

# The Acidic Environment

## 2.1 Indicators

### 2.1.1 Classify common substances as acidic, basic or neutral

### 2.1.2 Solve problems by applying information about the colour changes of indicators to classify some household substances as acidic, neutral or basic

- An **acid** is a substance which, in solution, produces hydrogen ions,  $H^+$  (or  $H_3O^+$ , hydronium ions).
- A **base** is a substance which either contains the oxide  $O^{2-}$  or hydroxide ion  $OH^-$  or which in solution produces the hydroxide ion. Bases are usually metal hydroxides or metal oxides.
  - A soluble base is an **alkali** (a subgroup of bases).

|                   | Acidic  | Basic  | Neutral   |
|-------------------|---|--|---|
| <i>Properties</i> | <ul style="list-style-type: none"> <li>• Sour taste; corrosive</li> <li>• In solution, acids conduct electricity.</li> <li>• Acids turn <b>blue</b> litmus <b>red</b>.</li> <li>• <math>pH &lt; 7</math></li> </ul>                               | <ul style="list-style-type: none"> <li>• Bitter taste; soapy feel</li> <li>• In solution, alkalis are good conductors of electricity.</li> <li>• Mainly insoluble in water (aqueous bases are alkalis).</li> <li>• Bases turn <b>red</b> litmus <b>blue</b>.</li> <li>• <math>pH &gt; 7</math></li> </ul>                                | <ul style="list-style-type: none"> <li>• <math>pH = 7</math></li> <li>• Neutral substances do not react with most metals and do not react with fats.</li> </ul> |
| <i>Examples</i>   | <ul style="list-style-type: none"> <li>• vinegar (acetic acid)</li> <li>• vitamin C (ascorbic acid)</li> <li>• lemon juice (citric acid)</li> <li>• aspirin (salicylic acid)</li> <li>• 'fizzy' drinks (carbonic acid)</li> <li>• milk</li> </ul> | <ul style="list-style-type: none"> <li>• oven/drain cleaners (sodium hydroxide)</li> <li>• household cleaners (ammonia)</li> <li>• antacid tablets (calcium carbonate)</li> <li>• baking powder (sodium bicarbonate)</li> <li>• washing powder (sodium carbonate <math>Na_2CO_3</math>)</li> <li>• blood</li> <li>• sea water</li> </ul> | <ul style="list-style-type: none"> <li>• pure water</li> <li>• salt water</li> <li>• sugar</li> </ul>   |

### 2.1.3 Identify that indicators such as litmus, phenolphthalein, methyl orange and bromothymol blue can be used to determine the acidic or basic nature of a material over a range, and that the range is identified by change in indicator colour

- An **indicator** is a substance (usually a vegetable dye) that, in solution, changes colour depending on whether the solution is acidic or basic (i.e. at different  $pH$  levels).
- How indicators work:
  - An indicator is a solution containing a **weak acid** in equilibrium with its **conjugate base**:
 
$$HIn + H_2O \rightleftharpoons In^- + H_3O^+$$
  - It has one colour (1) in acidic form ( $HIn$ ) and colour 2 ( $In^-$ ) in its conjugate base form.
  - The colour will change depending on the concentration of  $H^+$ .

### 2.1.4 Identify data and choose resources to gather information about the colour changes of a range of indicators

| Indicator               | Colour in acid | Colour in base | pH Range            |
|-------------------------|----------------|----------------|---------------------|
| <i>Litmus</i>           | Red            | Blue           | 5.0 – 8.0           |
| <i>Phenolphthalein</i>  | Colourless     | Pink           | 8.3 – 10.0 (basic)  |
| <i>Methyl Orange</i>    | Red            | Yellow         | 3.1 – 4.4 (acidic)  |
| <i>Bromothymol Blue</i> | Yellow         | Blue           | 6.0 – 7.6 (neutral) |

### 2.1.5 Identify and describe some everyday uses of indicators including the testing of soil acidity/basicity

- Testing pH of soils:
  - Some plants only grow within narrow *pH* ranges. Soil acidity is tested to ensure that the plants intended for the area have suitable *pH* in which to live.
  - Soil *pH* is measured using electronic instruments or universal indicator.
  - If using indicator, the soil can hide any colour change, so neutral, white barium sulfate is added to damp soil then indicator is added so that any colour change is visible.
- Testing pH of swimming pools:
  - Ideal *pH* is near neutral (close to 7.4) to prevent skin irritation.
  - Sodium hypochlorite ( $\text{NaOCl}$ ) is added to swimming pools to kill microbes. Hypochlorous acid ( $\text{HOCl}$ ) is the active form, which kills microbes but is relatively unstable.
 
$$\text{OCl}^- + \text{H}_2\text{O}_{(l)} \rightarrow \text{HOCl} + \text{OH}^-$$
    - The presence of  $\text{OH}^-$  ions makes the water basic, so  $\text{HCl}$  is added to return to neutrality. This must be done to protect the eyes and throats of swimmers from becoming irritated.
  - A pool test kit is used to test samples of the pool water, or *pH* paper soaked in indicator can be used.
- Monitoring pH of chemical wastes:
  - The *pH* of the acidic wastes produced from laboratories must be neutralised before disposal.
  - Indicators are used to measure *pH*, and substances added to neutralise it.

### 2.1.6 Perform a first-hand investigation to prepare and test a natural indicator

- Aim: To prepare and test the natural indicator found in red cabbage.
- Equipment: 500 mL beaker, 0.01 M solutions of cloudy ammonia, vinegar,  $\text{NaOH}$ , soda water,  $\text{HCl}$  and salt water.
- Method:
  1. A leaf of red cabbage was added to a beaker containing 250 mL of water, and the mixture was boiled gently until a rich coloured extract was formed.
  2. The mixture was allowed to cool, and the reddish purple indicator solution was poured off.
  3. The indicator was tested by adding a few drops to samples of cloudy ammonia, vinegar,  $\text{NaOH}$ , soda water,  $\text{HCl}$  and salt water. The indicator was added drop wise until a definite colour could be seen.
  4. The testing was repeated using Universal Indicator.
- Risk Assessment:  $\text{HCl}$  is corrosive and  $\text{NaOH}$  is caustic. Dilute  $\text{NH}_3$  solution is mildly toxic, so its fumes should not be inhaled.



### 2.2.3 Define Le Chatelier's principle

- ***If a chemical system at equilibrium is disturbed, then the system adjusts itself so as to minimise the disturbance.***
- Characteristics of a system at equilibrium:
  - It is a **closed system** (no matter or energy can enter or leave the system).
  - **Macroscopic properties** will stay **constant** (macroscopic properties can be observed or measured; e.g. state, colour, temperature, pressure).
  - **Concentrations** of reactants and products stay **constant** but *not necessarily equal*.
  - Continual **microscopic change** occurs between reactants and products.
  - The **rate of forward reaction** is *equal* to **rate of backward reaction** (equilibrium is dynamic).
  - A **catalyst** will increase the rate of a reversible reaction in both directions. It will make a system **reach equilibrium faster**, but will not change the concentration of substances at equilibrium or the equilibrium position.

