

Module 2: The Acidic Environment

1. Indicators were identified with the observation that the colour of some flowers depends on soil composition.

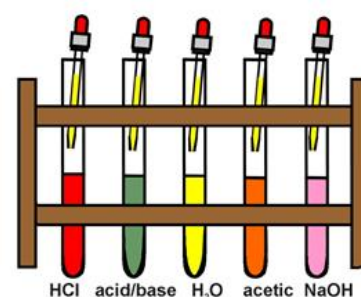
Students learn to:

- Acids** are any substance that has a pH of less than seven. They have a sour taste and sting or burn the skin and also decompose metals. Common **examples** of acids include milk, wine, vinegar, orange and lemon juice, soft drinks and toothpaste. **Bases** are any substance that has a pH of greater than seven. They taste bitter and have a soapy feel when reacting with lipids. Common **examples** include caustic soda, otherwise known as oven cleaner, drain cleaner, window cleaner and other household cleaning agents. **Neutral** substances have a pH of seven and include pure water, ethanol, oils, and various salts, eg sodium chloride.
- Indicators** are used to determine whether a substance is acidic or basic by colour change. Many common flowers contain compounds that **change colour** in the presence of acidic or basic environments. Many different types of indicators are used because one indicator will only change colour in reaction to different pHs over a certain pH scale, for instance 8 – 10. Examples of **common indicators** are shown right. All display prominent colour changes.
- The most obvious **everyday use** of indicators is to differentiate between acids and bases on the pH scale. This is utilised for **swimming pool maintenance** in **acidity testing kits**. This is to test whether the pool remains within the safe acidity levels of 7.2 to 7.6 and to ensure an adjustment if necessary. A sample of the pool water is taken in a small vial then indicator added, hence analysed by **digitally** by a testing device or **visually** using a colour chart. **Soil testing** is also important as many plants do not grow well in acidic conditions as they affect the **supply of nutrients** to the plant. Therefore **horticulturalists** and farmers must test the acidity and make adjustments, for instance if it is too acidic the **lime** (calcium oxide) can be added to make the soil more effective. Generally, this test is achieved by adding a **white powder**, barium sulfate or talc, and adding a drop of indicator where the colour change is clearly visible. **Acid-base titrations** used in **chemical research** are another use discussed later.

Indicator	Colour Change	pH Range
Litmus	Red to Blue	4.5 ↔ 8.3
Phenolphthalein	Colourless to Cerise (Pinky Purple)	8.2 ↔ 10.0
Methyl Orange	Red to Yellow	3.1 ↔ 4.4
Bromothymol Blue	Yellow to Blue	6.0 ↔ 7.6

Students:

- Practical Investigation:** **Aim:** to prepare and test a natural indicator. **Independent Variable** – the substance being tested; **Dependent Variable** – colour change in the indicator. **Method:** Grind up either flower samples or red cabbage with water and sand. Decant the resulting pigment and drop it into various strength acidic and basic substances (right). Observe colour changes. **Results:** Flowers of plants may contain pH sensitive pigments. Some pigments give clear changes across a range of pHs but some will indicate specific ranges, ie acids and not bases. Many pigments are also 'once only' pigments such that changing their acidity will not change the colour, they only react once.



2. While we usually think of the air around us as neutral, the atmosphere naturally contains acidic oxides of carbon, nitrogen, and sulfur. The concentrations of these acidic oxides have been increasing since the Industrial Revolution.

Students learn to:

- **Oxides of non-metals often act as acids**, examples including nitrous oxides (NO_x), carbon dioxide (CO_2), sulfur dioxide or sulfur trioxide (SO_2/SO_3), and phosphorous oxide (P_4O_{10}). While by definition these oxides are not acids (don't donate hydrogen nuclei), they react as acids. That is, they **react with water to form acids** (eg. $\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{CO}_3(aq)$) and/or **neutralise bases to form salts** (eg. $\text{CO}_2(g) + 2\text{NaOH}(aq) \rightarrow \text{H}_2\text{O}(l) + 2\text{NaCO}_3(aq)$).

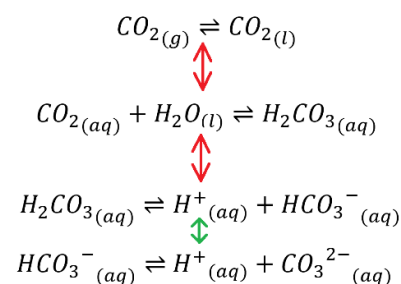
Acidic oxide		Basic oxide		Amphoteric oxide			
Li_2O	BeO	B_2O_3	CO_2	N_2O_5		OF_2	
Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7	
K_2O	CaO	...	Ga_2O_3	GeO_2	As_2O_5	SeO_3	Br_2O_7
Rb_2O	SrO	...	In_2O_3	SnO_2	Sb_2O_5	TeO_3	I_2O_7
Cs_2O	BaO	...	Ti_2O_3	PbO_2	Bi_2O_5	PoO_3	At_2O_7

- The acidic nature of the oxides can be applied to the entire periodic table. In fact the **acidity of any given oxide increases diagonally upwards left to right**, ie across the periodic table. Most **metals are basic oxides**, in that they neutralise with acids to form salts and do not react with basic solutions. eg. $\text{CuO}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CuSO}_4(aq) + \text{H}_2\text{O}(l)$ and $\text{Fe}_2\text{O}_3(s) + 6\text{HNO}_3(aq) \rightarrow \text{Fe}(\text{NO}_3)_3(aq) + 3\text{H}_2\text{O}(l)$. Some metals are **amphoteric oxides**, ie they can react as both acidic and metallic oxides. All **non-metals are acidic oxides** as described above.

