EXCEL YEAR 12 CHEMISTRY PASS CARDS

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YOUR PATH TO SUCCESS!
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In chemical systems the particles are always in constant motion at a fixed temperature.

In a static chemical equilibrium, both forward and backward reactions have come to a halt as no changes occur at the molecular level.

In a dynamic chemical equilibrium the forward and reverse reactions occur at the same rate.

In chemical systems reactions may occur in the forward and reverse directions. They are said to be reversible.

The attainment of equilibrium depends on whether the system is open or closed.

A closed system is a system in which components cannot escape. Chemical reactions are therefore reversible in closed systems.
The following equilibrium exists in a solution of cobalt (II) chloride:

$$\text{Co(H}_2\text{O)}_6^{2+}(aq) + 4\text{Cl}^- (aq) \rightleftharpoons \text{CoCl}_4^{2-}(aq) + 6\text{H}_2\text{O}(l)$$

The Co(H$_2$O)$_6^{2+}$ ion is pink and the CoCl$_4^{2-}$ ion is blue.

The addition of HCl or NaCl solutions increases the chloride ion concentration so that the equilibrium shifts to the right and the system becomes more blue. A new equilibrium position is established.

The addition of more water causes the equilibrium to shift to the left and the system becomes more pink. A new equilibrium position is established.

Repeated changes to the concentration of chloride ions or water show that this reaction is reversible.
When hydrocarbons undergo complete combustion in an excess of oxygen, carbon dioxide and water are formed. These reactions are strongly exothermic:

\[
\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})
\]

The release of heat energy in this exothermic reaction drives the reaction in the forward direction. The reaction is spontaneous as the Gibbs free energy change is negative (\(\Delta G < 0\)).

The high activation energy for the reverse reaction reduces the chance that products will recombine to form reactants.

As combustion reactions occur in open systems, the products can escape into the surroundings and therefore they cannot recombine to produce reactant molecules.
Photosynthesis

Photosynthesis occurs in the chloroplasts of green plant cells. Solar energy is absorbed by chlorophyll molecules inside the chloroplasts.

Chlorophyll selectively absorbs red and violet light in the visible spectrum.

This energy is used to convert carbon dioxide and water into glucose and oxygen:

\[ 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \]

The Gibbs free energy change for photosynthesis is positive (\( \Delta G > 0 \)) and therefore the reaction is non-spontaneous. This reaction requires solar energy to occur.

The reaction products are lost from the system and this prevents the reverse reaction occurring.
In an **endothermic process** the activation energy for the forward reaction is much greater than the activation energy for the reverse reaction. Heating the system increases the forward rate at which reactants are turned into products. The equilibrium shifts to the right as more products form.

In an **exothermic process** the activation energy for the reverse reaction is much greater than for the forward reaction. If the system is heated the rate of the reverse reaction increases and more reactants form. The equilibrium shifts to the left.

The **rate of a reaction** is dependent on the frequency of collision between reacting particles. The greater concentration of the reacting particles, the greater the collision frequency. Over time the reacting particles are consumed and their concentration decreases.

**Equilibrium** is achieved when the rate of the forward reaction equals the rate of the reverse reaction.
Le Chatelier’s principle states:
When a change is made to an equilibrium system, the system moves to counteract the imposed change and restore the system to a new equilibrium.

The new equilibrium position differs from the old equilibrium position. The position of an equilibrium refers to the comparative concentration of reactants and products.

Example: $2\text{CrO}_4^{2-}(aq) + 2\text{H}^+(aq) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(aq) + \text{H}_2\text{O}(l)$
- The chromate ion ($\text{CrO}_4^{2-}$) is yellow and the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is orange.
- Increasing the concentration of hydrogen ions is a change in the system.
- According to Le Chatelier’s principle, to counteract the change the hydrogen ion concentration is decreased by chromate ions reacting with some of the hydrogen ions to produce more dichromate ions. Thus the system becomes more orange. A new equilibrium position is established.
In **homogeneous gaseous systems**, changes in pressure (caused by changes in the volume of the vessel) will lead to changes in concentrations of reactants or products.

In general an **increase in total pressure by volume reduction** causes a gaseous equilibrium to shift to the side of fewer gas molecules. If the number of particles is the same on each side of the equilibrium, then a change in total pressure has no effect.

**Example:** \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \)

- \( \text{N}_2\text{O}_4 \) is colourless and \( \text{NO}_2 \) is brown.
- If the volume of the reaction vessel is increased, the total pressure decreases (Boyle’s law).
- According to Le Chatelier’s principle, the system counteracts the change by shifting to the right to increase the number of particles. The system will become more brown.
A saturated sodium chloride solution is an example of a heterogeneous equilibrium. Solid salt crystals are in equilibrium with ions in solution:

\[ \text{NaCl}(s) \rightleftharpoons \text{Na}^+(aq) + \text{Cl}^-(aq) \]

If drops of concentrated hydrochloric acid are added to the saturated solution, the concentration of chloride ions increases. This disturbance shifts the equilibrium to the left to counteract the change. More NaCl crystals form.

If additional NaCl crystals are added to the saturated solution, no change is observed as the sodium and chloride ions are already at their maximum concentration in the water.

Adding water will dilute the concentration of the ions. The equilibrium shifts to the right as more salt crystals dissolve to restore the system to saturation.
FACTORS THAT AFFECT EQUILIBRIUM

Heterogeneous equilibria 2

The **thermal decomposition** of solid calcium carbonate in a closed system is an example of a heterogeneous reaction because the carbon dioxide produced is gaseous:

$$\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$$

The **equilibrium** is endothermic in the forward direction. If the system is heated to a higher temperature, the equilibrium shifts to the right (according to Le Chatelier’s principle) to counteract the change and the partial pressure of carbon dioxide increases.

The **addition of more solid calcium oxide** or solid calcium carbonate causes no change to the equilibrium position.

The **addition of more carbon dioxide** gas raises the gas pressure and causes the equilibrium to shift to the left to counteract the change. The partial pressure of carbon dioxide will decrease until the new equilibrium is established.
The equilibrium constant expression

- The position or extent of a chemical equilibrium can be expressed quantitatively using the equilibrium constant ($K_{eq}$). If the value of $K_{eq}$ is large then the equilibrium lies to the product side. If $K_{eq}$ is small then the equilibrium lies to the reactant side.

- Consider the following homogeneous gaseous equilibrium:

\[ 2A_2(g) + 3B_2(g) \rightleftharpoons 2A_2B_3(g) \]

- The equilibrium constant for this equilibrium is:

\[ K_{eq} = \frac{[A_2B_3]^2}{[A_2]^2[B_2]^3} \]

- If $K_{eq} >> 1$, then the equilibrium lies to the right.

- If $K_{eq} << 1$, then the equilibrium lies to the left.
Determining the equilibrium constant

- The decomposition equilibrium for ammonia is:
  \[2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)\]
- The \(K_{eq}\) expression is 
  \[K_{eq} = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}\]
- The following equilibrium data was collected at 30 MPa and 427 °C:

<table>
<thead>
<tr>
<th>[\text{NH}_3] (mol/L)</th>
<th>[\text{N}_2] (mol/L)</th>
<th>[\text{H}_2] (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.42</td>
<td>0.71</td>
<td>2.14</td>
</tr>
</tbody>
</table>

- The value of \(K_{eq}\) can now be calculated:
  \[K_{eq} = \frac{[0.71][2.14]^3}{[1.42]^2} = 3.5\]
- \(K_{eq} > 1\). The equilibrium lies slightly to the right.
The dimerisation equilibrium for nitrogen dioxide is:

$$2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$$

The following experimental equilibrium data was collected at two temperatures:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>NO$_2$ (mol/L)</th>
<th>N$_2$O$_4$ (mol/L)</th>
<th>$K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.370</td>
<td>9.815</td>
<td>71.7</td>
</tr>
<tr>
<td>43</td>
<td>2.58</td>
<td>8.71</td>
<td>1.31</td>
</tr>
</tbody>
</table>

The equilibrium lies further to the right at 0 °C.

The equilibrium is exothermic in the forward direction because higher temperatures reduce the value of the equilibrium constant as the equilibrium shifts to the left.
Dissociation of ionic compounds

- Ionic compounds have different solubilities in water. At 25 °C a saturation equilibrium is achieved when the salt reaches its maximum solubility.

- The product of the ion concentrations of the salt is called the ionic product (IP).

- IP increases as more salt dissolves and reaches a constant value once saturation is achieved.

- For CaI$_2$, the dissociation equilibrium is:
  \[
  \text{CaI}_2(\text{s}) \leftrightharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq})
  \]
  For a saturated solution of CaI$_2$, $IP = [\text{Ca}^{2+}][\text{I}^-]^2 = 0.34 \text{ mol}^3 \text{ L}^{-3}$
The degree of dissociation of a weak acid can be calculated by measuring the concentration of hydronium ions formed from a solution of the acid of known concentration.

Consider a weak acid, HA. The dissociation equilibrium equation is:

\[ \text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-\text{(aq)} \]

The degree of dissociation can be determined using the equation:

\[ \text{Degree of dissociation} = \frac{[\text{H}_3\text{O}^+]}{[\text{HA}]} \times 100/1\% \]

A solution of hydrofluoric acid at 25 °C has a hydronium ion concentration of 0.00412 mol/L and a HF concentration of 0.0250 mol/L.

The degree of dissociation is

\[ \frac{0.00412}{0.0250} \times 100 \times 1 = 16.5\% \]

See Excel Year 12 Chemistry p. 39
SOLVED EQUILIBRIA

Solubility

- **Ionic and molecular compounds** vary in their water solubility. In general solubility increases with increasing temperature.

- For **ionic compounds undergoing dissolution** the ions are stabilised in the water by attraction between the ions and water dipoles.

