen.

<i>Central element in oxyacid</i>	<i>More oxygen (highest oxidation state)</i>		<i>Less oxygen (lowest oxidation state)</i>	
Chlorine	Perchloric acid (HClO_4)	Chloric acid (HClO_3)	Chlorous acid (HClO_2)	Hypochlorous acid (HClO)
Bromine	Perbromic acid (HBrO_4)	Bromic acid (HBrO_3)	Bromous acid (HBrO_2)	Hypobromous acid (HBrO)

Common Acids and Bases

Examples of common acids and bases

Table: common examples of strong and weak acids

<i>Strong acid</i>		<i>Weak acid</i>	
Molecular formula	Name	Molecular formula	Name
HClO_4	Perchloric acid	H_3PO_4	Phosphoric acid
HI	Iodic acid	HF	Hydrofluoric acid
HBr	Hydrobromic acid	CH_3COOH	Ethanoic acid (acetic acid)
H_2SO_4	Sulfuric acid	CH_2OOH	Methanoic acid
HCl	Hydrochloric acid	$\text{C}_6\text{H}_8\text{O}_7$	Citric acid
HNO_3	Nitric acid		

Table: common examples of strong and weak bases

<i>Strong base</i>		<i>Weak base</i>	
Molecular formula	Name	Molecular formula	Name
NaOH	Sodium hydroxide	NH_3	Ammonia
KOH	Potassium hydroxide	NaHCO_3	Sodium bicarbonate
Ba(OH)_2	Barium hydroxide	CH_3NH_2	Methylamine
Ca(OH)_2	Calcium hydroxide	$(\text{CH}_3\text{CH}_2)_2\text{NH}$	Diethylamine

Acids ranked by their dissociation constant, K_a , in water

Name	Formula	K_a (25 °C)
Perchloric acid	HClO ₄	Large
Hydriodic acid	HI	Large
Hydrobromic acid	HBr	Large
Sulfuric acid	H ₂ SO ₄	Large
Hydrochloric acid	HCl	Large
Nitric acid	HNO ₃	Large
HYDRONIUM ION	H ₃ O ⁺	55
Sulfurous acid	H ₂ SO ₃	1.2×10^{-2}
Hydrogen sulfate ion	HSO ₄ ⁻	1.0×10^{-2}
Phosphoric acid	H ₃ PO ₄	7.1×10^{-3}
Citric acid ^b	H ₃ C ₆ H ₅ O ₇	7.1×10^{-4}
Nitrous acid	HNO ₂	7.1×10^{-4}
Hydrofluoric acid	HF	6.8×10^{-4}
Formic acid	HCO ₂ H	1.8×10^{-4}
Barbituric acid ^c	HC ₄ H ₃ N ₂ O ₃	9.8×10^{-5}
Ascorbic acid ^d	H ₂ C ₆ H ₆ O ₆	7.9×10^{-5}
Acetic acid ^e	HC ₂ H ₃ O ₂	1.8×10^{-5}
Carbonic acid	H ₂ CO ₃	4.5×10^{-7}
Hydrogen sulfide (aq)	H ₂ S	9.5×10^{-8}
Hydrogen sulfite ion	HSO ₃ ⁻	6.6×10^{-8}
Dihydrogen phosphate ion	H ₂ PO ₄ ⁻	6.3×10^{-8}
Hypochlorous acid	HOCl	3.0×10^{-8}
Hydrogen cyanide (aq)	HCN	6.2×10^{-10}
Ammonium ion	NH ₄ ⁺	5.7×10^{-10}
Bicarbonate ion	HCO ₃ ⁻	4.7×10^{-11}
Monohydrogen phosphate ion	HPO ₄ ²⁻	4.5×10^{-13}
Hydrogen sulfide ion	SH ⁻	1×10^{-19}
WATER	H ₂ O	1.8×10^{-16}
Hydroxide ion	OH ⁻	(est) 1×10^{-36}

- Strong acids (complete ionisation) are positioned above hydronium ion ($K_a > 55$) and weak acids are positioned below.

- Strongest acid has the greatest K_a at a given temperature. This will correspond to the lowest pK_a .

- K_a provides an indication of the tendency of an acid to lost its proton(s).