Chemical Equilibrium: Most (there's always an exception in chemistry) chemical reactions are actually **reversible**, they don't just react one way, ie after the products are produced, they can re-react to form the reactants. eg. $\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{H}_3\text{O}^+(aq)$. When reacted in a **closed system** (ie there is no energy or matter input, a closed can for instance) the initial reaction will decrease in frequency as the concentrations of reactants decrease. Of course similarly, the reversible reaction will then dominate and decrease as the concentration of the products lower. Eventually these reactions will balance out and reach chemical equilibrium; from then on a **macroscopic constancy** is reached, ie to our eyes nothing changes. However on a molecular level the reversible reactions are still proceeding, just at **equal rates** so they cancel known as **dynamic chemical equilibrium**.

- **Le Chatelier's principle** defined is: "If a chemical system at equilibrium is subjected to a change in conditions, the system will adjust to re-establish equilibrium in such a way as to partially counteract the imposed change." That is if the conditions are changed, then the equilibrium shifts to favour one side of the reaction, thus relieving the stress put on that side and counteracting or resisting the forced change by removing products or reactants.
- Below are the factors which will **affect a dynamic equilibrium** under Le Chatelier's principle:
 - **Concentration:** If the concentration of either the reactants or products is increased or decreased, the equilibrium will obey Chatelier and attempt to counteract this change. This means that increasing the concentration of one substance will cause the system to favour the direction that will decrease the concentration of that substance, and vice versa. Importantly, in reaction below, if say A is increased, then C and D will correspondingly increase but B will also slightly decrease as there will be more A 's for him to run into $\uparrow A + \downarrow B \rightleftharpoons \uparrow C + \uparrow D$ and the system will readjust accordingly. Also, if the volumes are increased, then this will not have an effect, only the concentrations.
 - **Pressure hence Volume:** Increasing the external pressure will reduce the volume occupied and thus increase the concentrations of all molecules (reverse if pressure decreased). If there are equal moles on either side of the reaction the equilibrium will be maintained however if there are unequal moles, ie $2A \rightleftharpoons B$, then the reaction will shift to favour the side with least molecules, thus reducing the imposed pressure. Thus the immediate effect on increasing pressure would result in increased concentrations on both sides of the reaction however the equilibrium would shift so there was less A .

- **Temperature:** The effect of temperature is discovered by considering the heats of reaction. If the temperature is increased, the system will resist the change by favouring the endothermic reaction, thus cooling the system. If the temperature is decreased, the exothermic reaction is favoured resisting the change.
- **Catalysts:** Catalysts decrease activation energy for both sides of the reaction thus do not change the dynamic equilibrium. However they do help to reach that equilibrium faster.



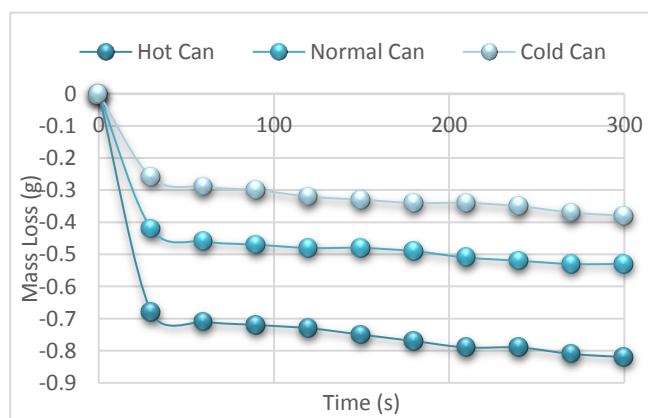
- The **solubility of Carbon Dioxide** in water is an extremely multi-staged process. Firstly, carbon dioxide is slightly soluble in water thus dissolves reacting with the water to form carbonic acid. This carbonic acid then **doubly dissociates** in two more reactions to form a carbonate ion. Thus carbon dioxide undergoes up to four dynamic equilibriums to finally acidify the water as shown right. This is why rain is slightly acidic, it has collected CO₂ on its path through the atmosphere. A **can of softdrink** is the best example of **Le Chatelier's Principle** with CO₂. If **pressure is increased** as it is when the softdrink is sealed (4-5 times the normal atmospheric pressure is pumped in), this increases the concentration above the drink, thus more dissolves and it favours the left hand side of the whole chain up so the drink becomes more acidic. The reverse happens when the drink is opened and the pressure relieved, the carbon dioxide shifts to the right and is displaced out of the drink, hence the bubbles. **Temperature** has a similar effect, as the dissolving reaction is exothermic, if the temperature is increased then the gaseous reactants will be favoured displacing CO₂, hence the drink tastes better (less flat) at colder temperatures. If any **acids** (food acids) are added to the drink, this effects the concentration of hydronium ions on the lower end and thus the equilibrium is shifted accordingly. ie, when acid is added, CO₂ is released; oppoiste when base is added.
- **Sulfur Dioxide** is released **naturally** when bacteria decompose organic matter to form hydrogen sulfide, as follows $2\text{H}_2\text{S}_{(g)} + 3\text{O}_{2(g)} \rightarrow \text{SO}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$. Other natural source include from volcanic gases released during eruptions/geysers and smoke from bushfires. **Industrial sources** of sulfur dioxide are mainly the burning of fossil fuels and the smelting of sulfide ores. Fossil fuels, for instance coal, often contain sulfide impurities that are oxidised when burnt, ie $4\text{FeS}_{2(s)} + 11\text{O}_{2(g)} \rightarrow 2\text{Fe}_2\text{O}_{3(s)} + 8\text{SO}_{2(g)}$. An example of smelting plant pollution is the extraction of Zinc involving the roasting of Zinc Sulfide, ie $2\text{ZnS}_{(s)} + 3\text{O}_{2(g)} \rightarrow 2\text{ZnO}_{(s)} + 2\text{SO}_{2(g)}$. **Nitrogen Oxides** are formed both naturally and industrially in high temperature combustion environments which allow the nitrogen in the atmosphere to react with the oxygen in the following reactions: $\text{N}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{(g)}$ and then $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_2_{(g)}$. NO is neutral but NO₂ is acidic. The main **natural** production of nitric oxide (NO) is lightning, the high temperature allowing the reaction. Nitrogen oxide (NO₂) is hence produced. **Industrially** humans majorly increase NO_x (generally refering to both NO and NO₂) rates through the comubstion of fossil fuels in both power stations and vehicles.
- The data to accurately track sulfur and nitrogen oxides in the atmosphere was not properly developed until the 1950's. From the start of the **Industrial Revolution** (early 1800's) air quality significantly decreased in industrial cities and areas. This caused the major **acid rain problems** outlined below but also a series of pollution incidents in London and North-East USA which caused many deaths. This resulted in **strict regulations** being put in place like the US's Clean Air Act which significantly reduced SO₂ concentrations to a safe steady level of about 0.1 ppm, ten times the natural level, which is maintained today. This was achieved by devices such as **scrubbers**, which pass SO₂ through a saturated solution, for example, magnesium hydroxide which reacts to form magnesium oxide and sulfuric acid, thus removing SO₂. NO_x concentrations only became a problem in the 20th century when **electrical and vehicle combustion** reached significant levels. This led to **photochemical smog** and dangerous intoxications within cities but was soon controlled using **catalytic converters** which utilise catalysts to favour the production of NO back to N₂ and O₂. However the sheer number of new nitric oxide produces being added as countries expand and develop has made it difficult to adequately control NO_x concentrations. Thus there is **strong evidence for increased concentrations** of oxides of sulfur and nitrogen which are still challenging to control.