- **Ionic sulfides, oxides and carbonates** are generally insoluble in water, whereas nitrates, chlorides and sulfates are generally soluble.

- **Polar organic molecules** contain polar functional groups (e.g. OH, COOH, NH$_2$) that improve solubility, particularly if they can hydrogen bond with water molecules.

- **Toxic polar organic compounds** found in some plants and fruits can slowly be removed by continued washing of the crushed flesh with water. This technique was used by Indigenous Australians to make various native fruits edible.
The **solubility rules** are used to identify ions in solution.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Solubility rule</th>
</tr>
</thead>
<tbody>
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<td>NO$_3^-$</td>
<td>All nitrates are soluble.</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>Most chlorides are soluble except AgCl and PbCl$_2$.</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>Most bromides are soluble except AgBr and PbBr$_2$.</td>
</tr>
<tr>
<td>I$^-$</td>
<td>Most iodides are soluble except AgI and PbI$_2$.</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>Most sulfates are soluble except BaSO$_4$, PbSO$_4$.</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>Most carbonates are insoluble except Group 1 carbonates.</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>Most hydroxides are insoluble except Group 1 hydroxides and Ba(OH)$_2$.</td>
</tr>
</tbody>
</table>

All sodium and potassium salts are soluble.

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**MODULE 5: EQUILIBRIUM AND ACID REACTIONS**

See *Excel* Year 12 Chemistry p. 49
For any saturated solution of an ionic solid $M_x N_y$, the dissolution equilibrium equation is:

$$M_x N_y(s) \leftrightharpoons xM^{y+}(aq) + yN^{x-}(aq)$$

The equilibrium constant expression for this solubility equilibrium is called the solubility product constant, symbol $K_{sp}$.

$$K_{sp} = [M^{y+}]^x[N^{x-}]^y$$

Examples:

1. $\text{PbCl}_2(s) \leftrightharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq); \quad K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.7 \times 10^{-5}$

2. $\text{PbI}_2(s) \leftrightharpoons \text{Pb}^{2+}(aq) + 2\text{I}^-(aq); \quad K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 = 9.8 \times 10^{-9}$

$\text{PbI}_2$ is more insoluble than $\text{PbCl}_2$ as the $K_{sp}$ is smaller for $\text{PbI}_2$. See Excel Year 12 Chemistry p. 51
**SOLUTION EQUILIBRIA**

**Predicting precipitation**

**Question:**
20 mL of 0.0010 mol/L magnesium nitrate is added to 20 mL of 0.0010 mol/L sodium carbonate. Determine whether or not precipitation of magnesium carbonate will occur.

\[ K_{sp} (\text{MgCO}_3) = 2 \times 10^{-5} \]

**Answer:**

\[ n(\text{Mg}^{2+}) = (0.0010)(0.020) = 2.00 \times 10^{-5} \text{ mol} \]

\[ n(\text{CO}_3^{2-}) = (0.0010)(0.020) = 2.0 \times 10^{-5} \text{ mol} \]

Volume on mixing = 20 + 20 = 40 mL = 0.040 L

\[ [\text{Mg}^{2+}] = \frac{2.0 \times 10^{-5}}{0.040} = 5.0 \times 10^{-4} \text{ mol/L} \]

\[ [\text{CO}_3^{2-}] = \frac{2.0 \times 10^{-5}}{0.040} = 5.0 \times 10^{-4} \text{ mol/L} \]

\[ IP = [\text{Mg}^{2+}][\text{CO}_3^{2-}] = (5.0 \times 10^{-4})(5.0 \times 10^{-4}) = 2.5 \times 10^{-7} \]

\[ IP < K_{sp}. \text{ Therefore no precipitate of MgCO}_3 \text{ will form.} \]
Common laboratory acids include:
- hydrochloric acid (HCl)
- nitric acid (HNO₃)
- sulfuric acid (H₂SO₄)

Common laboratory bases include:
- sodium hydroxide (NaOH)
- potassium hydroxide (KOH)
- ammonia solution (NH₃(aq))

Common household acids include:
- acetic acid (in vinegar)
- citric acid in oranges/lemons
- carbonic acid (in soda water)

Common household bases include:
- baking soda (NaHCO₃)
- washing soda (Na₂CO₃)
- ammonia solution in floor/window cleaners
### Properties of acids and bases

<table>
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<th>Acids</th>
<th>Bases</th>
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<tbody>
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<td>weak diluted acids taste sour</td>
<td>weak diluted bases taste bitter</td>
</tr>
<tr>
<td>turn blue litmus red</td>
<td>turn red litmus blue</td>
</tr>
<tr>
<td>neutralise bases</td>
<td>neutralise acids</td>
</tr>
<tr>
<td>react with and dissolve active metals</td>
<td>generally do not react with active metals</td>
</tr>
<tr>
<td>react with carbonates with the evolution</td>
<td>do not react with carbonates</td>
</tr>
<tr>
<td>of carbon dioxide gas</td>
<td></td>
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</tbody>
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See [Excel Year 12 Chemistry p. 59](#)
Acid–base indicators change colour as the acidity of the surroundings change.

The following table summarises the changes.

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<th>Low acidity</th>
<th>Neutral</th>
<th>Low alkalinity</th>
<th>High alkalinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl orange</td>
<td>red</td>
<td>orange to yellow</td>
<td>yellow</td>
<td>yellow</td>
<td>yellow</td>
</tr>
<tr>
<td>litmus</td>
<td>red</td>
<td>red</td>
<td>purple</td>
<td>blue</td>
<td>blue</td>
</tr>
<tr>
<td>bromothymol blue</td>
<td>yellow</td>
<td>yellow</td>
<td>green</td>
<td>blue</td>
<td>blue</td>
</tr>
<tr>
<td>phenolphthalein</td>
<td>colourless</td>
<td>colourless</td>
<td>colourless</td>
<td>pink</td>
<td>crimson</td>
</tr>
</tbody>
</table>
PROPERTIES OF ACIDS AND BASES

Acid–base reactions

When an **acidic solution reacts with a base**, such as a metal oxide or metal hydroxide, a neutralisation reaction occurs. The products of such acid–base reactions are water and a salt.

**Examples:**

1. Copper (II) oxide is neutralised by dilute sulfuric acid to form copper (II) sulfate and water. The black copper (II) oxide solid gradually dissolves and the blue copper (II) sulfate product is water soluble:
   \[
   \text{CuO(s)} + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CuSO}_4(aq) + \text{H}_2\text{O(l)}
   \]

2. Cobalt (II) hydroxide is neutralised by the hydrochloric acid to form cobalt (II) chloride and water. The purple cobalt (II) hydroxide solid gradually dissolves and a solution of pink-red cobalt (II) chloride forms:
   \[
   \text{Co(OH)}_2(s) + 2\text{HCl(aq)} \rightarrow \text{CoCl}_2(aq) + 2\text{H}_2\text{O(l)}
   \]
PROPERTIES OF ACIDS AND BASES

Acid–carbonate reactions

When an acid–carbonate reaction occurs, a neutralisation reaction occurs. The products of such reactions are carbon dioxide, water and a salt.

Examples:
1. Copper (II) carbonate is neutralised by the nitric acid to form copper (II) nitrate, carbon dioxide and water. The green solid gradually dissolves and a solution of blue copper (II) nitrate forms:
   \[
   \text{CuCO}_3(s) + 2\text{HNO}_3(aq) \rightarrow \text{Cu(NO}_3)_2(aq) + \text{H}_2\text{O(l)} + \text{CO}_2(g)
   \]
2. Baking soda (sodium hydrogen carbonate) is a white solid that is neutralised by a solution of citric acid to form a colourless solution of sodium citrate, carbon dioxide and water. This reaction is used in cooking as a rising agent because of the evolved carbon dioxide:
   \[
   3\text{NaHCO}_3(s) + \text{C}_3\text{H}_5\text{O(COOH)}_3(aq) \rightarrow \text{Na}_3(\text{C}_3\text{H}_5\text{O(COO)}_3)(aq) + 3\text{H}_2\text{O(l)} + 3\text{CO}_2(g)
   \]
The reaction of active metals with dilute hydrochloric or sulfuric acid is an example of an oxidation-reduction reaction rather than a neutralisation reaction.

The metal is oxidised to form a metal ion. The hydronium ions in the acidic solution are reduced to hydrogen gas. Water is also formed.

Examples:

1. Zinc solid dissolves in dilute hydrochloric acid and a colourless solution of zinc chloride and hydrogen gas are formed:
   \[
   \text{Zn(s)} + 2\text{H}_3\text{O}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g) + 2\text{H}_2\text{O}(l)
   \]

2. Iron solid dissolves slowly in dilute sulfuric acid to form a pale-green solution of iron (II) sulfate. Hydrogen gas is evolved:
   \[
   \text{Fe(s)} + 2\text{H}_3\text{O}^+(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{H}_2(g) + 2\text{H}_2\text{O}(l)
   \]
Neutralisation can be used to reduce the symptoms of gastric acid reflux.

Commercial antacids are used to neutralise excess acid. These antacids contain weak bases such as magnesium hydroxide, aluminium hydroxide and sodium hydrogen carbonate.

The neutralisation reactions remove the excess hydrochloric acid that burns the oesophagus during gastric reflux:

\[
\text{Mg(OH)}_2(s) + 2\text{H}_3\text{O}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + 4\text{H}_2\text{O}(l)
\]

\[
\text{Al(OH)}_3(s) + 3\text{H}_3\text{O}^+(aq) \rightarrow \text{Al}^{3+}(aq) + 6\text{H}_2\text{O}(l)
\]

\[
\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{Na}^+(aq) + 2\text{H}_2\text{O}(l) + \text{CO}_2(g)
\]
Optimal plant growth depends on the acidity or pH of the soil. Camellias grow best in moderately acidic soils (pH 4.5–5.5) whereas chrysanthemums grow best in mildly acidic soils (pH 6.0–6.3).