### 2.2.4 Identify factors which can affect the equilibrium in a reversible reaction

- Concentration:
  - If a reactant or product is added to a **solution** or **gas phase** reaction mixture at equilibrium, then the equilibrium moves in the direction which consumes some of the added substances.
$$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{Cr}_2\text{O}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq})$$
    - Increase  $[\text{Cr}_2\text{O}_7^{2-}]$ , equilibrium shifts to the right.
    - Increase  $[\text{Cr}_2\text{O}_4^{2-}]$ , equilibrium shifts to the left.
$$\text{Ca}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$$
    - Increase  $[\text{Ca}^{2+}]$  and  $[\text{OH}^-]$  will shift equilibrium to the left.
    - **BUT** increase in the amount of  $\text{Ca}(\text{OH})_2(\text{s})$  will have no effect on the equilibrium.
- Pressure: (only affects **gases**)
  - If the pressure on a reaction system is increased, the equilibrium moves in the direction which tends to reduce pressure. This is the direction which corresponds to a decrease in the no. of moles of gas (since a decrease in no. of moles of gas in a container of fixed volume leads to a decrease in pressure).
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
    - Increase in pressure, equilibrium shifts to the right.
    - Decrease in pressure, equilibrium shifts to the left.
  - Note: If the no. of moles of gases of reactants is equal to the no. of moles of gases of products, then a change in pressure will NOT affect the position of equilibrium.
$$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$$
- Temperature:
  - If the temperature of a reaction mixture at equilibrium is increased, the equilibrium moves in the direction which absorbs heat (and thus minimises the applied temperature rise).
$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) + \text{heat} \quad [\text{exothermic: } \Delta H < 0]$$
    - Increase in temperature will shift equilibrium to the left.
$$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{heat} \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g}) \quad [\text{endothermic: } \Delta H > 0]$$
    - Increase in temperature will shift equilibrium to the right.
  - As temperature rises, exothermic reactions move to the left and endothermic reactions move to the right.

- Volume: (think in terms of pressure; ↑ volume, ↓ pressure)
  - If the volume of the reaction system is increased, and the reaction involves **gases**, the equilibrium will shift to increase the total no. of molecules.
 
$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)} + heat$$
    - Increase in volume will shift equilibrium to the left.
- Addition of water:
  - If water is added to change the total volume of a reaction mixture NOT involving gases, the equilibrium will shift to oppose the change.
 
$$HCl_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$
    - Increase in amount of water will shift equilibrium to the right.
- Addition of a reagent:
  - If the addition of a reagent reacts with a reactant or product, the equilibrium will shift to oppose the change.
 
$$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$$
    - If a dilute acid is added, the  $H^+$  will react with  $OH^-$  to form  $H_2O$ , so the equilibrium will shift to the right.

### 2.2.5 Describe the solubility of carbon dioxide in water under various conditions as an equilibrium process and explain in terms of Le Chatelier's principle

- The carbon dioxide, water and carbonic acid system is made up of three equilibria:
  1. The solution of carbon dioxide gas in water:
 
$$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$$
  2. The reaction of dissolved carbon dioxide with water:
 
$$H_2O_{(l)} + CO_{2(aq)} \rightleftharpoons H_2CO_{3(aq)} + heat$$
  3. Carbonic acid behaves as an acid by releasing a hydrogen ion:
 
$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO_3^-_{(aq)}$$
  - Net Equation:
 
$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HCO_3^-_{(aq)}$$

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \quad [\Delta H < 0]$$
    - An equilibrium shift to the left releases carbon dioxide gas.
    - An equilibrium shift to the right dissolves carbon dioxide gas.
- Increasing pressure:
  - Increasing pressure of  $CO_2$  gas shifts equilibrium to the right, which increases the concentration of  $H^+$  and hence lowers the  $pH$ .
- Increasing temperature:
  - If temperature is increased, equation 2 shifts to the left. The higher  $[CO_{2(aq)}]$  will cause equation 1 to shift to the left also, and more  $CO_{2(g)}$  is released. This causes dissolved carbon dioxide to lower, so raising the temperature of a solution lowers the solubility of the gas.
- Adding acids and bases: From the net equation:
  - If an acid is added,  $[H^+]$  will increase, so the equilibrium will shift to the left, producing more carbon dioxide gas.
  - If a base is added, the  $OH^-$  will react with the  $H^+$  (to produce  $H_2O$ ), so the equilibrium will shift to the right to replace the  $H^+$ .
  - If sufficient basic substance is added, the reaction could go to completion.

## 2.2.6 Identify natural and industrial sources of sulfur dioxide and oxides of nitrogen

- **Sulfur dioxide ( $SO_2$ )**
  - *Natural*: volcanic gases, bushfires, geothermal hot springs.
  - *Industrial*: combustion of fossil fuels, smelting of metal sulphides, power stations.
- **Nitric oxide ( $NO$ ) and nitrogen dioxide ( $NO_2$ )** – collectively referred to as  $NO_x$ 
  - *Natural*: the reaction of atmospheric nitrogen and oxygen due to high temperatures of lightning produces *nitric oxide*, which then slowly reacts with oxygen to form *nitrogen dioxide*.
  - *Industrial*: combustion of fossil fuels in cars and power stations.
- **Nitrous oxide ( $N_2O$ )**
  - *Natural*: formed by the action of bacteria on nitrogenous material in soils; use of nitrogenous fertiliser increases raw material for the bacteria, increasing levels of nitrous oxide.
  - *Industrial*: fuel for racing cars, sedative/analgesic.
- Note:  $NO_2$  is acidic;  $NO$  and  $N_2O$  are neutral.

## 2.2.7 Describe, using equations, examples of chemical reactions which release sulfur dioxide and chemical reactions which release oxides of nitrogen

## 2.2.8 Analyse information from secondary sources to summarise the industrial origins of sulfur dioxide and oxides of nitrogen and evaluate reasons for concern about their release into the environment

- Oxides of nitrogen:
  - Nitric oxide (colourless) is produced when lightning *rapidly* combines nitrogen and oxygen, or in high temperature combustion reactions in engines or power stations:
 
$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$$
  - Nitrogen dioxide (brown) is formed when nitric oxide reacts *slowly* with oxygen in the air:
 
$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$
- Sulfur dioxide:
  - Sulfur dioxide is formed by either the combustion of burning of sulfur-rich coal and other fossil fuels or the processes of roasting and extraction of metals from metal sulfides:
 
$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$

$$2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$$

$$4FeS_{2(s)} + 11O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$$
- Impacts of their release into the environment:
  - Sulfur and nitrogen oxides are detrimental to the environment, as they cause health problems and affect the surrounding environment through acid rain and photochemical smog.
  - **Health Problems**: Both sulfur dioxide ( $SO_2$ ) and nitrogen dioxide ( $NO_2$ ) are *respiratory irritants* as they cause breathing difficulties, especially for asthmatics. At higher concentrations,  $NO_2$  causes *extensive tissue damage* as it forms nitric acid,  $HNO_3$ .
  - **Photochemical smog**: The main problem with  $NO_2$  is that it causes *photochemical smog* in the form of ozone, an *air pollutant* which affects visibility due to small particles in the air.
    - Nitrogen dioxide absorbs UV radiation to form nitric acid and oxygen atoms.
 
$$NO_{2(g)} \xrightarrow{UV} NO_{(g)} + O \cdot_{(g)}$$
    - Oxygen atoms combine with molecular oxygen to form **ozone**.
 
$$O \cdot_{(g)} + O_{2(g)} \rightarrow O_{3(g)}$$

- **Acid rain:** Sulfur and nitrogen oxides can cause *acid rain* through dissolution in water, forming strong acids which can adversely affect the environment and humans.
- Policies to reduce emissions:
  - The **Environmental Protection Authority** (EPA) now requires copper producers to treat exhaust gases being emitted to the atmosphere to limit the maximum  $SO_2$  content.
  - Sulfur dioxide can be removed by **scrubbers**, which pass gaseous emissions through a saturated solution of magnesium hydroxide, for example. The magnesium sulfite produced must be disposed of as landfill or converted by another process back to magnesium hydroxide.
$$SO_{2(g)} + Mg(OH)_{2(aq)} \rightarrow MgSO_{3(aq)} + H_2O_{(l)}$$
  - Motor vehicles are fitted with **catalytic converters** which convert nitric oxide emissions back to nitrogen gas, thus removing  $NO$  from the exhaust gas.
$$2NO_{(g)} + 2CO_{(g)} \rightarrow N_{2(g)} + 2CO_{2(g)}$$
  - The  $SO_2$  produced by smelting metal sulfides can be collected and used to make  $H_2SO_4$ .
  - There are aims to reduce our **reliance on fossil fuels** by using other forms of power production (e.g. hydroelectricity and solar power).