- Avogadro** postulated when discovering the mole that equal moles of gas under controlled temperature and pressure should occupy equal volumes. This is known as the **ideal gas law** which basically says that every gas acts as a tiny pool ball due to the kinetic theory and thus takes up equal volumes. There are two standard pressures used in our calculations, **Standard Temperature and Pressure (STP)** which occurs at 273.15K or 0°C and 100 kPa and produces 22.71 L of ideal gas. **Standard Laboratory Conditions (SLC)** occur at 298.15K or 25°C and 100 kPa and produces 24.79 L of ideal gas. The volume of any gas can thus be calculated under these conditions when the number of moles is known, and vice versa, using the equation above where v is the volume being calculated, n is the moles and V is the volume of one mole at whatever standard you are using, STP or SLC.
- Both **Sulfur Dioxide** and **Nitrogen Oxides** react with the water in the atmosphere to produce the **sulfuric acid** (H_2SO_4) and **nitric acid** (HNO_3). Thus the increases of these acidic oxides due to **industrial activity** causes increases in the acidity of pure rain which, due to carbon dioxide, is about 5.6. SO_2 and NO_x have been recorded to decrease to pH levels of rain to 2.4 although acid rain is defined as any rain with a pH less than 5. **Acid precipitation** comes in two varieties, **wet deposition** which is the typical rain and snow falls with high acidity, but also **dry deposition** where particles deposit themselves on the ground and is how half of the acidic oxides return to earth. When it precipitates, these oxides react with the rain making the runoff even more acidic than the rain alone. Acid rain has many dangerous effects. For instance, in lakes and estuaries, increased acidity levels **kills off all aquamarine life**, acidity levels of below 4.2 make it impossible for any marine life to survive. Thus many lakes and rivers in northern America and Europe are now devoid of life. It also has an effect on trees and other flora because it increases the acidity levels of the soil making it unbearable, but also the H^+ ions **react with nutrients** and minerals of the soils, hence starving the trees and making them far more susceptible to **other damage** like breakages. By the same token many **toxic metals** to humans such as mercury react with the increased acidity levels and congregate in dangerous quantities, fish in Sweden are now inedible due to mercury levels; copper in drinking water from the pipes was also a problem. Acid rain also **dissolves stone**, especially limestone ($CaCO_{3(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$) which degrades building and historical monuments and statues. This is because when the calcium reacts, the CO_2 evaporates, crumbling the stone.