Decreasing soil acidity can be achieved by adding weakly basic substances that neutralise excess soil acidity. Adding powdered limestone (CaCO$_3$) to an acidic soil reduces the acidity of the soil water as calcium carbonate is a weak base and a neutralisation reaction occurs:

$$\text{CaCO}_3(s) + 2\text{H}_3\text{O}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + 3\text{H}_2\text{O}(l) + \text{CO}_2(g)$$

To monitor the acidity of soil water during these pH adjustments a wet soil sample is placed in a Petri dish and white barium sulfate is applied to the wet soil surface. The soil water absorbs into the BaSO$_4$ layer. When universal indicator is added to the white layer the colour change reveals the pH of the soil water.
Example:
50.0 mL of 1.0 mol/L potassium hydroxide solution and 50.0 mL of 1.0 mol/L hydrochloric acid were mixed in a polystyrene foam calorimeter. The mixture had a mass of 0.1038 kg and the temperature increased by 6.5 °C during the neutralisation. (Assume $c = 4.2 \times 10^3 \text{ J/kg/K}$)

Answer:

\[
\text{HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H}_2\text{O(l)}
\]

\[
q = mc\Delta T = (0.1038)(4.2 \times 10^3)(6.5) = 2834 \text{ J}
\]

\[
n(\text{HCl}) = (1.0)(0.050) = 0.050 \text{ mol;}
\]

\[
n(\text{KOH}) = (1.0)(0.050) = 0.050 \text{ mol}
\]

\[
\Delta H = -\frac{q}{n} = -\frac{2834}{0.050} = -5668 \text{ J/mol} = -56.7 \text{ kJ/mol}
\]
PROPERTIES OF ACIDS AND BASES

Theories of acids 1

- **Antoine Lavoisier (1776)—the oxygen theory**
  - Lavoisier demonstrated that non-metallic oxides (e.g. sulfur trioxide) dissolved in water made the water acidic.
  - Lavoisier proposed that oxygen was the cause of acidity. Lavoisier’s theory could not explain why metal oxides were not acidic.

- **Humphry Davy (1810)—the hydrogen theory**
  - Davy observed that when HCl gas and H$_2$S gas dissolved in water they produced acidic solutions. These molecules contained no oxygen atoms. Davy’s theory attributed acidity to the presence of replaceable hydrogen. These results were not consistent with Lavoisier’s oxygen theory.
  - Davy’s theory could not explain why not all hydrogen compounds were acidic.
Svante Arrhenius (1884)—the hydrogen ion theory

- **Arrhenius observed** that acidic solutions conducted electricity just like salt solutions. He proposed that acids released hydrogen ions when they dissolved in water.

- **Arrhenius proposed** that alkalinity was due to the presence of hydroxide ions in solution.

- **Arrhenius explained** how acid solutions neutralised alkaline solutions in terms of the interaction of the aqueous hydrogen ions and hydroxide ions:
  \[ \text{OH}^- (\text{aq}) + \text{H}^+ (\text{aq}) \rightarrow \text{H}_2\text{O}(l) \]

- **Arrhenius’s theory also explained** the difference between strong acids such as hydrochloric acid (HCl) and weak acids, such as hydrofluoric acid (HF) as being due to their different degrees of dissociation in water.
Johannes Brønsted and Thomas Lowry (1923)—the proton theory

- Hydrogen ions are protons. These protons associate with water molecules to form hydronium ions ($\text{H}_3\text{O}^+$). B/L acids donate protons and B/L bases accept protons.
- Bases include substances that neutralise acids but which are not classified as alkalis as no $\text{OH}^-$ ions are present. In the following equation the hydronium ion donates a proton to the carbonate ion:

$$\text{H}_3\text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{HCO}_3^-(\text{aq})$$

Gilbert Lewis (1923)—the electron pair theory

- A Lewis acid accepts an electron pair and a Lewis base donates an electron pair.
- When hydrogen ions and hydroxide ions undergo neutralisation, the $\text{H}^+$ ion accepts a pair of non-bonding electrons from the oxygen atom of the $\text{OH}^-$ ion to form a covalent bond in the resulting water molecule.
The pH of a solution is defined as:

\[
pH = -\log_{10}[H^+] = -\log_{10}[H_3O^+]
\]

Acidic solutions have a pH < 7. Alkaline solutions have a pH > 7.

**Example:** Calculate the pH of a 0.00250 mol/L nitric acid solution.

**Answer:** Nitric acid is a strong monoprotic acid and completely dissociates in water:

\[
\text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq})
\]

\[
[H_3O^+] = [\text{HNO}_3] = 0.00250 \text{ mol/L}
\]

\[
pH = -\log_{10}[0.00250] = 2.60
\]
The pOH of a solution is defined as:

\[
pOH = -\log_{10}[OH^-]
\]

Acidic solutions have a pOH > 7. Alkaline solutions have a pOH < 7.

[H\(^+\)], [OH\(^-\)] and \(K_w\) (water ionisation constant) are related:

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

pH and pOH are related: \(\text{pH} + \text{pOH} = 14\)

Example: Calculate the pH of a 0.00850 mol/L NaOH solution.

Answer: NaOH is a strong base and fully dissociated in water:

\[
[OH^-] = [\text{NaOH}] = 0.00850 \text{ mol/L}
\]

\[
pOH = -\log_{10}[OH^-] = -\log_{10}(0.00850) = 2.07
\]

\[
\text{pH} = 14 - \text{pOH} = 14 - 2.07 = 11.93
\]
When a solution of a strong acid is mixed with a strong base solution in the correct mole ratio, the final solution will have a pH of 7. If the acid and base solutions are not mixed in the correct mole ratios, then the final mixture will be either acidic or alkaline.

Example:
Calculate the final pH of a solution formed by mixing 200 mL of 0.100 mol/L HNO₃ and 200 mL of 0.100 mol/L Ba(OH)₂.

Answer:

\[ 2\text{HNO}_3(aq) + \text{Ba(OH)}_2(aq) \rightarrow \text{Ba(NO}_3)_2(aq) + 2\text{H}_2\text{O(l)} \]

Stoichiometry = HNO₃ : Ba(OH)₂ = 2 : 1

\[ n(\text{HNO}_3) = (0.100)(0.200) = 0.0200 \text{ mol; } n(\text{Ba(OH)}_2) = (0.100)(0.200) = 0.0200 \text{ mol} \]

The nitric acid is limiting and is completely neutralised, leaving an excess of Ba(OH)₂.

\[ n(\text{Ba(OH)}_2(\text{excess})) = 0.0100 \text{ mol; } n(\text{OH}^-) = 2 \times 0.0100 = 0.0200 \text{ mol} \]

\[ [\text{OH}^-] = \frac{0.0200}{0.400} = 0.0500 \text{ mol/L; } p\text{OH} = -\log_{10}(0.0500) = 1.30; \text{pH} = 14 - 1.3 = 12.7 \]
USING BRØNSTED–LOWRY THEORY

Acid–base conjugate pairs

➔ In the Brønsted–Lowry theory each acid has a corresponding base called the conjugate base. Each Brønsted–Lowry (B/L) base has a corresponding conjugate acid.

➔ A strong Brønsted–Lowry (B/L) acid has a weak conjugate base (e.g. HCl/Cl⁻).

➔ A strong Brønsted–Lowry base has a weak conjugate acid (e.g. OH⁻/H₂O).

Examples:

<table>
<thead>
<tr>
<th>B/L acid</th>
<th>Conjugate base</th>
<th>B/L base</th>
<th>Conjugate acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>HSO₄⁻</td>
<td>SO₄²⁻</td>
<td>HSO₄⁻</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td>H₂O</td>
<td>NH₃</td>
<td>NH₄⁺</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>H₂PO₄⁻</td>
<td>PO₄³⁻</td>
<td>HPO₄²⁻</td>
</tr>
</tbody>
</table>

See Excel Year 12 Chemistry p. 78

MODULE 6: ACID–BASE REACTIONS
When strong acids and strong bases react the products are weak conjugate acids and bases. These neutralisation reactions go to completion. The hydronium ion is a strong acid and the hydroxide ion is a strong base. Water is produced when these ions react:

$$\text{H}_3\text{O}^+ (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) + \text{H}_2\text{O}(l)$$

When a strong acid reacts with a weak base, or a strong base reacts with a weak acid, the reaction also goes to completion:

$$\text{H}_3\text{O}^+ (aq) + \text{NH}_3 (aq) \rightarrow \text{H}_2\text{O}(l) + \text{NH}_4^+ (aq)$$
$$\text{OH}^- (aq) + \text{HF}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{F}^- (aq)$$

When weak acids and weak bases react an equilibrium is established. These reactions do not proceed to completion:

$$\text{NH}_3 (aq) + \text{HF}(aq) \rightleftharpoons \text{NH}_4^+ (aq) + \text{F}^- (aq)$$
In the Brønsted–Lowry theory some species are amphiprotic. This means they can behave as either a Brønsted–Lowry acid or a Brønsted–Lowry base, depending on the other chemical substances present.

**Example:** The hydrogen phosphate ion (HPO$_4^{2-}$)

- **HPO$_4^{2-}$** is a B/L acid:
  \[ \text{HPO}_4^{2-}(aq) + \text{OH}^-(aq) \rightarrow \text{PO}_4^{3-}(aq) + \text{H}_2\text{O}(l) \]

- **HPO$_4^{2-}$** is a B/L base:
  \[ \text{HPO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \]
Hydrolysis of salts

➔ **Water** is a common amphiprotic substance. Water can act as a proton donor or a proton acceptor.