### 2.2.9 Explain the formation and effects of acid rain

- **Acid rain** is any rain that has a  $pH$  of less than 5 (i.e.  $H^+$  concentration higher than  $10^{-5} \text{ mol/L}$ ).
- Rainwater can become quite acidic due to the **high solubility** of acidic oxide gases (e.g.  $SO_2$  and  $CO_2$ ). Pure rainwater is *slightly acidic* because of dissolved  $CO_2$ .
- Formation of acid rain:
  - *Sulfur dioxide* reacts with rain in the atmosphere, forming *sulfurous acid*:
$$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$$
  - *Sulfurous acid* is catalytically oxidised to *sulfuric acid*:
$$2H_2SO_{3(aq)} + O_{2(g)} \rightarrow 2H_2SO_{4(aq)}$$
  - *Nitrogen dioxide* also reacts with rain, producing strong *nitric acid* and weak *nitrous acid*:
$$2NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{3(aq)} + HNO_{2(aq)}$$
  - *Nitrous acid* is catalytically oxidised to *nitric acid*:
$$2HNO_{2(aq)} + O_{2(g)} \rightarrow 2HNO_{3(aq)}$$
  - $HNO_3$  is soluble in water and so falls as acid rain.
- Effects of acid rain:
  - *Environmental damage:*
    - Acid rain causes **defoliation** of plant life, resulting in destruction of **forests** and **vegetation**. This effect is also amplified due to the lowering of soil  $pH$ , causing acids to dissolve minerals and release toxic metals into the soil, thus affecting plant growth.
    - It leads to increased **acidity of lakes** which has a detrimental effect on aquatic organisms. Acid rain disrupts the  $CO_2$  gaseous/aqueous equilibrium and stresses fish life and reproduction.
  - *Structural damage:*
    - Acid rain corrodes man-made **metallic** structures such as bridges.
$$Fe_{(s)} + 2H^+_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)}$$
    - Acid rain causes erosion of **limestone** and **marble** structures. Calcium carbonate is dissolved by acid rain, forming soluble calcium hydrogen carbonate.
$$CaCO_{3(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

### 2.2.10 Assess the evidence which indicates increases in atmospheric concentration of oxides of sulfur and nitrogen

- Oxides of sulfur:
  - Both the *increase in combustion of coal* for energy and the *increase in smelting of metals* since the Industrial Revolution have led to a dramatic increase in the amount of oxides of sulfur being released into the atmosphere.
    - For example, the roasting of zinc sulfide minerals releases sulfur dioxide:
 
$$2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$$
    - Sulfur dioxide is acidic and can dissolve in rain to form acid rain:
 
$$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$$

$$2H_2SO_{3(aq)} + O_{2(g)} \rightarrow 2H_2SO_{4(aq)}$$
  - Oxides of sulfur eventually form sulfate ions, most of which are water soluble, so finding evidence for increases in atmospheric concentrations of oxides of sulfur is difficult.
  - However, some evidence has come from the **analysis of gases** trapped in ice cores, showing increased concentrations of sulfates, and observations that in Europe and North America, many **lakes are now too acidic** to support fish life (with the *pH* in some lakes so low that biodiversity has been reduced).
  - Other evidence comes from the **destructive effects of acid rain** on historically important buildings. For example, statues in affected areas in Europe are showing signs of deterioration due to acid rain which has attacked the calcium carbonate in their stonework.
 
$$CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(aq)} + CO_{2(g)} + H_2O_{(l)}$$
- Oxides of nitrogen ( $NO_x$ ):
  - $NO_x$  is mainly produced from internal combustion engines and coal-burning power stations.
 
$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$$
    - In the presence of sunlight,  $NO$  is oxidised to  $NO_2$ :
 
$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$
  - The concentrations of  $NO_x$  have increased with the rapid increase in use of motor vehicles since the Industrial Revolution.
  - The evidence for this comes from both **direct measurements of gas concentrations** in the atmosphere (made by statutory bodies, e.g. EPA) and indirectly through increases in levels of **photochemical smog** in cities and **increased levels of acid rain**. For example, increases in photochemical smog (in the form of ozone) have been observed in major cities (e.g. Sydney):
 
$$NO_{2(g)} \xrightarrow{UV} NO_{(g)} + O \cdot_{(g)}$$

$$O \cdot_{(g)} + O_{2(g)} \rightarrow O_{3(g)}$$
- Assessment of evidence:
  - The **quantitative** measurements (analysis of gases in ice core samples and direct measurements of gas concentrations in the atmosphere) are accurate and reliably point to increases in concentrations of  $NO_x$ , however the technology for measuring low concentrations has only been available in recent times.
  - The **qualitative** evidence for smog and acid rain is less reliable, as these issues could be caused by other acidic oxides and other factors may have led to their increase.



### 2.2.11 Identify data, plan and perform a first-hand investigation to decarbonate soft drink and gather data to measure the mass changes involved and calculate the volume of gas released at 25°C and 100kPa

- Aim: To measure mass changes involved and to measure the volume of gas released at 25°C and 100 kPa when a carbonated drink is decarbonated.
- Equipment: bottle/can of carbonated soft drink, electronic balance.
- Method & Discussion: There are several methods that can be used for this experiment, each with their limitations. All of them involve initially weighing the carbonated drink on the electronic balance, then weighing the drink again after it has been decarbonated.
  - Method 1: **Shaking**
    - The can is shaken, opened and left out in the open.
    - The lower air pressure of the external surroundings will cause carbon dioxide to move from the aqueous to the gaseous state, thereby decarbonating the soft drink:
$$CO_2(g) \rightleftharpoons CO_2(aq)$$
    - However, this will take a long time to occur, making this method less feasible to conduct in the school laboratory
  - Method 2: **Heating**
    - The can is heated on a hot plate or with a Bunsen burner.
    - Since the equation  $CO_2(g) \rightleftharpoons CO_2(aq)$  is exothermic, heat is a product of the reaction. The increased temperature will shift equilibrium to the left, by Le Chatelier's Principle. This depletes the  $CO_2(aq)$  in the soft drink, eventually decarbonating the drink.
    - However, heating also evaporates the *water* content of the soft drink, which means that the mass change of the soft drink will not accurately reflect the mass of  $CO_2$  lost.
  - Method 3: **Adding salt**
    - Salt is added to the can of soft drink.
    - Salt is more soluble than  $CO_2$ , so adding salt will force the  $CO_2(aq)$  out of solution and escape as  $CO_2(g)$ , again decarbonating the drink.
    - However, the addition of salt is not always entirely accurate and would affect the mass change of the soft drink.