Students:

- Practical Investigation – Decarbonating Soft Drink. Aim:** to measure the mass change as a soft drink decarbonates, i.e. loses some dissolved CO_2 . **Independent Variable** – the pressure conditions of the soft drink; **Dependent Variable** – the mass loss of the drink. **Method:** place a can of hot soft drink (40°C) on an electronic balance and zero the weight. Crack the can and record the mass lost after every 30 s for 5 minutes. Repeat above steps with room temperature can and cold (almost frozen) can. **Results:** as below.
- For **sulfur dioxides**, **industry** contributes about **40%** to emissions. This is as a result of **burning coal** for energy production, for **metal smelting**, and for **oil refining**; as above. **Transport** emissions only contribute about **2%** to sulfur emissions, mainly from the **combustion of petrol**. **Nitrogenous oxides** are mostly formed by **transport**, **72%**, from cars and trucks as above. Only **4%** comes from **industrial sources of oil**

Time (s)	Hot Can	Normal Can	Cold Can
0	0.68	0.42	0.26
30	0.70	0.45	0.28
60	0.71	0.46	0.29
90	0.72	0.47	0.30
120	0.73	0.48	0.32
150	0.75	0.48	0.33
180	0.77	0.49	0.34
210	0.79	0.51	0.34
240	0.79	0.52	0.35
270	0.81	0.53	0.37
300	0.82	0.53	0.38



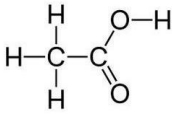
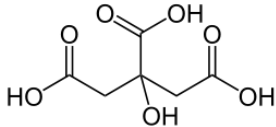
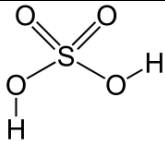
refining and **coal burning**. Together, they cause **acid rain** which can be a major problem, as above. They also cause **photochemical smog**, which creates the unattractive haze seen above cities. Sulfur dioxide in

- the smog also causes **respiratory problems** which can be dangerous for **asthma** patients. Nitrogenous oxides also cause **irritation of eyes**, reducing the quality of life. These are serious problems if left unchecked and can cause **massive damage** thus policies need to be enforced to monitor their emission. Currently, such policies, like the **USA's Clean Air Act** are very effective in **preventing sulfur oxides and acid rain**, but nitrogenous oxides are still a **significant problem** that is not adequately dealt with, mainly because of the massive increase in the number of **vehicles** in existence.

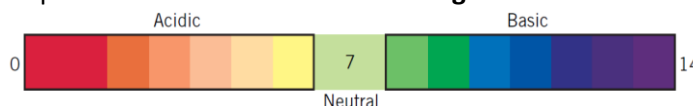
3. Acids occur in many foods, drinks and even within our stomachs.

Students learn to:

- Acids are **proton donors**. As standard hydrogen is an electron orbiting a proton, the proton's acids donate are thought of as **ionised hydrogens**, written as H^+ . These protons are **never found unbonded**, and as water is the most common solvent are often referred to as **hydronium ions**, H_3O^+ . Thus, when an acid ionises, releases its loosely held hydrogen ions, these ions form hydronium ions in the water, in an **equilibrium acid** that is determined by the strength of the acid. When HCl, typically a gas, dissolves in water, it ionises as shown, $HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$. The hydrogen ions **dissociate** to form hydronium ions leaving chlorine ions behind. All acids dissociate in this way.
- Some common acids that you MUST remember are displayed below.

Acid	Acetic	Citric	Hydrochloric	Sulfuric
Alternate Name	Ethanoic	2-hydroxypropane-1,2,3-tricarboxylic	-	-
Chemical Formula	CH_3COOH	$C_6H_8O_7$	HCl	H_2SO_4
Structural Formula			$H-Cl$	
Ionisation	Monoprotic	Triprotic	Monoprotic	Diprotic
Example	Vinegar, wines.	Citric fruits, eg. lemons	Gastric Juices	Acid Rain

- For any given solute at LTP, the **ionisation constant** is the product of the **concentration of hydrogen** ions multiplied by the **concentration of hydroxide** ions. For water, $K_w = [H^+] \times [OH^-] = 10^{-14}$. Thus, for neutral water, $[H^+] = [OH^-] = 10^{-7}$, and for any acidic substance, the concentration of hydrogen ions increases which is opposed by a decrease in hydroxide ions. The inverse is true for basic substances. The **pH scale** is a measure of the acidity or basicity of substances and is the $-\log_{10}[H^+]$. Thus acidic substances with **high concentrations of protons** have a low pH whilst basic substances with **high concentrations of hydroxide** ions have high pH values. This is displayed right, in a colourful fashion.



- There is a difference between **concentration and strength**. The **concentration of a solution** is dependent on the **number of moles** dissolved in the substance. Thus a **concentrated solution** is one with lots of substance dissolved, say 10 molL^{-1} . A **dilute substance** is hence one with little substance dissolved, say 0.001 molL^{-1} . The strength of an acid is something entirely different. When considering **identical concentrations** of acids, not all of them have the same pH. A **strong acid** is one where all **donatable hydrogens dissociate completely**. A **weak acid** is where some of the acid's protons remain attached, only a **percentage dissociate**. But more later.
- As the **pH scale** is based on **concentrations of hydrogen ions** in terms of **indices**, it is represented as a **negative logarithmic scale** or $-\log_{10}[H^+]$. Thus, a change in a pH of 1 results in a change in the concentration of hydrogens by a **factor of 10**, as it is indices. Thus a pH of 2 is 1000 times more
- concentrated than a pH of 5. To **calculate the pH** given $[H^+]$, take the $-\log_{10}[H^+]$. Inversely, to calculate the $[H^+]$ from pH, take 10^{-pH} .