➔ The **salts of weak bases** (e.g. NH$_4$Cl) hydrolyse in water to form acidic solutions as hydronium ions are formed. The ammonium ion acts as a B/L acid and water acts as a B/L base:

\[
\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)
\]

➔ The **salts of weak acids** (e.g. NaCH$_3$COO) hydrolyse in water to form alkaline solutions as hydroxide ions are formed. The acetate ion acts as a B/L base and water acts as a B/L acid:

\[
\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq)
\]
**Indicators and the Brønsted–Lowry theory**

- **Acid–base indicators** are weak acids. Acid–base indicators exist in two forms, the unionised Brønsted–Lowry acid (HIn) and its conjugate base (In\(^-\)):

  \[ \text{HIn (aq)} \rightleftharpoons \text{H}^+(aq) + \text{In}^-(aq) \]

- **The HIn indicator molecule** has a different colour to the In\(^-\) ion.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>HIn</th>
<th>In(^-)</th>
<th>pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl orange</td>
<td>red</td>
<td>yellow</td>
<td>3.1 – 4.4</td>
</tr>
<tr>
<td>bromothymol blue</td>
<td>yellow</td>
<td>blue</td>
<td>6.0 – 7.6</td>
</tr>
<tr>
<td>phenolphthalein</td>
<td>colourless</td>
<td>crimson</td>
<td>8.3 – 10.0</td>
</tr>
</tbody>
</table>

**Example:** Methyl orange is red when the pH < 3.1 and yellow when the pH > 4.4. In the pH range 3.1–4.4 the indicator is orange.
Volumetric analysis is a quantitative laboratory technique used to determine the concentration of a solution by reacting it with another solution of known concentration.

The first step in acid–base volumetric analysis involves the preparation of a solution of known concentrations called the primary standard.

Anhydrous sodium carbonate is one of the most commonly used primary standard bases. It is stable, pure and readily dried so that it can be weighed easily and accurately.

To prepare 250.0 mL of a 0.100 mol/L solution of sodium carbonate, 2.65 g of dried Na₂CO₃ is weighed out, dissolved in water and the solution is quantitatively transferred to a 250 mL volumetric flask. Water is added until the base of the meniscus is on the engraved mark in the volumetric flask. The solution is mixed thoroughly.

See Excel Year 12 Chemistry p. 90
A titration is a volumetric procedure in which a primary standard is used to determine the concentration of a solution of unknown concentration.

Clean a conical flask and a 25 mL pipette with water. Rinse the pipette with the standard sodium carbonate solution. Fill the pipette with the sodium carbonate solution and transfer the solution to the conical flask.

Clean a 50 mL burette with water and then rinse the burette with the acid solution. Discard the washings and fill the burette with the acid (e.g. HCl) solution.

Add four drops of the appropriate indicator (e.g. methyl orange) to the flask and add the acid to the flask until the indicator turns from yellow to orange. The volume of acid is recorded. This volume (called the titre) is used to calculate the acid concentration.
Example:
25.00 mL of the standard 0.0500 mol/L \( \text{Na}_2\text{CO}_3 \) was titrated with a solution of \( \text{HNO}_3 \) of unknown concentration using methyl orange indicator. The average of three titres was 23.45 mL. Calculate the concentration of the nitric acid solution.

Answer:
\[
\text{Na}_2\text{CO}_3 (\text{aq}) + 2\text{HNO}_3 (\text{aq}) \rightarrow 2\text{NaNO}_3 (\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2 (\text{g})
\]

\[
n(\text{Na}_2\text{CO}_3) = c \cdot V = (0.0500)(0.02500) = 1.25 \times 10^{-3} \text{ mol}
\]

Reaction stoichiometry: \( \text{Na}_2\text{CO}_3 : \text{HNO}_3 = 1 : 2 \)

\[
n(\text{HNO}_3) = 2 \times 1.25 \times 10^{-3} = 2.50 \times 10^{-3} \text{ mol}
\]

\[
c(\text{HNO}_3) = \frac{n}{V} = \frac{(2.50 \times 10^{-3})}{0.02345} = 0.107 \text{ mol/L}
\]
To select the most appropriate indicator for the titration, the pH at the equivalence point must be matched to the pH range in which the indicator changes colour. The end point of a titration occurs when the indicator just changes colour.

The indicator must change colour when the pH has its greatest rate of change during the titration.

<table>
<thead>
<tr>
<th>Titration</th>
<th>Suitable indicator(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>strong acid–strong base</td>
<td>methyl orange; phenolphthalein</td>
</tr>
<tr>
<td>strong acid–weak base</td>
<td>methyl orange</td>
</tr>
<tr>
<td>weak acid–strong base</td>
<td>phenolphthalein</td>
</tr>
</tbody>
</table>
Acid dissociation constant ($K_a$)

The equation for the dissociation of a weak acid (HA) in water is:

$\text{HA(aq) + H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$

The equilibrium constant is called the acid dissociation constant ($K_a$):

$K_a = [\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}]$

The smaller the value of $K_a$, the weaker the acid:

- Formic acid (HCOOH): $K_a = 1.8 \times 10^{-4}$
- Acetic acid (CH$_3$COOH): $K_a = 1.7 \times 10^{-5}$

$pK_a$ is defined as $pK_a = -\log_{10}K_a$. The larger the $pK_a$, the weaker the acid.
Applications of acid–base analysis

- **Acid–base titrations** can be used to determine the concentration of sodium hydroxide in a liquid drain cleaner.

- **A pH meter and glass electrode** can be used to determine the acidity of wine.

- The **ascorbic acid content of Vitamin C tablets** can be determined by titrating a solution of the Vitamin C tablet with standardised NaOH using phenolphthalein indicator. Chemists can also determine the Vitamin C content of traditional foods used by Indigenous Australians (e.g. Quandong fruits).

- **A pH titration** can be performed on samples of diluted vinegar to determine the acetic acid content.
Buffers are solutions that resist large changes in pH on the addition of small quantities of strong acids or bases. Buffer solutions contain a weak Brønsted–Lowry acid and its conjugate base, or a weak Brønsted–Lowry base and its conjugate acid.

The greatest buffering effect is obtained if the buffer solution contains equimolar concentrations of the weak acid and its conjugate base.

Example:
Buffer = CH$_3$COOH(aq) + NaCH$_3$COO(aq)

Changes:
1. Add drops of NaOH solution.
2. Add drops of HCl solution.

Buffering action:
1. The hydroxide ions are neutralised by the acetic acid molecules.
2. The hydronium ions are neutralised by the acetate ions.
The **pH of our blood** must remain in the range 7.35 to 7.45. Buffers are used to maintain blood pH. One important buffer system in the blood is the carbonic acid–hydrogen carbonate buffer.

The **buffering equations** are:

1. \( \text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) \)
2. \( \text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq) \)

By **breathing deeper and faster** the carbon dioxide is removed from the blood and the pH rises as both equilibria shift to the left and the hydronium ion concentration decreases.

The **kidneys excrete HCO}_3^- into the blood**. By altering the level of this conjugate base the pH of the blood can be stabilised over a narrow range.
Alkanes are saturated hydrocarbons that contain only carbon–carbon single bonds. The general formula of alkanes is:

\[ C_nH_{2n+2} \quad (n = 1, 2, 3 \ldots) \]

All alkanes are named using the suffix –ane.

The first four alkanes are:
- methane \((n = 1)\) \((CH_4)\);
- ethane \((n = 2)\) \((C_2H_6)\);
- propane \((n = 3)\) \((C_3H_8)\);
- butane \((n = 4)\) \((C_4H_{10})\)

Methyl groups \((CH_3)\) and ethyl groups \((CH_2CH_3)\) are common alkyl groups that form branches along an alkane chain.

Example: \(CH_3CH_2CH(CH_3)CH_2CH_2CH_3 = 3\)-methylhexane
Alkenes and alkynes

- **Alkenes** have a double carbon–carbon bond and alkynes have a triple carbon–carbon bond. They are unsaturated hydrocarbons.

- **Alkene general formula** = \( C_n H_{2n} \);
  alkynie general formula = \( C_n H_{2n-2} \)

- **Alkenes are named** using the –ene suffix.
  Alkynes use the –yne suffix.

**Examples:**
- \( \text{CH}_3 \text{CH}_2 \text{CHCHCH}_2 \text{CH}_2 \text{CH}_3 \): name = hept-3-ene
- \( \text{CH}_3 \text{CH}_2 \text{C(CH}_3\text{)} \text{CHCH}_2 \text{CH}_3 \): name = 3-methylhex-3-ene
- \( \text{CHCCH}_2 \text{CH}_2 \text{CH}_3 \): name = pent-1-yne

See *Excel* Year 12 Chemistry p. 112
Alcohols are organic compounds that contain the hydroxyl functional group (OH).

Alkanols are derivatives of alkanes and their general formula is: \( C_n \text{H}_{2n+1} \text{OH} \). Alkanols are named using the –ol suffix. The –ol suffix has priority over alkyl groups in allocating locant positions of functional groups.

Examples:

\( \text{CH}_3\text{CH(OH)CH}_3 \): name = propan-2-ol
\( \text{CH}_3\text{CH(OH)CH}_2\text{CH(CH}_3\text{)CH}_3 \): name = 4-methylpentan-2-ol
**Alkanols** can be classified as primary, secondary or tertiary. This classification is based on the position of the hydroxyl functional group in the alkanol molecule (R₁, R₂, R₃ = alkyl groups).

- Primary alkanol: R₁CH₂OH
- Secondary alkanol: R₁R₂CHOH
- Tertiary alkanol: R₁R₂R₃COH

**Examples:** Figure PC.1 shows the structural formulas of three alkanols.

<table>
<thead>
<tr>
<th>Primary</th>
<th>Secondary</th>
<th>Tertiary</th>
</tr>
</thead>
<tbody>
<tr>
<td>H H H H H C C C OH H</td>
<td>H H H H H C C C - C - C - H H</td>
<td>H H C - C - C - C - H H</td>
</tr>
<tr>
<td>propan-1-ol</td>
<td>butan-2-ol</td>
<td>2-methylbutan-2-ol</td>
</tr>
</tbody>
</table>

See Excel Year 12 Chemistry p. 114
Carboxylic acids are organic molecules containing the carboxyl (COOH) functional group. This group is always on the first carbon atom in the chain.