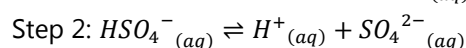
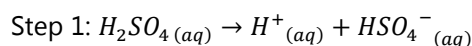
## 2.3 Acids and pH

### 2.3.1 Define acids as proton donors and describe the ionisation of acids in water

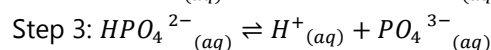
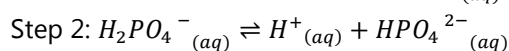
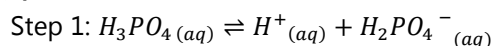
- **Acids** are **proton-donors**. In water, acids ionise, releasing a proton and a negative ion. The proton,  $H^+$ , can attach to a water molecule,  $H_2O$ , to form the hydronium ion  $H_3O^+$ .
$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$
- $HCl$  is acidic only because of the presence of water; hence water is often called an *ionising solvent*.

### 2.3.2 Gather and process information from secondary sources to write ionic equations to represent the ionisation of acids

- A **monoprotic** acid (e.g.  $HCl$ ) forms *one* proton ( $H^+$ ) per molecule of acid:
$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
- A **diprotic** acid (e.g.  $H_2SO_4$ ) ionises in solution to form *two* protons per molecule of acid. The ionisation of a diprotic acid occurs stepwise:



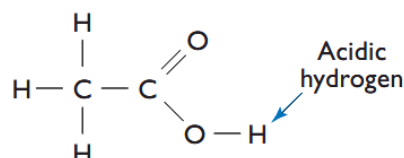
- A **triprotic** acid (e.g.  $H_3PO_4(aq)$ ) ionises in solution to form *three* protons per molecule of acid:



### 2.3.3 Identify acids including acetic (ethanoic), citric (2-hydroxypropane-1,2,3-tricarboxylic), hydrochloric and sulfuric acid

- **Acetic Acid:**

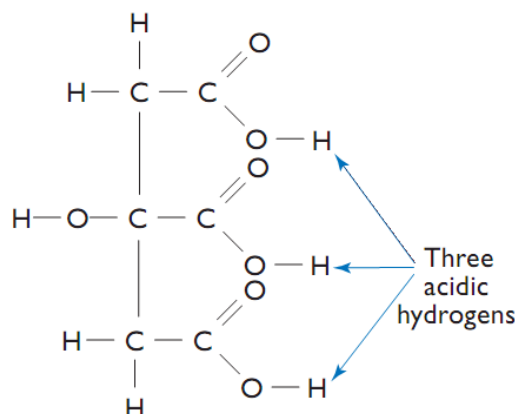
- *Systematic name:* Ethanoic acid
- *Molecular formula:*  $CH_3COOH$
- It is the weak acid present in vinegar.



- **Citric Acid:**

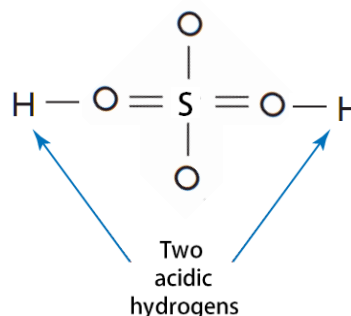
- *Systematic name:* 2-hydroxypropane-1,2,3-tricarboxylic acid
- *Molecular formula:*  $C_6H_8O_7$
- It is a triprotic acid, and is weak as it only partially ionises in water. It occurs in citrus fruit (e.g. lemons, limes) and is widely used as a food additive.
- Neutralisation of citric acid:  

$$C_6H_8O_7 + 3NaOH \rightarrow Na_3C_6H_5O_7 + 3H_2O$$



- **Sulfuric Acid:**

- *Molecular formula:*  $H_2SO_4$
- It is a strong acid used to make batteries, fertilisers, ethanol, etc. and is the most industrially produced chemical.
- It is also found in acid rain.



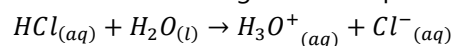
- **Hydrochloric Acid:**

- *Molecular formula:*  $HCl$
- It is a strong acid that is produced in the stomach to aid in digestion. Industrially, it is made in large quantities.

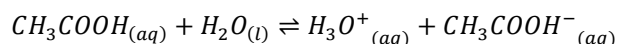
### 2.3.4 Describe acids and their solutions with the appropriate use of the terms strong, weak, concentrated and dilute

### 2.3.5 Describe the difference between a strong and a weak acid in terms of an equilibrium between the intact molecule and its ions

- A **strong** acid is one in which acid molecules have completely ionised. There are no neutral acid molecules present. Ionisation reaction with water goes to completion:

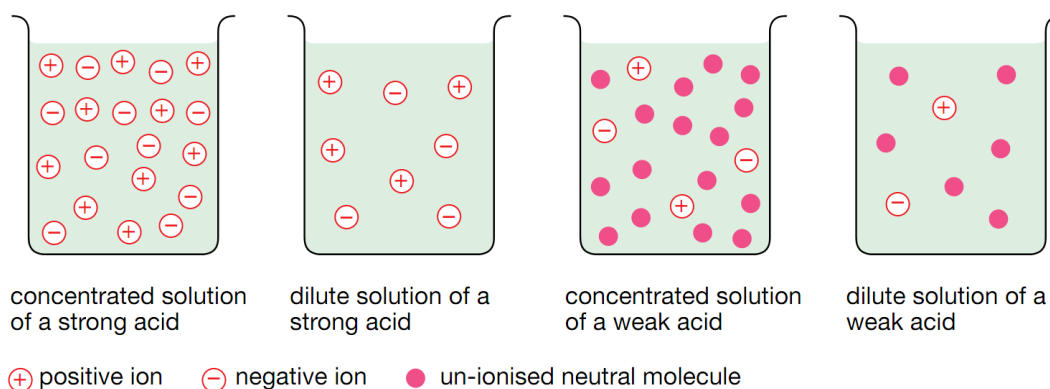


- A **weak** acid is one in which acid molecules have partially ionised. Some molecules remain intact in solution. The ionisation reaction of a weak acid with water is an equilibrium reaction that does not go to completion:



- A **concentrated** solution has a high molarity of acid particles per unit volume of solution.
- A **dilute** solution has a low molarity of acid particles per unit volume of solution.
- Strong acids:
  - Mainly:
    - Hydrochloric acid, **HCl**
    - Sulfuric acid, **H<sub>2</sub>SO<sub>4</sub>**
    - Nitric acid, **HNO<sub>3</sub>**
  - Also strong are:
    - Hydrobromic acid, **HBr**
    - Hydriodic acid, **HI**
    - Perchloric acid, **HClO<sub>4</sub>**
  - Consider all other acids as weak
- Strong bases:
  - Sodium hydroxide, **NaOH**
  - Potassium hydroxide, **KOH**
  - Barium hydroxide, **Ba(OH)<sub>2</sub>**
  - Magnesium hydroxide, **Mg(OH)<sub>2</sub>**
  - Calcium hydroxide, **Ca(OH)<sub>2</sub>**
- Weak bases:
  - Ammonia, **NH<sub>3</sub>**
  - Sodium carbonate, **Na<sub>2</sub>CO<sub>3</sub>**

### 2.3.6 Use available evidence to model the molecular nature of acids and simulate the ionisation of strong and weak acids



### 2.3.7 Identify pH as $-\log_{10} [\text{H}^+]$ and explain that a change in pH of 1 means a ten-fold change in $[\text{H}^+]$

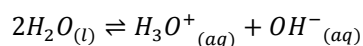
- The *pH* of a solution:  $\text{pH} = -\log_{10}[\text{H}^+]$
- A change in *pH* of 1 means a 10-fold change in  $[\text{H}^+]$ .