- The following table contains the pH of the above four acids at 0.01 molL⁻¹. They have to be kept at **equal concentrations** because according to Le Chatelier, if more water (more diluted) is added, then this pressure on one side of the equilibrium **favours the production of ions** whilst at the same time diluting the ions. Thus it is extremely complex to determine cross concentrations. Hydrochloric is a strong acid, thus it **dissociates completely**. 100% of its protons have been donated, thus the concentration of hydronium is the same as the concentration of HCl. However acetic, same concentration as HCl, obviously **does not dissociate completely**. To determine this **degree of ionisation**, divide the concentration of hydronium ions by the concentration of the acid, and that gives the **percentage ionised**. **Degree of ionisation** = $\frac{[H^+]}{[acid]}$. For acetic, $10^{-3.38} = 4.17 \times 10^{-4}$. Therefore, degree of ionisation = $\frac{4.17 \times 10^{-4}}{1 \times 10^{-2}} = 4.17\%$. Similarly, citric acid has a degree of ionisation of 8%.
- If a **strong acid dissociates** completely into its ions, then it is **not an equilibrium reaction** as there is **no reactants remaining**. Take HCl, $HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$. There are **no intact molecules** of HCl gas remaining in the solution, only the **ions**. **Weak acids** are different because they **dissolve in equilibrium**, i.e. there is some **intact molecules left** and some **dissociated ions**. $CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$ Acetic is a weak acid, thus when it dissociates, 99% of the acid remains intact whilst 1% dissociates into ions. Thus a weak acid is an acid in equilibrium.
The final thing about acids is not all of them **only have one proton to donate**. HCl and Acetic only have one, so they are called **monoprotic**. But Sulfuric has two hydrogens to donate, thus is **diprotic**. Citric has three, so is **triprotic**. This is important to remember when **calculating acid concentrations** and hydronium concentrations, the concentration of hydronium is not necessarily equal to the concentration of acid.

Students:

- Practical Investigation – pH Testing. Aim:** to distinguish between acidic, neutral, and basic chemicals using indicators and pH probes. **Independent Variable** – acidity/basicity of chemical; **Dependent Variable** – indicator colour and pH reading. **Method:** gather several different samples of substances, preferably differing in acidity. First, add universal indicator to the samples. The colour chart on the previous page indicates the corresponding pH level. Then test using the pH probe, calibrated prior, which gives exact reading. **Results:** varied and simple. The indicator is a destructive test as it contaminates the solution whilst the pH probe is not destructive, it does not contaminate, if cleaned properly.
 - Practical Investigation – Concentration and Strength. Aim:** to measure the pH of different acids with identical concentrations. **Independent Variable** – the acid being tested; **Dependent Variable** – the corresponding pH. **Method:** using a pH probe and universal indicator, test quantitatively and qualitatively the pH of acetic, citric, hydrochloric and sulfuric acids at a stable concentration (e.g. 0.01 molL⁻¹). Compare. **Results:** as in table in top right hand corner.
 - When writing equations for **strong acids**, they **dissociate completely** so the reaction **proceeds to completion**. Thus use \rightarrow . **Weak acids dissociate in equilibrium**, thus use the reversible arrows, \rightleftharpoons .
 - Use your imagination, electron dot diagrams, structural and condensed structural formula, ball and stick modelling kits and the table on the previous page to have loads of fun! :D
 - Acids can be used as food additives for many different reasons. Sometimes the acid might have a particular taste, like ethanoic acid used in salt and vinegar flavouring, that is desirable to be added. They can also be used to improve the quality of food, or as preservatives to extend the shelf life. For instance, some meats are treated with sulfur dioxide gas to prevent microbial growth and hence decomposition. Some common acidic food additives are sulfur dioxide, lactic acid, acetic acid, propanoic acid.
 - To the right, some naturally occurring acids bases and their chemical composition.
- | Acid/Base | pH | Formula | Found Naturally |
|-------------|------|--|--|
| Oxalic Acid | 1.3 | COOHCOOH | Spinach and rhubarb leaves. |
| Formic Acid | 2.3 | HCOOH | Poison in ant stings and stinging nettle. |
| Ammonia | 11.6 | NH ₃ | Volcanic gases and in organic decomposition. |
| Caffeine | 7.5 | C ₈ H ₁₀ N ₄ O ₂ | Coffee, tea, cola nuts, guarana, etc. |

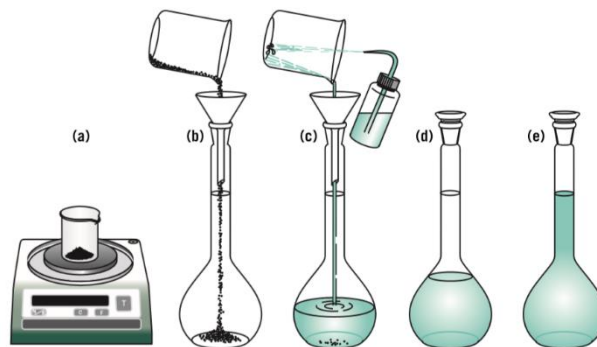
4. Because of the prevalence and importance of acids, they have been used and studied for hundreds of years. Over time, the definitions of acid and base have been refined.

Students learn to:

- Because of the importance of acids, their definition has been a long process. Originally an acid was something tasting sour that reacted with certain metals. **Antoine Lavoisier** first decided that all acids must **contain oxygen** because he observed that ethanoic, carbonic, sulfuric and nitric acid all contained oxygen (oxygen the name is in fact derived from the Greek “acid former”). **Sir Humphrey Davy** proved that hydrochloric acid did not contain oxygen and thus postulated that all acids must contain **replaceable hydrogen** (displaced in metallic reactions) rather than oxygen. **Svante Arrhenius** proposed that since acids are electrolytes that they must **ionise hydrogen ions** in water and similarly bases are those who ionise hydroxide ions. In fact ideas similar to Arrhenius’ are expressed in syllabus point 3. However Arrhenius’ theory does not take into due account the **importance of the solvent** on the acids properties or consider that acids can react outside of solvents.
- The **Brönsted-Lowry theory** of acids and bases states that an acid is a **proton donor**, and a base is a **proton acceptor**. For example, in the equation $HCl_{(g)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$ hydrochloric acid is the acid as it donates the proton, and hence water is the base as it accepts the proton. Ammonia in water, $NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$, the ammonia accepts the proton and is thus the base despite having no hydroxide ion to donate, the water hence the acid.
- As an acid **reacts in equilibrium**, once the acid has **donated** its proton, it can subsequently **accept** another proton to return to its original state, thus acting as a base. Although strong acids are considered to completely dissociate, this is not always necessarily the case so can still be represented as an equilibrium reaction, sort of. Consider the above equation, $HCl_{(g)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$. The HCl donates their hydrogen ions as acids, but then the Cl^- ions can subsequently accept those hydrogen ions back, the opposite equation in the equilibrium, thus acting as a base. Thus HCl and Cl^- form a **conjugate acid-base pair**. Similarly with the H_2O and the H_3O^+ , they form a base-acid conjugate pair. The stronger the acid, the weaker its conjugate base will be and there is little incentive to return the other way. Thus HCl is a strong acid while Cl^- is a weak base. Similarly, H_2O is a weak base while the H_3O^+ is a strong acid.
- A salt is defined as an ionic compound whose cation is anything other than H^+ and whose anion is anything other than OH^- or O^{2-} , ie excluding all acids/bases. A salt however does not have to be neutral but can be neutral, acidic or basic; this is because when the ions in the salt react with water (known as hydrolysis), H^+ and OH^- ions can be produced as they are often conjugate acids or bases. **Neutral** salts include **Sodium Chloride ($NaCl$)** and **Calcium Nitrate ($Ca(NO_3)_2$)**. **Acidic** salts include **Ammonium Chloride (NH_4Cl)** and **Sodium Hydrogen Sulfate ($NaHSO_4$)**. **Basic** salts include **Sodium Acetate ($NaCH_3COO$)** and **Potassium Fluoride (KF)**. The way to predict or determine whether a salt will be neutral, basic or acidic is to look at the reactants in the neutralisation reaction that formed it. If the salt formed from a strong acid (eg HCl) and a weak base (eg NH_3) then the resulting salt (NH_4Cl) will be slightly acidic, the Chlorine ions do not want to accept at all while the ammonium ions will want to donate, thus when reacting with water the solution will be acidic. Similarly if the salt has ions from a strong base ($NaOH$) and a weak acid (CH_3COOH) then the salt ($NaCH_3COO$) will be slightly basic. Neutral salts are formed from reacting either a weak acid with a weak base or a strong acid with a strong base ($NaCl$).
- Depending on the equilibrium status and the so called stress on one side of the equation, some substances can react as both Brönsted-Lowry theory bases and acids. These substances are called **amphiprotic** and are defined as being able to act as **both Brönsted-Lowry theory bases and acids** as opposed to *amphoteric* substances which merely react as either acids or bases, but are not necessarily proton acceptors and donors. Examples include water, best seen in the reaction $H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$. The hydrogen carbonate ion (HCO_3^-) is another example, shown above and the hydrogen sulphate ion (HSO_4^-) also reacts both ways.
- Since an acid donates protons and a base accepts protons, a **neutralisation reaction** can be considered as the transfer of a proton to nullify the acidic/basic nature of the reactants. These reactions are many of the

basic formulae you remembered in year 10 with the assistance of the toilet door. As the neutral state is much more stable, this reaction is highly exothermic.

- **Acid-base Titrations** are a form a **volumetric analysis** which enables chemists to determine the concentration of an unknown acid/base. If we have a **known volume** and **concentration** of an acid/base, we can volumetrically add the unknown base/acid until the **neutralisation reaction** is complete, which by then examining the equation, we can determine the concentration. To start with, we must have a solution of **accurately known concentration**,



- (a) Accurately weigh out a mass of sodium carbonate (primary standard).
- (b) Transfer the Na_2CO_3 to a volumetric flask.
- (c) Ensure complete transfer of Na_2CO_3 by washing with water.
- (d) Dissolve the Na_2CO_3 in water.
- (e) Add water to make the solution up to the calibrated mark.

termed as a **standard solution**. A **primary standard** is the first standard solution and is prepared **gravimetrically**, whose solid substance is inert in the atmosphere so it cannot gather any impurities and has a high molecular mass to minimise weighing errors. It is then **dissolved in a solvent** and the concentration determined. It is then possible to **standardise** other solutions using titration to make them standard solutions as many times as you want (with increasing error). Sodium hydroxide for instance **deliquesces** very easily so must be standardised against something like anhydrous sodium carbonate.