Alkanoic acids are carboxylic acids formed from alkanes.

The general formula of alkanoic acids is:

\[ C_nH_{2n+1}COOH \quad (n = 0,1,2,3 \ldots) \]

Alkanoic acids are named using the -oic acid suffix. The preferred IUPAC name for the first two alkanoic acids is their common name rather than their systematic name.

Examples:
- HCOOH: name = formic acid (or methanoic acid)
- CH₃COOH: name = acetic acid (or ethanoic acid)
- CH₃CH₂CH₂CH₂COOH: name = pentanoic acid
The carbonyl group (C=O) is present in both aldehydes and ketones. Aldehydes and ketones formed from alkanes are called **alkanals** and **alkanones**.

**Aldehydes** have the carbonyl group at the first (terminal) carbon. Thus the functional group for aldehydes is CHO. Ketones have the carbonyl group on non-terminal carbon atoms in the chain.

**Alkanals have the general formula** RCHO. Alkanones have the general formula $R_1R_2CO$.

**Alkanals are named** using the $-al$ suffix. Alkanones are named using the $-one$ suffix.

**Examples:**
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$: name = hexanal
- $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$: name = heptan-3-one
Amines and amides

**Amines** are organic molecules containing the amino \((\text{NH}_2)\) functional group. The general formula for primary amino alkanes is:

\[
\text{C}_n\text{H}_{2n+1}\text{NH}_2 \quad (n = 1, 2, 3 \ldots)
\]

Primary amino alkanes are named using the –amine suffix.

**Example:** \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2\): name = butan-1-amine

**Amides** are derivatives of carboxylic acids. The OH group of the carboxylic acid is replaced by an amine \((\text{NH}_2)\) group. The general formula for amides is:

\[
\text{C}_n\text{H}_{2n+1}\text{CONH}_2 \quad (n = 0, 1, 2 \ldots)
\]

Amides are named using the –amide suffix.

**Example:** \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2\): name = butanamide
Halogenated hydrocarbons

- **Halogens** can bond to hydrocarbon molecules to form halohydrocarbons.

- **Halogens are functional groups.** The halogen functional groups are:
  - $\text{Br} = \text{bromo}$; $\text{Cl} = \text{chloro}$; $\text{F} = \text{fluoro}$; $\text{I} = \text{iodo}$

  The halogen functional groups are named using prefixes in the name of the hydrocarbon molecule.

- **The halogens are named alphabetically** in a halogenated hydrocarbon.

  **Examples:**
  - $\text{CH}_3\text{CH}_2\text{CHI}_2$: name = 1,1-diiodopropane
  - $\text{CH}_2\text{CHFCBr}_2\text{CH}_2\text{CH}_2\text{CH}_3$: name = 3,3-dibromo-2-fluorohexane
  - $\text{CHF}_2\text{CH}_2\text{CBr}_2\text{CH}_2\text{CHCl}_2$: name = 3,3-dibromo-1,1-dichloro-5,5-difluoropentane
Isomers are molecules with the same molecular formula but different structural formulas.

1. **Chain isomers**—these isomers differ due to chain branching:
   - \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \) (hexane)
   - \( \text{CH}_3\text{CH}_2\text{CH}((\text{CH}_3))\text{CH}_2\text{CH}_3 \) (3-methylpentane)

2. **Position isomers**—these isomers differ due to different positions of the functional groups:
   - \( \text{CH}_3\text{CHFCH}_2\text{CH}_2\text{F} \) (1,3-difluorobutane)
   - \( \text{CH}_2\text{FCH}_2\text{CH}_2\text{CH}_2\text{F} \) (1,4-difluorobutane)

3. **Functional group isomers**—these isomers differ due to different functional groups:
   - \( \text{CH}_3\text{CH}_2\text{COCH}_3 \) (butanone); \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} \) (butanal)
The structural formulas of hydrocarbons represent the arrangement of atoms in the molecules in two dimensions.

Figure PC.2 shows the structural formulas of an alkane, an alkene and an alkyne.

2-methylpentane

4-methylhex-2-ene

5-methylhept-3-yne
Hydrocarbons are three-dimensional molecules (see Figure PC.3).

In alkanes, carbon–carbon single bonds are formed by the overlap of sp³ hybrid orbitals. This results in a tetrahedral arrangement of atoms around each carbon.

In alkenes, carbon–carbon double bonds are formed by the overlap of sp² hybrid orbitals and p orbitals. This results in a planar arrangement of atoms around the double bond.

In alkynes, carbon–carbon triple bonds are formed by the overlap of sp hybrid orbitals and two sets of p orbitals. This results in a linear arrangement of the triple bond.

Figure PC.3

propane
propene
propyne
Physical properties of hydrocarbons

- **Hydrocarbons** are non-polar molecules. The dispersion intermolecular forces between these molecules are caused by the interaction of temporary dipoles and induced dipoles.

- These dispersion forces are much weaker than the intramolecular chemical covalent bonds joining the atoms together within the molecule.

- The **boiling points of hydrocarbons** increase as the molecular weight of the molecules increases. The larger the molecule, the greater the dispersion forces.

- In general the boiling points of straight chain alkanes and alkenes with the same number of carbon atoms per molecule decrease in the order alkanes > alkenes > alkynes.

- **Low molecular weight hydrocarbons** are volatile and pose a safety risk during use and storage. Sparks can cause fires when exposed to hydrocarbon vapour–air mixtures.
The majority of hydrocarbons are extracted from organic sources such as petroleum and natural gas located in geological structures. Petroleum is a fossil fuel formed by the decay of the remains of plankton and algae over long periods of geological time.

The petroleum is a mixture of crude oil with dissolved hydrocarbon gases. The components of crude oil are separated into fractions containing mixtures of various hydrocarbons.

The petrol fraction (7–9 carbon atoms) is used as a fuel for cars. The kerosene fraction (11–16 carbon atoms) is used as aviation fuel and a solvent. Heavy fractions with greater than 20 carbon atoms are used as waxes, greases and bitumen surfacing of roads.

Hydrocarbons release carbon dioxide on combustion. The increase in atmospheric levels of CO$_2$ over the last 200 years has led to increases in global warming.
PRODUCTS OF REACTIONS INVOLVING HYDROCARBONS

Addition reactions

➔ **Unsaturated hydrocarbons** have reactive double or triple carbon–carbon bonds. These bonds have high electron density and this property promotes reactions with other molecules such as halogens that have high electronegativity.

➔ **Alkenes** react with chlorine to form chlorinated alkanes. Alkenes react with hydrogen bromide to form brominated alkanes via addition reactions.

➔ Alkenes react with hydrogen (over a nickel catalyst) to form alkanes.

**Examples:**

\[
\text{CH}_2\text{CH}_2 + \text{Cl}_2 \rightarrow \text{CH}_2\text{ClCH}_2\text{Cl}; \text{ name of product = 1,2-dichloroethane}
\]

\[
\text{CH}_2\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br}; \text{ name of product = bromoethane}
\]

\[
\text{CH}_2\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3; \text{ name of product = ethane}
\]
PRODUCTS OF REACTIONS INVOLVING HYDROCARBONS

Substitution reactions

- **Alkanes** are relatively unreactive towards many common chemical reagents.

- UV light is used to make alkanes reactive towards molecules such as chlorine. The UV creates reactive free radicals. In **substitution reactions** the halogen atoms replace hydrogen atoms:

  \[
  \text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) + \text{UV} \rightarrow \text{CH}_3\text{Cl}(\text{l}) + \text{HCl}(\text{g})
  \]

- The **chlorinated products** are now more reactive and other compounds can be synthesised from them. Alcohols can be manufactured from these chlorinated products. Methanol can be manufactured from chloromethane:

  \[
  \text{CH}_3\text{Cl}(\text{l}) + \text{KOH}(\text{aq}) \rightarrow \text{CH}_3\text{OH}(\text{aq}) + \text{KCl}(\text{aq})
  \]
Physical properties of alcohols

- **Alcohols** are organic compounds that contain the hydroxyl functional group (OH).

- **Alkanols** are polar molecules due to the polar hydroxyl group. The boiling points of alkanols increases with increasing chain length.

- **Alkanols** are less volatile and much more water soluble than the corresponding alkane. Apart from dipole–dipole attraction, hydrogen bonding is also a significant intermolecular force for short chain alkanols.