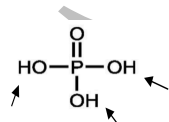
For example, carbonic acid has lower tendency to lose its protons compared with acetic acid.

Deprotonation/ionisation of acids

- Not all hydrogen atoms (protons) of an acidic species can be deprotonated or donated away.
- Some acidic species may be able to donate more than one proton per acid molecule.
 - Monoprotic – an acid molecule can only donate one proton. E.g. HCl, HNO₃, CH₃COOH (acetic acid)
 - Diprotic – an acid molecule can donate up to two protons. E.g. H₂SO₄
 - Triprotic – an acid molecule can donate up to three protons. E.g. H₃PO₄

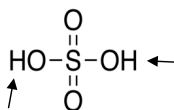
If there are more than one proton that could be donated, each has a different K_a value. This means diprotic and triprotic acids typically have multiple K_a and pK_a values. Consequently, the strength of acidic nature of these protons varies.

- The number of ionisable protons **does not** indicate acid strength. A triprotic acid (e.g. H₃PO₄) can have lower K_a values than a monoprotic acid e.g. HCl.

Phosphoric acid (H₃PO₄)

Triprotic

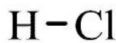
K_{a1}	7.1×10^{-3}
K_{a2}	6.3×10^{-8}
K_{a3}	4.5×10^{-13}

Sulfuric acid (H₂SO₄)

Diprotic

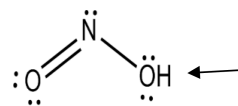
K_{a1}	Large
K_{a2}	1.2×10^{-2}

Hydrochloric acid (HCl)



Monoprotic

K_{a1}	Large
----------	-------

Nitric acid (HNO₃)

Monoprotic

K_{a1}	Large
----------	-------

Acidic Hydrogens

- Davy's hydrogen theory did not account of the acidic nature of hydrogens in hydrogen-containing molecules. Not all hydrogens can be ionised or deprotonated. Hydrogen atoms that can be deprotonated is referred to as the acidic hydrogen.
- Evidently, the pK_a scale can be as low as -8 and as high as 50 . Technically, all hydrogens can be deprotonated but ones with extraordinarily high pK_a values are effectively not acidic because it is very unlikely for these hydrogens to be deprotonated.
- Polarity**
When all other factors are kept constant, acids become stronger as the X-H bond becomes more polar. The second-row nonmetal hydrides, for example, become more acidic as the difference between the electronegativity of the X and H atoms increases. HF is the strongest of these four acids, and CH_4 (methane) is one of the weakest Brønsted-Lowry acids known.

When these compounds act as an acid, a H-X bond is broken to form H^+ and X^- ions. The more polar this bond, the easier it is to form these ions. Thus, the more polar the bond, the stronger the acid.

- Atomic Radius of the X Atom**

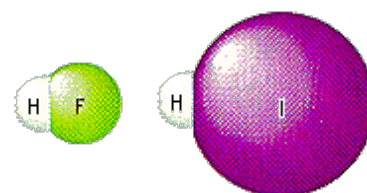
At first glance, we might expect that HF, HCl, HBr, and HI would become weaker acids as we go down this column of the periodic table because the X-H bond becomes less polar. Experimentally, we find the opposite trend. These acids actually become stronger as we go down this column.

Acids become stronger as the X-H bond becomes weaker, and bonds generally become weaker as the atoms get larger as shown in the figure to the right.

Short pK_a table

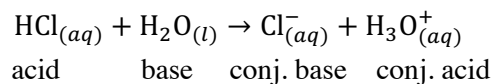
Functional group	Example	pK_a
Alkane	CH_4	~ 50
Amine	$:NH_3$	~ 35
Alkyne	$R-C\equiv C-H$	25
Water	$HO-H$	16
Protonated amines	$NH_4^+ Cl^-$	10
Carboxylic acids	$H_3C-C(=O)OH$	5
Hydrochloric acid	HCl	-8

Weaker acid
↓
Stronger acid

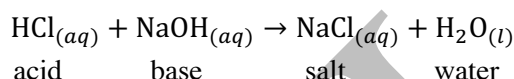


Acid-Base Reactions

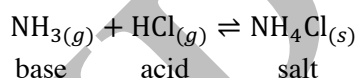
- Acid-base reactions encompass a wide range of different reactions. They are more commonly referred to as neutralisation reactions because acids and bases neutralise each other's chemical properties.
- Acid-base reactions, in the Brønsted-Lowry theory, are reactions that involve transfer of protons or H^+ ions. This type of reaction is best exemplified by the dissociation of acid (or base) in water. In this reaction, water acts as both a solvent and base because it accepts a proton from the acid.