In **Titration**; a **pipette** is used to deliver the standard solution with known volume to a volumetric flask. A **burette** is then used to accurately deliver a volume between 0.0 mL to 50.0 mL of the unknown solution. An **indicator** has been added to the **volumetric flask** such that when the point at which the neutralisation reaction completes, called the **equivalence point**, is reached, the indicator will **change colour**. This occurs when the **mole ratio** in solution is equal to the mole ratio in the complete reaction equation and is known as the **end point** in titration. The equivalence point is reached by just one drop of the unknown solution, as shown on the graphs below. In a titration between a **strong acid** and **strong base**, the equivalence point will be near seven. With a **strong base** but **weak acid**, the equivalence point will be slight basic (because the salt produced will be slightly basic), thus phenolphthalein is a common indicator. Similarly a **strong acid** and **weak base** will form a slightly acidic equivalence point, thus methyl orange is useful. A titration between a **weak base** and a **weak acid** will not create such a rapid change near the equivalence point so indicator titration is generally not usable. Once the volumes are determined, and the mole ration determined, then the titration formula (right) is used to determine the concentration of the solution. And we are finished!

$$\frac{C_A \cdot V_A}{n_A} = \frac{C_B \cdot V_B}{n_B}$$

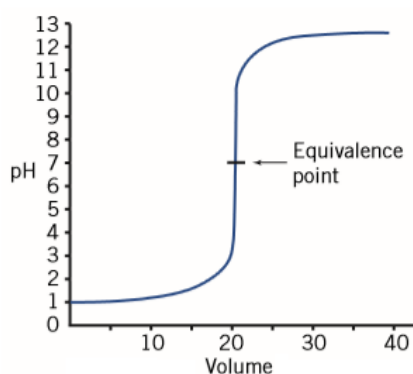


Figure 10.4 Titration curve for strong acid–strong base

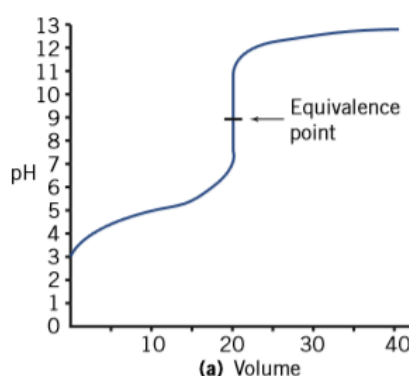
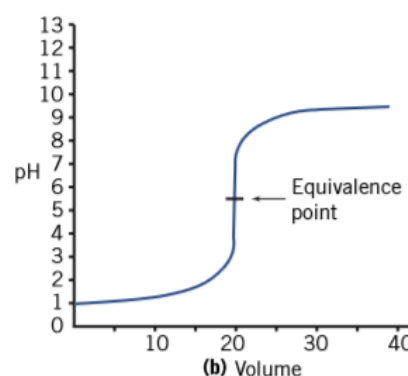


Figure 10.5 Titration curves for (a) weak acid, strong base and (b) strong acid, weak base



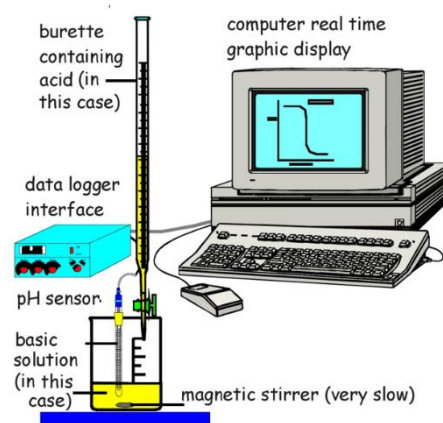
- **Buffers** are substances that are in **equilibrium** and thus **resist a change in pH**, sometimes reducing the change by a factor of 400. Buffers contain approximately equal amounts of a **weak acid** and its **conjugate base**. Thus when either hydroxide or hydronium ions are added to the solution, the equilibrium shifts to resist this change. A good example is within **biological organisms**. Biochemical processes can only be

conducted within a very narrow pH range, the blood for instance has a pH of about 7.4. If this fluctuates to less than 7.35 or greater than 7.45, a life threatening condition occurs although death occurs at about 6.8 or 7.8. Thus a **carbonic/ hydrogen carbonate buffer system** is used $H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$. This is also linked to the carbon dioxide in the **lungs**, which enables the body to maintain a pH of 7.4.

Students:

- Ignoring, same as first few dot points in *Students Learn To*.
- **Practical Investigation – Acid/Base Salt Solutions.** Aim: to identify the pH of a range of salt solutions. **Independent Variable** – salt being tested; **Dependent Variable** – the corresponding pH of solution. **Method:** Prepare a wide variety of salts, ammonium chloride (NH₄Cl), sodium chloride (NaCl), sodium carbonate (Na₂CO₃) and potassium acetate (KCH₃COO), and create solutions of equal molar value. Use a data logger and probe to measure the different salt solutions. **Results:** as in table.
- **Practical Investigation – Titration.** Titrate, you know how to do it.
- **Practical Investigation – Concentration of a Domestic Acid.** Conduct a titration against a domestic acid, say vinegar, but stick a probe in there. The endpoint is where the titration curve changes most rapidly. Setup is as right.
- When corrosive acids or bases are involved in spills or accidents, neutralisation is an efficient measure to alleviate the damage. **Sodium hydrogen carbonate** is particularly effective as it contains the **amphiprotic hydrogen carbonate ion**. This means it can neutralise both acidic and basic spills and is even more effective as it **reacts quickly**. It's also **solid** and thus **easily stored** and **quickly distributed**. It is also **relatively cheap** and thus can be bought in **relatively large quantities**, which is necessary since it is a **weak acid/base**. It is **not itself corrosive** and thus can be used **liberally**, particularly efficient as it is impractical to calculate the required moles to perfectly neutralise a spill without leaving excess. However, as **neutralisation reactions are highly exothermic**, if it was used to neutralise on human flesh for instance, it would **cause severe burns**. Thus, for human spills, douse with **copious quantities of water**. Thus neutralisation reactions are particularly effective at cleaning spills on inanimate/ robust objects however on heat vulnerable objects, it is even more damaging and thus counterproductive.