- **Ethanol** is an important solvent. The non-polar ethyl (C$_2$H$_5$) group in ethanol assists some low-molecular weight non-polar solutes to dissolve in ethanol. Ethanol–water mixtures are used in many pharmaceutical products.
ALCOHOLS

Enthalpy of combustion of alcohols

- **Calorimetry experiments** can be used to determine the enthalpy of combustion of alcohols.
- The **calorimeter consists** of a Pyrex or metal beaker containing a known mass of water.
- The **alcohol is placed in a weighed spirit burner**. The burning alcohol heats the water and the temperature rise and the mass of alcohol burnt is determined.
- **The results obtained for Δ\(_c\)H using different alkanols** are much lower than the published data because considerable heat is lost to the surroundings and the combustions are incomplete.
- The **longer the hydrocarbon chain of the alkanols**, the more incomplete is the combustion. The flames become increasingly smoky due to the formation of soot:

\[
C_5H_{11}OH(l) + 6O_2(g) \rightarrow 3CO_2(g) + CO(g) + C(s) + 6H_2O(l)
\]

See Excel Year 12 Chemistry p. 145
Reactions of alcohols

Substitution reaction:
- Alkanols undergo substitution reactions when they react with hydrogen halides. An acid catalyst is required:
  \[ \text{CH}_3\text{CH}_2\text{OH}(l) + \text{HBr}(g) \rightarrow \text{CH}_3\text{CH}_2\text{Br}(l) + \text{H}_2\text{O}(l) \]

Dehydration reaction:
- When alkanols are dehydrated, alkenes are formed. Concentrated sulfuric acid is a common dehydrating agent:
  \[ \text{C}_3\text{H}_7\text{OH} (l) \rightarrow \text{C}_3\text{H}_6 (g) + \text{H}_2\text{O}(l) \]

Complete combustion:
- Alkanols undergo complete combustion in excess oxygen to produce CO\(_2\) and H\(_2\)O:
  \[ 2\text{CH}_3\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \]
ALCOHOLS

Oxidation of alcohols

- **Primary alkanols** can be oxidised by a mild oxidant (e.g. $\text{H}^+$/CrO$_3^-$) to form alkanals:
  \[
  \text{C}_3\text{H}_7\text{OH}(l) \rightarrow \text{CH}_3\text{CH}_2\text{CHO}(l) \text{ (product = propanal)}
  \]

- **Strong oxidants** (e.g. $\text{H}^+$/MnO$_4^-$) oxidise primary alkanols to form alkanoic acids:
  \[
  \text{C}_3\text{H}_7\text{OH}(l) \rightarrow \text{CH}_3\text{CH}_2\text{COOH}(l) \text{ (product = propanoic acid)}
  \]

- **Secondary alkanols** can be oxidised by strong oxidants to form alkanones:
  \[
  \text{CH}_3\text{CH(OH)}\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3 \text{ (product = pentan-2-one)}
  \]

- **Tertiary alkanols** cannot be oxidised by these oxidants.

See *Excel* Year 12 Chemistry p. 148
Sugarcane is grown for sugar (sucrose) production. A by-product is a dark-brown syrup called molasses. The sucrose sugar (C₁₂H₂₂O₁₁) in the molasses is first hydrolysed to produce simple sugars such as glucose (C₆H₁₂O₆).

Glucose can then be anaerobically fermented at 37 °C by genetically modified yeast to produce ethanol (C₂H₅OH):

\[
C₆H₁₂O₆ \text{(aq)} \rightarrow 2C₂H₅OH(l) + 2CO₂(g)
\]

Fractional distillation of the fermented solution produces hydrous ethanol (95% ethanol).

Anhydrous ethanol is produced by removing the remaining water using absorbent solids (e.g. zeolites).
Types of fuels

- **Petrol, kerosene, diesel and natural gas** are fossil fuels because they are derived from petroleum that formed over millions of years from the fossilised remains of marine organisms.

- **Coal** is also a fossil fuel that is used to generate electricity in many power stations. Coal is the fossilised remains of swamp plants.

- **Ethanol and biodiesel** are examples of biofuels because they are derived from biological materials such as plant matter.

- Ethanol is a 10% component of E10 petrol.

- **Biodiesel** is a biofuel manufactured from organic sources such as fats and oils.
Alkanols

- **Alkanols** are molecules containing the hydroxyl (OH) functional group. Alkanols are neutral, polar molecules. Low molecular weight alkanols are water soluble.

- Primary alkanols can be oxidised by strong oxidants to form alkanoic acids. Secondary alkanols can be oxidised to form alkanones.

Alkanals

- **Alkanals** are molecules containing the carbonyl (CO) functional group on the terminal carbon. Alkanals can be formed by mild oxidation of primary alkanols. Alkanals can also be oxidised by strong oxidants to form alkanoic acids.

Alkanones

- **Alkanones** are molecules containing the carbonyl (CO) functional group on the non-terminal carbon atoms. Alkanones can be formed by strong oxidation of secondary alkanols. Alkanones are not oxidised further.
Amines and amides

- **Amines** are polar organic molecules containing the amine (NH$_2$) functional group.

- **Amines** are weak bases in aqueous solution. They react with strong acids to form salts. Methanamine forms methylammonium chloride when reacted with HCl:

  
  \[
  \text{CH}_3\text{NH}_2(aq) + \text{HCl}(aq) \rightarrow \text{CH}_3\text{NH}_3\text{Cl}(aq)
  \]

- **Amides** are strongly polar organic molecules containing the amide (CONH$_2$) functional group.

- The boiling points of amides are considerably higher than the equivalent alkanol or alkanoic acids.

- Amides are very weak bases in water solution.

See *Excel* Year 12 Chemistry p. 159
Carboxylic acids and esters

Carboxylic acids are organic molecules containing the carboxyl (COOH) functional group. Carboxylic acids are highly polar molecules. Alkanoic acids are carboxylic acids with the carboxyl group on the terminal carbon atom.

Alkanoic acids are weak acids in water solution. Alkanoic acids can be neutralised by strong bases to form salts:

$$\text{CH}_3\text{COOH}(aq) + \text{KOH}(aq) \rightarrow \text{KCH}_3\text{COO}(aq) + \text{H}_2\text{O}(l)$$

Alkanoic acids react with alkanols in the presence of an acid catalyst to form esters. Esters are alkyl alkanoate molecules containing the ester (COO) functional group. These reactions are condensation reactions:

$$\text{CH}_3\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3 + \text{H}_2\text{O}$$
Esterification is the procedure used to make an ester. The reaction is kinetically slow and the yield of ester is quite variable.

The rate of the reaction can be increased by moderate heating (using an electric heating mantle), as well as by adding a catalyst such as concentrated sulfuric acid.

The equilibrium yield of ester can be increased by adding an excess of one reactant.

The reaction is performed using a reflux condenser that condenses the hot vapours and returns them to the reaction flask so that the reaction can reach equilibrium.

The condenser is open to the atmosphere so dangerous vapour pressure build-up is avoided. Boiling chips in the flask prevent large vapour bubbles from forming that can cause vibrations in the apparatus.
Soap

- **Sodium stearate** ($\text{NaCH}_3(\text{CH}_2)_{16}\text{COO}$) is a soap. It is the salt of the fatty acid called stearic acid. The soap consists of a long hydrocarbon ‘tail’ and a charged ‘head’ group ($\text{COO}^-$).

- The soap is made by heating a fatty ester called *tristearin* with concentrated sodium hydroxide solution. The soap curd is precipitated by adding saturated salt water:

$$\text{(C}_3\text{H}_5\text{O})(\text{OOC(CH}_2)_{16}\text{CH}_3)_3 + 3\text{NaOH} \rightarrow \text{C}_3\text{H}_5\text{O(OH)}_3 + 3\text{NaCH}_3(\text{CH}_2)_{16}\text{COO}$$

- **Soap** is an efficient cleaning agent. The hydrocarbon tails of the soap penetrate oily stains on clothes and form spherical structures called *micelles*, with the negative head groups on their surface. These charged groups interact with polar water molecules so the micelles lift off the clothes, dissolve in the water and are then washed away.
Detergents are cleaning agents. Most detergents are manufactured from petrochemicals. Like soap they have long hydrocarbon tails and a charged or polar head group.

Detergents are classified into three main categories:

- **Anionic detergents**: the head group is anionic (e.g. $-\text{C}_6\text{H}_4\text{SO}_3^-$)
- **Cationic detergents**: the head group is cationic (e.g. $-\text{N}({\text{CH}}_3)_3^+$)
- **Non-ionic detergents**: the head group is polar (e.g. $-(\text{CH}_2\text{CH}_2\text{O})_n$)

Anionic detergents are widely used in laundry detergents, dishwashing liquids and oven cleaners as they are strongly foaming.

Cationic detergents are used as fabric softeners and hair and fabric conditioners.

Non-ionic detergents are widely used in automatic dishwashing detergents and cosmetics.
Cellulosic biomass can be used to produce bioethanol fuel.

The bioethanol fuel can be produced by first converting biomass into glucose. The glucose undergoes anaerobic fermentation to produce ethanol. Figure PC.4 illustrates the process in the form of a flowchart.
Polyvinyl acetate production

Polyvinyl acetate is a synthetic polymer used for wood glues and other adhesives. It is also used in the preparation of latex paints and in the lamination of metal foils.

The steps used in its industrial production from crude oil are summarised below:

- The naphtha fraction of crude oil is extracted by fractional distillation.
- The naphtha fraction undergoes thermal (steam) cracking to produce smaller molecules, including reactive ethylene gas ($\text{C}_2\text{H}_4$).
- The ethylene gas is reacted with acetic acid and oxygen (using a palladium catalyst) to form the vinyl acetate ($\text{CH}_3\text{CO}_2\text{CHCH}_2$) monomer.
- The vinyl acetate monomer undergoes free radical addition polymerisation to form polyvinyl acetate.
Polyethylene

- **Ethylene monomers** can join together in long chains to form polymers. This type of polymerisation is called **addition polymerisation**.

- **Low density polyethylene** (LDPE) is produced by a free radical peroxide initiator method. The radical attacks the monomer to produce a monomer radical, which then attacks another monomer to form a dimer radical. During propagation chain growth continues via a series of addition reactions to produce a branching polymer chain.

- **The branches** cause the hydrocarbon chains to pack non-uniformly. This weakens the dispersion forces between the polymer chains.

- **LDPE** is soft and flexible and is used to manufacture plastic bags, squeeze bottles and electrical insulation.
Addition polymers—polystyrene

- **Polystyrene** (PS) is an important commercial polymer. It is manufactured from the styrene monomer \((\text{CH}_2\text{CHC}_6\text{H}_5)\). The IUPAC name for this monomer is phenylethylene.