### 2.3.8 Describe the use of the pH scale in comparing acids and bases

- The **pH scale** is used to determine the acidity or basicity of a substance by comparing the concentration of hydrogen ions in solution.
  - In a **neutral** solution (pure water without any dissolved gas),  $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol L}^{-1}$  so  $\text{pH} = 7$ .
  - In an **acidic** solution,  $[\text{H}^+] > 10^{-7} \text{ mol L}^{-1}$  so  $\text{pH} < 7$ .
  - In a **basic** solution,  $[\text{H}^+] < 10^{-7} \text{ mol L}^{-1}$  so  $\text{pH} > 7$ .
- The *pOH* scale uses  $[\text{OH}^-]$  instead of  $[\text{H}^+]$  as a measure:
 
$$\text{pOH} = -\log_{10}[\text{OH}^-]$$
- Relationship between *pH* and *pOH*:
 
$$\text{pH} + \text{pOH} = 14$$

- Self-ionisation of water:

- Water undergoes **self-ionisation** in all solutions



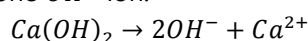
- In pure water, the  $[H^+] = [OH^-] = 10^{-7}$ ;  $pH = pOH = 7$
  - For acids,  $[H^+] > [OH^-]$ . For bases  $[OH^-] > [H^+]$ .
- $[H^+] \times [OH^-] = K_w = 1.0 \times 10^{-14} \text{ (mol L}^{-1}\text{)}^2$  at  $25^\circ\text{C}$ , 298K
  - $K_w$  is the *ionisation constant for water*. It is the same for all aqueous solutions no matter what it contains.
  - As the self-ionisation of water is an endothermic process, the value of  $K_w$  will change as the temperature changes. In hot water, the value of  $K_w$  is higher than it is in cold water.

- Degree of ionisation:

- In a strong acid solution, each acid molecule is assumed to fully ionise.
- Weak acids do not fully ionise. If the **degree of ionisation** (% of molecules that have ionised) is known, then  $pH$  can be determined.

$$\text{Degree of ionisation (at } 25^\circ\text{C)} = \frac{[H_3O^+]}{[HA]} \times 100\%$$

- Note: Bases can release more than one  $OH^-$  ion.



$$[OH^-] = 2 \times [Ca(OH)_2]$$

- To calculate  $pH$  of a solution after **dilution**, use  $c_1v_1 = c_2v_2$
- To find the  $pH$  of a **mixture of acid and base**, find the moles of acid and base and which one is in excess, then find  $[H^+]$  and  $[OH^-]$ .

### 2.3.9 Gather and process information from secondary sources to explain the use of acids as food additives

- Acids are used as food **preservatives** as lowering the  $pH$  inhibits enzymatic activity and prevents the growth of microbes which can spoil the food.
  - *Acetic acid*, as vinegar, is used as a food preservative and flavouring.
  - *Propanoic acid* is used as a preservative in bread.
  - *Citric acid* is a natural preservative, often added to jams and preserves.
- Acids are also used as **flavour enhancers** due to their sharp, sour taste (tartness).
  - *Carbonic acid* is added to soft drinks to add 'fizz'.
  - *Phosphoric acid* is used as a flavouring agent in soft drinks and jams.

### 2.3.10 Identify data, gather and process information from secondary sources to identify examples of naturally occurring acids and bases and their chemical composition

- Natural acids:

- **Hydrochloric acid:** Aqueous  $HCl$  is produced naturally by the lining of our stomachs and aids in the digestion of food.
- **Citric acid:** ( $C_6H_8O_7$ ) Citric acid occurs naturally citrus fruit, and is widely used as a food additive for flavour and as a preservative.
- **Acetic acid:** ( $CH_3COOH$ ) Acetic acid is found naturally in vinegar, which is produced by oxidation of ethanol:  $C_2H_5OH \xrightarrow{\text{oxidation in air}} CH_3COOH$

- **Ascorbic acid:** ( $C_6H_8O_6$ ; vitamin C) Ascorbic acid occurs in fruit and vegetables and is essential to our health and wellbeing.
- Natural bases:
  - **Ammonia:** ( $NH_3$ ) Ammonia is present in the stale urine of animals, and is also formed through the anaerobic decay of organic matter.
  - **Metallic oxides:** (e.g. iron(III) oxide, copper(II) oxide and titanium(IV) oxide) These insoluble oxides are solid bases found in minerals.
  - **Calcium carbonate:** ( $CaCO_3$ ) Calcium carbonate is found naturally as limestone.

### 2.3.11 Plan and perform a first-hand investigation to measure the pH of identical concentrations of strong and weak acids

### 2.3.12 Compare the relative strengths of equal concentrations of citric, acetic and hydrochloric acids and explain in terms of the degree of ionisation of their molecules

- Aim: To measure and compare the *pH* of equimolar solutions of strong and weak acids.
- Equipment: dropper bottles containing standard 0.1 M solutions of *HCl*, acetic acid and citric acid, *pH* meter and buffers, small beakers.
- Method:
  1. The *pH* meter was calibrated with acid buffers.
  2. The *pH* of each of the three acid solutions was measured, starting with acetic acid.
- Results:

| Acid (0.010 mol/L)       | Hydrochloric acid | Citric acid | Acetic acid |
|--------------------------|-------------------|-------------|-------------|
| Degree of ionisation (%) | 100.0             | 8.0         | 1.0         |
| <i>pH</i>                | 1.0               | 2.1         | 2.9         |

- Discussion:
  - The degree of ionisation of an acid is the percentage of molecules that have ionised.
  - The order of the acids from strongest to weakest, and in order of increasing *pH*, was hydrochloric acid, citric acid and acetic acid. This is due to the degree of ionisation of the molecules in water. Weak acids ionise less readily in water and require a much higher concentration to equal that of a stronger acid.
- Note: While there are degrees of weakness of weak acids, there are no degrees of strength for strong acids. If an acid is strong, it is completely ionised. If an acid is not completely ionised, it is not strong – it is weak.

### 2.3.13 Solve problems and perform a first-hand investigation to use pH meters/probes and indicators to distinguish between acidic, basic and neutral chemicals

- A ***pH* meter** is an instrument, consisting of a probe and a voltmeter, that measures *pH* directly.
  - A *pH* probe is a galvanic cell that contains electrodes and electrolyte. It is sensitive to  $[H^+]$  in the test sample – as the *pH* varies, the output voltage of the *pH* probe changes linearly.
- Advantages of using a *pH* meter:
  - It is a **non-destructive** way of testing a solution (it does not alter the *pH* of the solution or disturb any chemical equilibria involved).
  - It can be used to measure *pH* levels of **cloudy and coloured** solutions.
  - It is **portable**, and so can be used in environmental *pH* monitoring of soils and rivers.
  - It can monitor **continuous changes** in *pH* levels (using a computer).

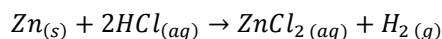
- Steps in using a pH meter:
  1. **Calibrate** the pH meter before use by placing the probe in a **buffer** solution of known pH and adjusting the meter to give appropriate readings.
  2. **Rinse** the probe with distilled water between measurements (so that the solutions tested are unaffected). Shake to remove excess water.
- Although pH meters give fairly accurate pH values, they are relatively expensive. A cheaper way of estimating pH is to use indicators, which change colours over fairly narrow pH ranges.
- Steps in using indicators:
  1. Drops of particular indicators are added to fresh small samples of the solution to be tested.
  2. Their colours are compared with a standard chart of indicator colours at different pH levels.
- Using **universal indicator** solution is a **destructive** way of testing, as the indicator will contaminate the portion of solution tested.