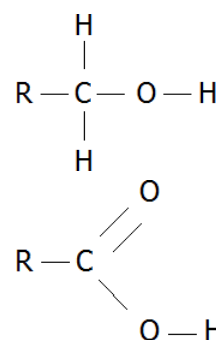
Salt	pH
NH ₄ Cl	5.2
NaCl	7.1
Na ₂ CO ₃	10.8
KCH ₃ COO	9.7



5. Esterification is a naturally occurring process which can be performed in the laboratory.

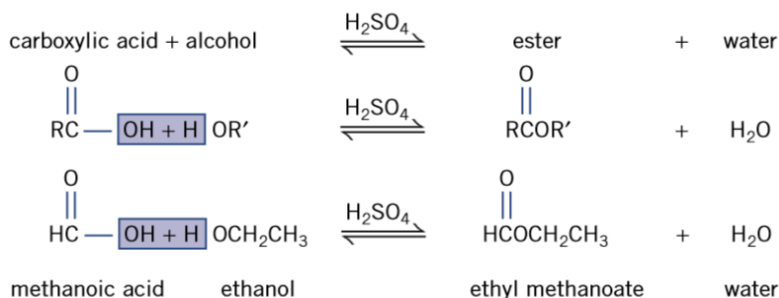
Students learn to:

- **Alkanols** are straight chained saturated hydrocarbons with a functional group **OH**. Alkanols are named by replacing the 'e' in alkane naming with an 'ol'. **Alkanoic Acids** are also straight chained saturated hydrocarbons with a functional group **COOH** (the carbon is attached to the chain). Alkanoic acids are named by replacing the 'e' with '-oic acid'. Thus alkanol and carboxylic acids only differ by replacing two hydrogens with a double bonded oxygen.
- **Esters** are produced by reacting Alkanols and Alkanoic acids. **IUPAC** names esters by taking the alkanol, and giving it branch status as an alkyl or aromatic group, '-yl'. The Alkanoic ending is replaced with '-oate'. For example, methanol and propanoic acid react to form **methylpropanoate**.
- Both Alkanols and Alkanoic acids having hydroxyl groups which form **hydrogen bonding**. Thus they have **much greater melting and boiling points** when compared to molecules of similar mass, Alkanoic acids more than Alkanols as the double bonded oxygen allows for extra hydrogen bonds. Due to these hydrogen



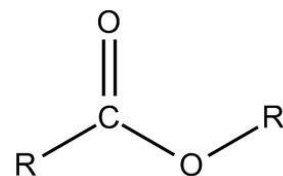
bonds, both Alkanols and Alkanoic acids are **soluble in water**. Esters on the other hand have no hydrogen bonds thus have low melting and boiling points compared to the reactants and are insoluble in water.

- **Esterification** is the reaction between an Alkanol and an Alkanoic acid. It is a **condensation reaction**



eliminating water where the hydroxyl functional group from the carboxylic acid bond with the hydrogen from the alkanol leaving the oxygen from the alkanol to bond with the carbon. Esterification is an **exothermic reaction** however esterification is conducted at temperatures from 333K to 370K, depending on the ester being produced, as this greatly **increases the rate of reaction**. This heat is provided indirectly to prevent combustion, e.g. through a water bath. The **reaction yield is increased** by adding excess alkanol. The general formula for an ester is displayed right and equations are above.

- A **concentrated sulfuric acid catalyst** is utilised in **esterification** to increase the rate of reaction by lowering the activation energy. As it is an equilibrium reaction, a catalyst increases both forward and backward reactions allowing it to reach equilibrium faster. It also reacts with the water produced to continue the reaction moving right.
- As many esters being produced are **volatile** (readily evaporate) a process called **refluxing** is required to prevent them from escaping before equilibrium is reached. **Refluxing** is similar to distilling involving a **condensation jacket** and a **dufton/ fractionating column** as pictured on next page. The reaction occurs at temperatures such that when the ester is formed, it evaporates however reflux dictates it condenses again back into the solution or into a separate catchment.
- **Esters** occur **naturally** and are often complex combinations, although some can be pinpointed as characteristic of a typical flavour or smell, for instance a ripe pineapple will contain mainly **ethyl ethanoate**. Esters are industrially produced for many reasons, mainly as **fragrances** in the **cosmetics industry** or as **artificial flavouring** in the **food industry**. The natural scent of flowers, etc. is produced by a complex mix of esters which can be recreated chemically by reproducing the significant ones. **Natural flavours**, also mainly esters can be similarly reconstructed in foods. **Short chain esters** can also be used as **industrial solvents** in nail polish remover, etc. **Solid animal fats** and **organic oils** are also complex esters formed from **glycerol** and either **saturated or unsaturated fatty acids**. Fats are generally from saturated acids while oils are largely composed of unsaturated acids. Margarine is produced from vegetable oils hydrogenated to make it solid. **Waxes** are produced from **long chain aliphatic** (compounds which do not contain weird electron sharing rings like benzene) Alkanols and Alkanoic acids making them harder than fats due to more dispersion forces.



Students:

- **Practical Investigation. Aim:** to prepare an ester. Variables inapplicable. **Method:** set up apparatus as shown right. Water bath to provide indirect heating, boiling chips to provide consistent boiling, alkanol and Alkanoic acid with small amount of concentrated sulfuric acid catalyst in flask, condensation jacket attached to fractionating column and flask for reflux. **Results:** esterification occurs with small amount of ester appearing as insoluble miscible layer on top of aqueous solution. Reflux allows volatile esters to form. Esters have a strong scent.