- **Commercial PS polymers** typically vary in length from 10,000 to 40,000 monomer units. The polymer is quite rigid due to the presence of the large phenyl group. The phenyl group \((\text{C}_6\text{H}_5)\) consists of a hexagonal ring of carbon atoms in which hybridised orbitals form a ring of electrons above and below the plane of the ring.

- Polystyrene is a transparent, hard plastic. The high stiffness of PS makes it suitable for car battery cases, plastic cutlery and handles for tools. Its high refractive index makes it suitable for clear containers such as plastic drinking glasses and packaging of CDs and DVDs.

- **Polystyrene can be converted into polystyrene foam** by heating and using blowing agents such as propane gas to expand the polymer droplets and create holes in the plastic. The polystyrene foam is white and has a very low density. It is an excellent thermal insulator.
Polyvinyl chloride (PVC) is an addition polymer made from the chloroethylene (vinyl chloride) monomer. PVC is a rigid polymer used to make drainage pipes. Polystyrene (PS) is manufactured from the styrene monomer. PS is a clear, rigid polymer used to make containers and tool handles. Polytetrafluoroethylene (PTFE) is made from the tetrafluoroethylene monomer. PTFE is used as non-stick coatings in frypans.

Figure PC.5 shows their structural formulas.
Condensation polymerisation involves monomers condensing together with the elimination of a smaller molecule such as water.

Polyesters are examples of condensation polymers. Polyesters form when an alkandiol monomer bonds (via an ester linkage (COO)) with a dialkanoic acid monomer. The monomers are linked by the ester functional group. Polyester fibres are strong and elastic and are extensively used in the production of textiles.

A common polyester used to make textiles is PET (polyethylene terephthalate; see Figure PC.6).

Figure PC.6
Polylactic acid (PLA) is an example of a synthetic biopolymer. PLA is a biodegradable condensation polymer that is strong and flexible. The monomer is lactic acid (CH$_3$CHOHCOOH), which is produced from starch waste using Lactobacillus bacteria. Plastic bags, composting bags, disposable plates and tableware can be made from PLA.

PLA is biocompatible and can be used in medical applications inside the body (Figure PC.7).

Figure PC.7
Environmental monitoring is critical to knowing whether the quality of our environment is getting better or worse. The systematic sampling of air, water, soil and living organisms are conducted in order to observe and study the environment.

Water quality is monitored to ensure the water is fit to drink. Chemists measure water acidity, total dissolved solids, hardness and dissolved oxygen levels in this monitoring process.

Air quality is monitored to determine the levels of polluting oxides such as CO, NO$_2$ and SO$_2$ produced by vehicles and industries.

Soil quality is tested to determine the levels of contamination of heavy metals and organic pesticides discharged by industries and farmers into the environment.
Qualitative tests can be performed to identify the presence of various cations in solution.

Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$ can be distinguished using several tests. Sulfuric acid produces white precipitates with Ca$^{2+}$ and Ba$^{2+}$. Sodium hydroxide produces only a white precipitate with Mg$^{2+}$. Calcium ions produce an orange-red flame colour and barium ions produce a yellow-green flame colour.

Pb$^{2+}$ and Ag$^{+}$ both form white precipitates with HCl. However, PbCl$_2$ is soluble in hot water.

Cu$^{2+}$ ions form a blue precipitate with NaOH solution. Fe$^{2+}$ ions form a green precipitate and Fe$^{3+}$ ions form a brown precipitate with NaOH solution.
When aqueous solutions of various metal ions are atomised in a blue (non-luminous) Bunsen burner flame, they produce a characteristic colour in the flame. A clean platinum wire loop is dipped into a solution of a salt and then held in the flame (see Figure PC.8).

**Flame colour examples:**
- $\text{Ba}^{2+} = \text{pale yellow-green}$
- $\text{Cu}^{2+} = \text{green}$
- $\text{Ca}^{2+} = \text{orange-red}$
Various acid–base and precipitation reactions can be used to identify various anions.

\(\text{CO}_3^{2-}\) and \(\text{OH}^-\) ions form alkaline solutions, which can be detected using a pH meter. Nitric acid causes effervescence of \(\text{CO}_2\) from \(\text{CO}_3^{2-}\) ions but not with \(\text{OH}^-\) ions.

\(\text{Cl}^-\) forms a white precipitate with \(\text{Ag}^+\), whereas \(\text{Br}^-\) forms a cream precipitate and \(\text{I}^-\) forms a pale-yellow precipitate. AgCl dissolves in dilute ammonia. AgBr dissolves in concentrated ammonia solution. AgI does not dissolve in concentrated ammonia solution.

\(\text{SO}_4^{2-}\) precipitates in an acidified solution of \(\text{Ba}^{2+}\), but \(\text{PO}_4^{3-}\) will not. The phosphate ion will precipitate with barium ions in a solution made alkaline with ammonia solution. Acetate (\(\text{CH}_3\text{COO}^-\)) ions do not precipitate with \(\text{Ba}^{2+}\) in acidic or alkaline solutions.

See Excel Year 12 Chemistry p. 193
The composition of a mixture can be determined by gravimetric analysis involving a precipitation reaction. The sulfate concentration of a fertiliser can be found this way.

A sample of fertiliser is weighed and dissolved in water. After filtration the mixture is acidified and excess barium nitrate is added to precipitate $\text{BaSO}_4$. The precipitate is filtered, washed and dried to constant weight. The percentage by weight of $\text{SO}_4^{2-}$ in the fertiliser can be calculated.

**Example:** mass (fertiliser) = 1.85 g; mass (BaSO$_4$) = 0.475 g

\[ n(\text{BaSO}_4) = \frac{0.475}{233.37} = 2.04 \times 10^{-3} \text{ mol}; \ n(\text{SO}_4^{2-}) \text{ in fertiliser} = 2.04 \times 10^{-3} \text{ mol} \]

\[ m(\text{SO}_4^{2-}) = (2.04 \times 10^{-3})(96.07) = 0.196 \text{ g} \]

\[ \%\text{SO}_4^{2-} \text{ in fertiliser} = \left( \frac{0.196}{1.85} \right) \times \frac{100}{1} = 10.6\%\text{w/w} \]
The concentration of bromide ions in an aqueous solution can be determined by a precipitation titration. Silver ions precipitate bromide ions in the titration.

A 0.100 mol/L silver nitrate solution was used to fill a burette. 25.00 mL of NaBr solution was pipetted into a conical flask. 1 mL of yellow K$_2$CrO$_4$ indicator was added. The silver nitrate is added and the end point occurs when the indicator turns from yellow to reddish-brown.

Example:
Average titre = 21.55 mL AgNO$_3$

\[ n(\text{AgNO}_3) = (0.100)(0.02155) = 2.115 \times 10^{-3} \text{ mol} \]

\[ \text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr(s)}; \quad n(\text{NaBr}) = 2.115 \times 10^{-3} \text{ mol} \]

\[ c(\text{Br}^-) = c(\text{NaBr}) = \left( \frac{2.115 \times 10^{-3}}{0.02500} \right) = 0.0846 \text{ mol/L} \]
ANALYSIS OF INORGANIC SUBSTANCES

Colourimetry

Colourimetry is an instrumental procedure to determine the concentration of a coloured ion, or molecule, in solution.

Light of a specific colour or wavelength is passed through the coloured solution and the amount of light absorbed (absorbance, $A$) is directly proportional to the concentration ($c$) of the coloured ion or molecule.

A series of dilution standards of known concentration are prepared and their absorbance measured. A calibration graph is constructed ($A$ versus $c$).

The absorbance of solutions of unknown concentration is measured and the calibration graph is used to determine the concentration of these solutions.

See Excel Year 12 Chemistry p. 198
The colourimetry analysis of the concentration of a coloured species relies on the **Beer–Lambert law**, which states that the light absorbance ($A$) is directly proportional to the concentration ($c$) of the coloured species and the path length ($l$) of the solution the light passes through. This law is expressed mathematically:

$$A = εcl$$

where $ε$ is a constant called the molar absorptivity.

As long as $l$ is constant, then the absorbance ($A$) is directly proportional to concentration ($c$).

The absorbance ($A$) is determined by measuring the intensity of the light ($I_0$) passing through a reference cell, with the light intensity ($I$) passing through the sample cell. The following equation shows that absorbance is a logarithmic function:

$$A = \log_{10}\left(\frac{I_0}{I}\right)$$

The greater the concentration of the coloured species, the more light that is absorbed and the less light that is transmitted to the detector.
UV-visible spectrometers are used to measure the absorbance of ultra violet or visible light by a solution in the wavelength range 190–700 nm.

UV-visible spectrophotometry is used to detect and measure the concentration of dyes and organic pigments as well as the presence of specific coloured-metal complex ions.

Example: The spectrum of chlorophyll-a in Figure PC.9 shows strong absorbance peaks in the violet and red regions of visible light. Chlorophyll-a is green as little green light is absorbed by this molecule.
Knowledge of the absorption peak maxima ($\lambda_{\text{max}}$) allows chemists to quantitatively determine the concentration of coloured ions in solution using visible absorption spectrophotometry.

The hexaaquacobalt (II) ion ($\text{Co(H}_2\text{O)}_6^{2+}$) is pink in aqueous solution and the ion shows a strong absorption in the blue-green end (511 nm) of the visible spectrum. This wavelength is used to determine the concentration of the ion in water.

The absorbance of five dilution standards of the $\text{Co(H}_2\text{O)}_6^{2+}$ ion are measured and a calibration graph is constructed. This graph can be used to determine the concentration of unknown solutions, following the determination of the absorbance of each solution.
Atomic absorption spectroscopy (AAS) is used to measure the concentration of specific metal ions in solution.

A hollow cathode lamp made from the metal to be analysed generates specific wavelengths of light. The light passes through a slot burner’s flame containing the atomised metal ions of the sample being analysed. The greater the concentration of the metal ion, the more light that is absorbed and the less that reaches the detector.