## 2.4 Acid/base Theories

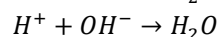
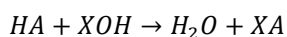
### 2.4.1 Outline the historical development of ideas about acids including those of Lavoisier, Davy, Arrhenius

### 2.4.2 Gather and process information from secondary sources to trace developments in understanding and describing acid/base reactions

- Lavoisier:
  - Lavoisier proposed that **acids contained oxygen**. He showed that many non-metal oxides, when dissolved in water, formed acids. For example, when  $H_2O$  was added to  $CO_2$ , an acidic solution was formed.
  - As a result, he hypothesised that the presence of oxygen in non-metal oxides gave these compounds their acidic properties.
  - However, this theory did not explain why oxides of metals (e.g.  $Na_2O$ ,  $CaO$ ) were not acidic nor why some acidic substances (e.g.  $HCl$ ) were distinctly acidic but contained no oxygen.
- Davy:
  - Davy was able to show that there were acids that did not contain oxygen (e.g.  $HCl$ ,  $HCN$ ,  $H_2S$ ).
  - He suggested that **acids contained replaceable hydrogen**, which gave them acidic properties.



- Acids reacted with metals to form salts. Bases reacted with acids to form salts and water.
- However, Davy did not explain why many compounds of hydrogen were not acidic (e.g. methane,  $CH_4$ ).
- Arrhenius:
  - Arrhenius proposed:
    - **Acids** produce **hydrogen ions**  $H^+$  when in solution.
    - **Bases** produce **hydroxide ions**  $OH^-$  when in solution.
  - Acids were strong if they ionised completely and weak if they ionised only slightly.
  - Arrhenius' theory explains the process of neutralisation. When an acid neutralises a base, it is the hydrogen ions and hydroxide ions that react to form neutral water:



- However, there are some limitations to Arrhenius' theory:
  - It does not recognise the role of the solvent in ionisation. Whether an acid is strong or weak depends on the nature of both the acid and the solvent it is dissolved in.
  - It does not explain why metallic oxides and carbonates are basic.
  - It does not explain why some solutions of various salts are acidic or basic rather than neutral. For example, a solution of  $\text{NaCl}$  is neutral, but a solution of  $\text{ZnCl}_2$  is acidic.

### 2.4.3 Outline the Brönsted-Lowry theory of acids and bases

- The **Brönsted-Lowry** theory of acids and bases:
  - An acid is a proton donor.
  - A base is a proton acceptor.
- The theory recognised the importance of hydrogen ions in explaining acid-base behaviour, which was considered as a proton exchange. A substance cannot act as an acid without another acting as a base. This explained how some substances could be both acidic and basic (i.e. amphiprotic).
- The role of the solvent became important, as it was not simply an inert liquid in which solutes dissolved. The theory focuses not only on the role of water as an ionising solvent, but also extends the concept of acids and bases to non-aqueous media.
- The self-ionisation of water can now be understood in terms of the Brönsted-Lowry theory. One water molecule behaves as a Brönsted-Lowry base and the other as a Brönsted-Lowry acid.
$$\text{H}_2\text{O}_{(l)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{OH}^-_{(aq)}$$
- In addition, the Brönsted-Lowry theory explained that the hydrolysis of salts to produce a  $pH$  different from 7.0 was due to simple acid or base reactions. It also provided a basis for the quantitative treatment of acid-base equilibria and  $pH$  calculations.

### 2.4.4 Describe the relationship between an acid and its conjugate base and a base and its conjugate acid

- A **conjugate base** is formed when an acid donates a proton.
$$\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-$$
  - $\text{HA}$  is the acid and  $\text{A}^-$  is the conjugate base.
- A **conjugate acid** is formed when a base accepts a proton.
$$\text{B} + \text{H}_2\text{O} \rightarrow \text{HB}^+ + \text{OH}^-$$
  - $\text{B}$  is the base and  $\text{HB}^+$  is the conjugate acid.
- The *conjugate base of a strong acid is an extremely weak base*, so it does not react with water to any significant extent. The stronger an acid, the weaker its conjugate base.
- The *conjugate base of a weak acid is a weak base*, so it does react with water.
- The *conjugate acid of a strong base is an extremely weak acid*, so it does not react with water to any significant extent. The stronger a base, the weaker its conjugate acid.

### 2.4.5 Identify conjugate acid/base pairs

- The conjugate base of an acid, under appropriate conditions, is capable of accepting a proton to form the acid again. The acid and base form a **conjugate pair**.
$$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+$$
  - $\text{HCl}$  and  $\text{Cl}^-$  form a conjugate acid/base pair.
  - $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  form a conjugate base/acid pair.

- Members of a conjugate pair differ from each other by the presence or absence of the transferable hydrogen ion.
- Note: By the Brönsted-Lowry definition, anions and cations as well as neutral molecules can be acids and bases.

#### 2.4.6 Identify a range of salts which form acidic, basic or neutral solutions and explain their acidic, neutral or basic nature

|  | Strong base ( $\text{NaOH}$ , $\text{KOH}$ )                      | Weak base ( $\text{NH}_3$ )  |
|--|---|--|
| Strong acid<br>( $\text{HCl}$ , $\text{HNO}_3$ )           | $\text{pH} = 7$<br>( $\text{NaCl}$ , $\text{KNO}_3$ )             | $\text{pH} < 7$<br>( $\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{NO}_3$ ) |
| Weak acid<br>( $\text{CH}_3\text{COOH}$ , $\text{HNO}_2$ ) | $\text{pH} > 7$<br>( $\text{NaCH}_3\text{COO}$ , $\text{KNO}_2$ ) | $\text{pH} = 7$<br>( $\text{NH}_4\text{CH}_3\text{COO}$ )                |

- Hydrolysis** is the reaction of a salt with water to produce a change in  $\text{pH}$ .
- Strong acid – Strong base
  - The salt of  $\text{NaOH}$  and  $\text{HCl}$  ( $\text{NaCl}$ ) is ionic and these ions do not react with water, so they do not disturb the  $\text{H}_3\text{O}^+/\text{OH}^-$  balance in the equilibrium of water. Thus, the  $\text{pH}$  is neutral ( $= 7$ ).  

$$\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$
 **$\text{Na}^+$  is a spectator ion**
- Strong acid – weak base
  - A solution of  $\text{NH}_4\text{Cl}$  is acidic. A weak base ( $\text{NH}_3$ ) forms a strong conjugate acid ( $\text{NH}_4^+$ ).  

$$\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$$
  - Since  $\text{NH}_4^+$  is strong, it will react with water.  

$$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$$
 **$\text{Cl}^-$  is a spectator ion**
  - The formation of excess hydronium ions makes the solution acidic.
- Weak acid – strong base
  - A solution of  $\text{NaCH}_3\text{COO}$  is basic. A weak acid ( $\text{CH}_3\text{COOH}$ ) forms a strong conjugate base ( $\text{CH}_3\text{COO}^-$ ).  

$$\text{NaOH} + \text{CH}_3\text{COOH} \rightarrow \text{NaCH}_3\text{COO} + \text{H}_2\text{O}$$
  - Since  $\text{CH}_3\text{COO}^-$  is strong, it will react with water.  