- Acid-base reactions, in the Arrhenius theory always produce water (in addition to salt) because H^+ ions (produced by acids) and OH^- ions (produced by bases) react in aqueous solution to form water.

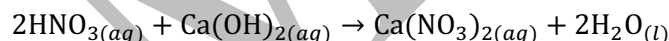


- Not all neutralisations produce water.** For example, the reaction between ammonia (base) and hydrogen chloride (acid):

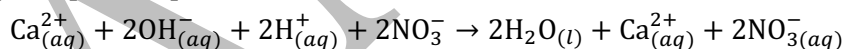


- All reactions with acids form **salts** which are defined as an ionic compound that consists of an anion of acid and a cation of base. In other words, a salt consists of a conjugate base and a conjugate acid. The ions which make up the salt are spectator ions because they remain dissolved as ions.

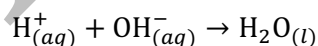
Neutral species equation:



Complete species equation:

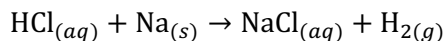


Net ionic equation:

**Acids + metals \rightarrow salt + hydrogen gas**

- Reaction between acids and metals is a type of acid-base reaction.

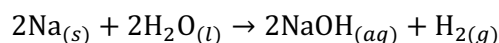
Overall equation



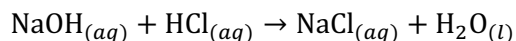
dilute acids + metal \rightarrow salt + hydrogen gas

- Stepwise equations*

Sodium metal reacts with water to form sodium hydroxide (strong base):



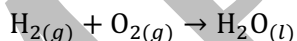
Sodium hydroxide then undergoes neutralisation with hydrochloric acid (HCl) to produce salt and water:



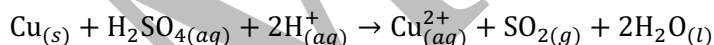
- The reaction between active metals (low ionisation energy) and dilute acids are extremely volatile. The products are, salt, hydrogen gas and heat – latter two react to produce explosions.

Metal	Observation
K, Na	effervesce very rapidly producing hydrogen gas, which may ignite
Ca, Mg	bubble rapidly releasing hydrogen
Al, Zn, Fe, Sn, Pb	bubble moderately to very slowly as hydrogen is released; reaction is faster in warm acid; lead stops reacting when coated with insoluble PbCl_2 or PbSO_4
Cu, Hg, Ag, Au	no reaction

- The production of hydrogen gas can be observed from bubbling and tested by conducting a ‘pop’ test. When hydrogen gas is lit in the presence of oxygen, they react to form water while producing a squeaky pop sound. The water condenses inside the test tube.



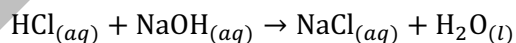
- Some metals e.g. copper can react with acid to form gases other than hydrogen gas. For example, the reaction between copper metal and concentrated sulfuric acid produces sulfur dioxide.



- Acids also under oxidation-reduction reactions with metals. The hydrogen ions from an acid gain electron from metals (reduction) to produce hydrogen gas. Conversely, metals lose electrons (oxidation) to produce cations.

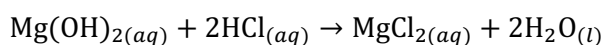
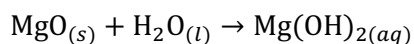
Acid + metal hydroxide → salt + water

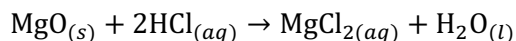
- Reaction between acid and metal hydroxide is considered an acid-base reaction in both the Arrhenius and Brønsted-Lowry definition.