The absorbance of a series of calibration standard solutions is measured and a calibration graph is constructed. The absorbance of the unknown sample can then be measured and the graph is then used to determine the concentration of the metal ion in the unknown.
The development of atomic absorption spectroscopy (AAS) has allowed chemists to detect and rapidly measure the concentration of metal ions in water systems (particularly those that may be polluted with heavy metals such as lead, mercury or cadmium) and in the tissues of animals and plants.

Using AAS to monitor the lead concentration in the air or in soil that is suspected of being contaminated is important for the health of people because high lead concentrations in the environment are associated with nervous system disorders and brain damage. According to the NHMRC Australian Drinking Water Guidelines, drinking water must have a lead concentration of less than 0.01 mg/L (0.01 ppm).

By using AAS as an analytical tool, chemists have discovered that trace elements have a variety of essential roles in our bodies. These include copper, which acts as a catalyst in the formation of haemoglobin and chromium, which is required for insulin action.
Functional group analysis

- **Unsaturated hydrocarbons**, alkanol and alkanoic acids can be distinguished by performing tests that are characteristic of their functional groups.

- The following table shows **observations for each test**. Alkanes give negative results for each test.

<table>
<thead>
<tr>
<th>Organic compound</th>
<th>Bromine water</th>
<th>Reaction with sodium metal</th>
<th>Reaction with sodium carbonate solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkenes</td>
<td>rapid decolourisation</td>
<td>no reaction</td>
<td>no reaction</td>
</tr>
<tr>
<td>alkynes</td>
<td></td>
<td>no reaction</td>
<td></td>
</tr>
<tr>
<td>alkanols</td>
<td>no reaction</td>
<td>effervescence</td>
<td>no reaction</td>
</tr>
<tr>
<td>alkanoic acids</td>
<td>no reaction</td>
<td>effervescence</td>
<td>effervescence</td>
</tr>
</tbody>
</table>
The carbon-13 nucleus has a property called spin. Spinning C-13 nuclei behave like tiny magnets as they create their own magnetic fields.

The spinning C-13 nucleus can absorb a photon of radio frequency radiation and move from a low energy state to a high energy state. Different chemical environments affect the radio frequencies absorbed by the C-13 nuclei in organic compounds.

The C-13 NMR spectra resonance peaks at different chemical shift (δ) values. The following chemical shift peaks are typical of various functional groups in organic compounds:
- C=C (90–150 ppm);
- C–OH (alcohols)(50–90 ppm);
- C=O (ketones)(205–220 ppm);
- C=O (esters and alkanoic acids)(160–185 ppm);
- C=O (aldehydes)(190–200 ppm)

Proton NMR can also be used to identify the different chemical environments of hydrogen atoms in organic compounds.

See Excel Year 12 Chemistry p. 211
Mass spectroscopy is used to analyse the composition of different materials. The sample is vaporised and ionised. The ions are accelerated through electric and magnetic fields.

The mass spectrogram in Figure PC.10 plots the intensity of each ion as a function of its mass to charge ratio (m/z). The ions may fragment to produce a characteristic fragmentation pattern.

Figure PC.10
Infrared spectroscopy is used to identify organic molecules and their functional groups.

Infrared radiation is absorbed by organic molecules and their bonds stretch and bend at specific frequencies, as shown in the table below. The IR spectrogram is analysed to match the recorded frequencies to specific functional groups.

<table>
<thead>
<tr>
<th>Compound type</th>
<th>Bond vibration</th>
<th>Frequency range (cm(^{-1}))</th>
<th>Compound type</th>
<th>Bond vibration</th>
<th>Frequency range (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkane</td>
<td>C–H stretch</td>
<td>2850–2960</td>
<td>alcohol</td>
<td>C–O stretch</td>
<td>1050–1150</td>
</tr>
<tr>
<td>alkane</td>
<td>C–H bend</td>
<td>1370–1480</td>
<td>carboxylic acid</td>
<td>O–H stretch</td>
<td>2500–3000</td>
</tr>
<tr>
<td>alkene</td>
<td>C–H stretch</td>
<td>3010–3090</td>
<td>carboxylic acid</td>
<td>C=O stretch</td>
<td>1700–1725</td>
</tr>
<tr>
<td>alkene</td>
<td>C=C stretch</td>
<td>1620–1680</td>
<td>ester</td>
<td>C=O stretch</td>
<td>1735–1750</td>
</tr>
</tbody>
</table>
CHEMICAL SYNTHESIS AND DESIGN

The chemical industry

- **Chemical industries** produce a wide variety of compounds. The reaction conditions that are selected represent a compromise between equilibrium, kinetic and economic factors.

- The **yield of product** depends on the extent of the equilibrium reactions involved. In chemical industries changes in temperature and concentration affect the yield.

- Raising the temperature and the use of suitable catalysts increases the rate of the reaction.

- The **environmental and social issues of the production of chemicals** need to be investigated during the planning stages of chemical factory construction.

- **Electrical power** must be readily available for many chemical industries. In some industries the site chosen may need to be close to the site of raw materials or feedstocks.
The Haber process—ammonia manufacture

- The **production of fertiliser** accounts for over 80% of the worldwide use of ammonia.

- **Nitrogen and hydrogen** are the feedstocks. The nitrogen is derived from the air and the hydrogen from natural gas and water. The Haber plant is usually located near natural gas supplies:

  \[
  \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}); \Delta H = -92 \text{ kJ/mol}
  \]

- **High pressures maximise ammonia** yield as the equilibrium shifts to the right. A compromise temperature increases reaction rate but does not reduce yield too much. A catalyst increases the reaction rate. Continuous removal of ammonia drives the reaction to the right.

- **Haber plants** are located near ports so that liquefied ammonia can be exported.
Sodium carbonate is used in glass, soap and detergent manufacture. Salt is obtained from sea water and calcium carbonate is obtained from limestone mines. The Solvay industry is located on the coast and near limestone mines.

The flowchart in Figure PC.11 summarises the steps to manufacture sodium carbonate. Ammonia is recycled to save costs and to avoid atmospheric pollution. Some CO$_2$ is also recycled.
Aspirin is a pharmaceutical containing acetylsalicylic acid. It is used for pain relief and as an anticoagulant to help prevent strokes and heart attacks. Acetylsalicylic acid is manufactured by a reaction between salicylic acid and acetic anhydride feedstocks.

The acetic anhydride is dissolved in liquid toluene, salicylic acid is then added and the mixture is heated under reflux for about 20 hours at 90 °C. The heating increases the reaction rate. Excess acetic anhydride is used to drive the equilibrium to increase product yield.

Large crystals of acetylsalicylic acid form during this time. Some acetylsalicylic acid remains dissolved and also has to be recovered. The unreacted salicylic acid and acetic anhydride are recovered from the solvent and recycled to minimise production costs. Pharmaceutical factories are located in urban areas to assist in the sales and distribution of the product.
Hair conditioners are examples of oil-in-water emulsions. The water continuous phase is compatible with the skin and hair and provides a medium to transfer the oily component onto the hairs.

The positively charged head groups of the cationic surfactants are attracted to the negative charges on the protein surfaces of the hair strands. The long hydrocarbon tails of the surfactant cling to the hair and make it feel soft and smooth and give it weight.

Hair conditioners are manufactured by large companies as well as small businesses. These factories are located in industrial zones in cities or large towns with suitable infrastructure and road networks.
Biodiesel is a general term referring to many types of fatty esters that can be used as renewable fuels in diesel vehicles.

The feedstock is typically beef fat (tallow) or recycled vegetable oil. The oil or fat is mixed with an excess of an alkanol such as methanol or ethanol and the mixture is heated and undergoes alkaline hydrolysis. The long-chain fatty acid esters are removed from the reaction mixture and form the final biodiesel product.

Fatty acid ester example: \( \text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3 \)

There is a social and environmental benefit in using waste fats and oils instead of dumping them. Biodiesel fuel use reduces greenhouse gas emissions.
The Contact process—production of sulfuric acid

- **Sulfuric acid has many uses**, including fertiliser production, anionic detergent manufacture and as the electrolyte in car batteries.

- **Sulfuric acid plants in Australia** are usually located near sulfide smelters that generate the SO\(_2\) feedstock. The sulfur dioxide is oxidised by an air stream (100–200 kPa) to form sulfur trioxide. The raised air pressure increases rate and yield. A vanadium (V) oxide catalyst increased the reaction rate. Because the reaction is exothermic a moderate temperature is used.

- **Recycling of unreacted SO\(_2\)** four times increases the net yield of SO\(_3\). The SO\(_3\) is initially dissolved in pre-prepared H\(_2\)SO\(_4\) to form H\(_2\)S\(_2\)O\(_7\), which is diluted carefully to form H\(_2\)SO\(_4\).

- High yields of sulfuric acid are achieved with very low toxic emission of sulfur dioxide to the atmosphere as required by government regulations.

See *Excel Year 12 Chemistry* p. 232
The aluminium industry and the chlor-alkali industry use electrolysis to produce elements or compounds from raw materials. Aluminium is extracted from bauxite (hydrated aluminium oxide) ore using electrolysis. Impurities are removed from the ore and the aluminium oxide is dissolved in molten cryolite ($\text{Na}_3\text{AlF}_6$) at 1000 °C. The mixture is electrolysed and the molten aluminium formed at the cathode is regularly tapped off and run into moulds. The electrolytic refinery must be located near electrical power stations to supply the large amounts of electricity used in the refining process.

Sodium hydroxide and chlorine are manufactured in the chlor-alkali industry. Salt is extracted from sea water and after purification it is electrolysed in electrolytic cells that use a polymer membrane to separate the two compartments. The sodium hydroxide produced is very pure. These industries must be located on the coast to extract the salt from the ocean.