$$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$$
 **$\text{Na}^+$  is a spectator ion**
  - The formation of excess hydroxide ions makes the solution alkaline.
- Weak acid – weak base
  - A solution of  $\text{NH}_4\text{CH}_3\text{COO}$  is close to neutral as both anion ( $\text{CH}_3\text{COO}^-$ ) and cation ( $\text{NH}_4^+$ ) react with water to small extents, and so cancel each other.  

$$\text{NH}_3 + \text{CH}_3\text{COOH} \rightarrow \text{NH}_4^+ + \text{CH}_3\text{COO}^-$$
  - Since  $\text{NH}_4^+$  is the strong conjugate acid of a weak base ( $\text{NH}_3$ ) it will react with  $\text{H}_2\text{O}$ .  

$$\text{NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{H}_3\text{O}^+$$
  - Since  $\text{CH}_3\text{COO}^-$  is the strong conjugate base of a weak acid ( $\text{CH}_3\text{COOH}$ ) it will react with  $\text{H}_2\text{O}$ .  

$$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{OH}^-$$
  - The  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  react so the solution is neutral.  

$$\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$$

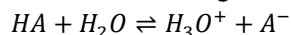


### 2.4.7 Identify amphiprotic substances and construct equations to describe their behaviour in acidic and basic solutions

- **Amphoteric** substances are capable of behaving as either acids or bases (refers to *oxides*).
  - Zinc oxide
    - $ZnO$  as a base:  $ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$
    - $ZnO$  as an acid:  $ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$
  - Aluminium oxide
    - $Al_2O_3$  as a base:  $Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$
    - $Al_2O_3$  as an acid:  $Al_2O_3 + 2KOH \rightarrow 2KAlO_2 + H_2O$   
 »  $KAlO_2$  is potassium aluminate
- **Amphiprotic** substances are capable of behaving as either Brønsted-Lowry acids or Brønsted-Lowry bases (i.e. proton donor or proton acceptor). They are a *subset* of amphoteric substances.
  - Water
    - $H_2O$  as a base:  $H_2O + HCl \rightarrow H_3O^+ + Cl^-$
    - $H_2O$  as an acid:  $H_2O + NH_3 \rightarrow NH_4^+ + OH^-$
  - Hydrogen carbonate ion
    - $HCO_3^-$  as a base:  $HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O \rightarrow CO_2 + 2H_2O$
    - $HCO_3^-$  as an acid:  $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

### 2.4.8 Qualitatively describe the effect of buffers with reference to a specific example in a natural system

- A **buffer solution** contains *comparable amounts* of a weak acid and its conjugate base, and is able to *resist changes* in *pH* when *small quantities* of a strong acid or base are added.



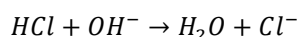
- $HA$  is a weak acid and  $A^-$  its conjugate base.
- For example:
 
$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$$
  - If  $H^+$  is added,  $[H_3O^+]$  increases. By Le Chatelier's principle, the equilibrium shifts to the left to minimise the change in  $[H_3O^+]$ . Instead of lowering the *pH*, the  $H_3O^+$  is used up in the buffer equilibrium.
  - If  $OH^-$  is added instead, it would react with the  $H_3O^+$ , causing the equilibrium to shift to the right to produce more  $H_3O^+$ .
- Buffers in nature:  $H_2CO_3 - HCO_3^-$  buffer solution
  - This occurs in natural systems (e.g. freshwater lakes and rivers) to maintain the *pH* between 6.5 and 7.5. Natural river bodies require this *pH* range for biological processes to occur favourably.
  - Carbon dioxide from the air dissolves in water to form carbonic acid, which establishes the  $H_2CO_3 - HCO_3^-$  buffer solution.
 
$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^-_{(aq)} + H_3O^+_{(aq)}$$
  - This buffer solution only works if there are carbonate rocks (limestone) available from which  $HCO_3^-$  can be formed.

- It was the absence of this buffering action in lakes in Scandinavia that resulted in falling  $pH$  from acid rain. The rocks from which the lakes had been carved contained no carbonate to provide  $HCO_3^-$  to make the buffer.
- Note: The same  $H_2CO_3 - HCO_3^-$  buffer controls the  $pH$  in parts of the human body, such as in the blood.

#### 2.4.9 Identify neutralisation as a proton transfer reaction which is exothermic

- **Neutralisation** reactions are **proton transfer reactions**. For example,  $HCl$  transfers a proton to the base  $OH^-$  to form  $H_2O$ .



- Net ionic reaction (removing the spectator ion  $Cl^-$ ):



- Neutralisation is an **exothermic** reaction, so heat energy is liberated. Enthalpy change,  $\Delta H$ , is negative. The amount of heat liberated per mole when a strong base is neutralised by a strong acid is almost the same no matter what acid or base is used.

#### 2.4.10 Analyse information from secondary sources to assess the use of neutralisation reactions as a safety measure or to minimise damage in accidents or chemical spills

- Neutralisation reactions are used for safety in cleaning up chemical spills involving strong acids and bases, as they are very corrosive. In particular, they are used to ensure effluents from factories and laboratories are neither acidic nor alkaline.
- Strong acids or bases are NOT used in cleaning up spills, as neutralisation is exothermic.
- To dilute an acid, always **add acid to water**; never add water to acid. Adding small quantities of concentrated acid to a large volume of water helps dissipate heat produced on dissolution. Water has a high heat capacity – it absorbs heat so that it is not converted to kinetic energy.
- **Sodium carbonate** ( $Na_2CO_3$ ) is suitable for neutralising acidic spills as:
  - It is a **stable** solid that is **safe** to handle.
  - It is the **cheapest** alkali available.
  - If too much of it is used, there is less danger than from excess sodium hydroxide or lime.
$$Na_2CO_{3(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$$
- **Sodium hydrogen carbonate** ( $NaHCO_3$ ) is also suitable as it is a **weak, non-toxic** base that is **stable, cheap** and **readily available**.
  - If an excess is used, there is **minimal safety risk** as it is weak.
  - It contains the **amphiprotic** hydrogen carbonate ion ( $HCO_3^-$ ) so it can neutralise both acids and alkalis.
    - For acid spills:  $NaHCO_{3(s)} + H^+_{(aq)} \rightarrow Na^+_{(aq)} + H_2O_{(l)} + CO_{2(g)}$
    - For basic spills:  $NaHCO_{3(s)} + OH^-_{(aq)} \rightarrow Na^+_{(aq)} + H_2O_{(l)} + CO_3^{2-}_{(aq)}$
  - It is easy to see when neutralisation is complete, as no more bubbles of  $CO_2$  gas are observed.
- Large scale neutralisations:
  - If large spills occur, large amounts of sand are used to prevent acid running off into drains or soil on the sides of roads.
  - Once the acid is absorbed, the sand is removed for neutralisation off-site.
  - Sodium carbonate powder followed by large quantities of water are used to neutralise and dilute any remaining acid.