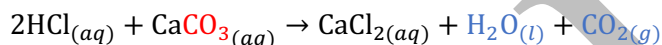
Acid + metal oxide → salt + water

- Metal oxides are considered *basic oxides* because they react with water to produce metal hydroxides which in turn produce OH^- ions in water.

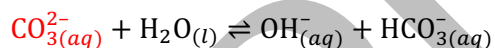


Overall equation**Acid + metal carbonates/hydrogen carbonates → salt + water + carbon dioxide**

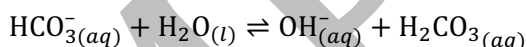
- Carbonates and hydrogen carbonates are polyatomic anionic bases in the Brønsted-Lowry theory because they do not dissociate into hydroxide ions in aqueous solution. Therefore, they are not considered as bases in the Arrhenius theory.
- Reactions between acids and carbonates/hydrogen carbonates produce salts, water and **carbon dioxide**.

Acid + carbonate:

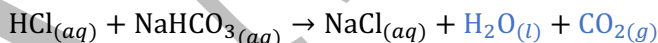
Carbonate ions is *hydrolysed* by water to form hydrogen carbonate. In this step, carbonate ions receive protons from water. Thus, they are basic under the Brønsted-Lowry theory.



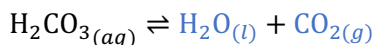
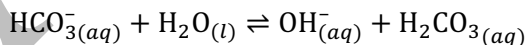
Hydrogen carbonate is *hydrolysed* by water to form carbonic acid



Carbonic acid decomposes to produce carbon dioxide

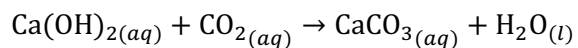
**Acid + hydrogen carbonate:**

Hydrogen carbonate undergoes the same steps to produce carbon dioxide. HCO_3^- receives a proton from water. Thus, it is a base (Brønsted-Lowry theory)



- Carbonate and hydrogen carbonate ions usually react with H_2O alone but in the presence of an acid, the equilibrium of each hydrolysis reaction lies more to the right side. This is because H^+ ions from the acid neutralises and reduces OH^- ions. According to Le Chatelier's principle, this shifts the equilibrium to the right side.

- Carbon dioxide can be identified using the lime water test. Bubbling carbon dioxide in calcium hydroxide, $\text{Ca}(\text{OH})_2$ to form milky calcium carbonate, CaCO_3 .



Practice Questions

- Write a balanced overall and net ionic equation for the reaction of phosphoric acid and potassium hydroxide.
- Distinguish between an Arrhenius acid with a Brønsted-Lowry acid. Provide a chemical equation in your answer.
- Write a balanced overall equation for the reaction between sulfuric acid and barium carbonate. Barium carbonate is insoluble.
 - Given that barium sulfate is also insoluble in water, write a net ionic equation for the reaction.
 - What would you observe as this reaction proceeds?

Neutralisation in Everyday Life and Industrial Processes

Neutralisation in Agriculture

- pH of soil in which plants are grown upon requires a specific range, otherwise it would negatively impact plant growth.
- If the soil is too acidic, powdered lime (CaO) or limestone (CaCO_3) are added to the soil to neutralise the H^+ ions and increase the pH.
- If the soil is too basic, rotting vegetables or leaves can be added. This is because the compost decomposes to release carbon dioxide gas which is acidic in nature.

Neutralisation in Industries

- Burning of fossil fuel releases sulfur dioxide (SO_2) which is acidic in nature. To prevent air pollution and onset of acid rain, lime and limestone are used to neutralise the gas.

Neutralisation in Medicine

- Antacid tablets e.g. $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ are used to treat gastric patients by neutralising the excessive acid (HCl) in their stomach.
- Vinegar is a common remedy for wasp and jelly fish stings because they are alkaline in nature.

Neutralisation at Home

- Baking powder contains sodium hydrogen carbonate (NaHCO_3), also known as bicarbonate of soda, and a weak acid. When water is added to a mixture of baking soda, the chemical reaction between the weak acid and hydrogen carbonate is stimulated. This produces carbon dioxide which causes the cake to rise.
- Toothpastes are alkaline which help prevent decaying food particles (acidic) in our teeth and subsequent tooth decay.