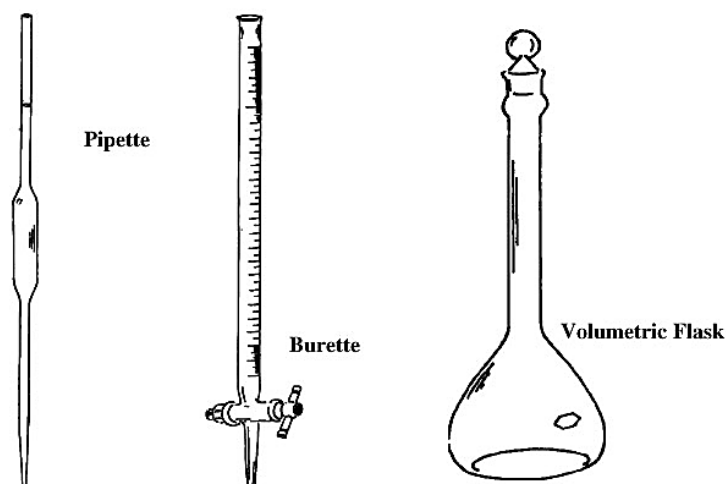
### 2.4.11 Describe the correct technique for conducting titrations and preparation of standard solutions

- **Volumetric analysis** is a quantitative analysis that involves measuring the volume of a solution of accurately known concentration (*standard solution*) that is required to react with a solution of the substance being determined.
  - Volumetric analysis is suitable when:
    - The reaction involves two solutions and the product is soluble.
    - The reaction equation is known and there are no unwanted side reactions.
    - There is some way to recognise when the reaction is complete (using indicator).
- **Titration is a procedure in volumetric analysis used to experimentally determine the unknown concentration of a solution.** One reactant is placed in a conical flask and the other solution (the *titrant*) is delivered in a measured volume (*titre*) from a burette until the equivalence point is reached.
  - The **endpoint** of the titration is marked by the colour change of a suitable indicator.
  - The **equivalence point** is the point at which the reaction is complete – reactants are present in the exact ratio shown in the equation. For a reaction between a strong acid and a strong base, equal moles of  $H^+$  and  $OH^-$  ions have been added together.
  - The difference between the equivalence point and the endpoint is the **titration error** – this is minimised by the correct choice of indicator:

| Reactants                 | pH at equivalence point | Indicator        |
|---------------------------|-------------------------|------------------|
| Strong acid + strong base | 7                       | Bromothymol blue |
| Strong acid + weak base   | 4-6                     | Methyl orange    |
| Weak acid + strong base   | 8-10                    | Phenolphthalein  |

- Preparation of standard solutions:
  - A **standard solution** is a solution of accurately known concentration.
    - A **primary standard** is made by dissolving an *exact* mass of solute in an accurate volume of water.
    - A **secondary standard** is one whose concentration is determined by titration against a primary standard.
  - *Characteristics of a good primary standard:*
    - Known and high degree of **purity**
    - Definite **composition**
    - **Stability** during storage and exposure to air
    - **Soluble**
    - High **molecular weight** (minimises weighing errors)
  - *Common primary standards:*
    - For analysing *acids*: **Anhydrous sodium carbonate** ( $Na_2CO_3$ ) (no water of crystallisation)
    - For analysing *bases*: **Hydrated oxalic acid** ( $H_2C_2O_4 \cdot 2H_2O$ )
  - *Substances unsuitable to use as a primary standard:*
    - $NaOH$  – it is **hygroscopic** (absorbs water from the air) and reacts with  $CO_2$  in the air.
    - $HCl$ ,  $HNO_3$ ,  $H_2SO_4$  – concentration of these acids changes with time.
    - $HCl$  and  $HNO_3$  are volatile, and  $H_2SO_4$  is hygroscopic.
    - $Na_2CO_3 \cdot 10H_2O$  (hydrated sodium carbonate) – it is **efflorescent** (loses water to the air).

- Apparatus used in volumetric analysis:



- **Pipettes**
  - For delivering an **aliquot** (*exact fixed volume*) of solution (25 mL).
  - It is filled by suction (using a pipette filler) to the graduation mark and drained by gravity.
  - It has an accuracy of  $\pm 0.05$  mL so it is more accurate than a measuring cylinder.
  - It is *rinsed with the solution to be transferred*.
- **Burettes**
  - For delivering *exact* volumes of solutions by turning the stop-cock.
  - Used to accurately determine volume of solution dispensed.
  - Burettes also have an accuracy of  $\pm 0.05$  mL.
  - It is *rinsed with the solution to be transferred*.
- **Volumetric flask**
  - For preparing and holding *exact* volume of standard solution.
  - It is filled so that the bottom of the meniscus is level with the graduation mark.
  - It is *rinsed with distilled water*.
- **Conical flask**
  - Holds the solution to be titrated and receives liquid from burette.
  - Placed on a white tile to reveal colour change in indicator.
  - Much *easier to swirl* without spilling than a beaker.
  - It is *rinsed with distilled water*.
- **Electronic balance**
  - Used to weigh solids for preparing primary standards or to determine the accurate mass of a sample to be analysed.

**2.4.12 Perform a first-hand investigation and solve problems using titrations and including the preparation of standard solutions, and use available evidence to quantitatively and qualitatively describe the reaction between selected acids and bases**

[Practical – Analysis of a Domestic Acidic Substance (Vinegar)]

**Part 1: Preparation of a Solution of a Primary Standard**

- Aim: To prepare 250 mL of a 0.05 molL<sup>-1</sup> solution of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (oxalic acid).
- Method:
  1. Calculate mass of oxalic acid required to prepare 250 mL of a 0.05 molL<sup>-1</sup> solution.
  2. Weigh the dry solid in a 100 mL beaker.
  3. Add distilled water and stir with a glass rod until completely dissolved.
  4. Rinse a 250 mL volumetric flask with distilled water.
  5. Transfer the solution into the volumetric flask using a water-rinsed glass funnel.
  6. Rinse the beaker and glass rod with distilled water and transfer all washings to the volumetric flask using a water-rinsed funnel.
  7. Add distilled water to the volumetric flask until about 1 cm below the line. Then add distilled water drop by drop until the bottom of the meniscus is in line with the 250 mL mark.
  8. Stopper the flask and invert many times it to mix thoroughly.
  9. Label the flask 0.05 molL<sup>-1</sup> H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O.

**Part 2: Determination of the Concentration of Household Vinegar**

- Aim: To determine the concentration of acetic acid in vinegar.
- Method: **Standardisation of the NaOH solution**
  1. Transfer about 75 mL of oxalic acid solution to a 100 mL beaker rinsed with oxalic acid.
  2. Using a pipette, transfer 25 mL of oxalic acid solution to a 250 mL conical flask.
  3. Transfer about 75 mL of NaOH solution to a 100 mL beaker rinsed with NaOH.
  4. Fill the burette with the NaOH solution, ensuring there are no air bubbles at the tip of the burette.
  5. Record the initial reading of the burette.
  6. Add 2 drops of phenolphthalein indicator into the conical flask and place it under the burette.
  7. Add the NaOH solution rapidly at first while swirling the conical flask. When the pink colour disappears more slowly, add the NaOH drop wise and occasionally.
  8. The titration is complete when the solution is permanently light pink.
  9. Repeat steps 1-7 until there are at least 3 concordant titres.
- Method: **Analysis of the vinegar**
  1. Using a pipette, transfer 25 mL of vinegar to a 250 mL volumetric flask.
  2. Dilute with distilled water to the mark and mix well.
  3. Titrate the diluted vinegar solution using the same technique as the standardisation of the NaOH, except that diluted vinegar solution is used instead of oxalic acid.
- Risk Assessment:
  - Oxalic acid is toxic and should be handled carefully.
  - Corrosive acids and bases are used.
  - Safety glasses should be worn during the titration.

**2.4.13 Choose equipment and perform a first-hand investigation to identify the pH of a range of salt solutions**

- Aim: To investigate the *pH* of a range of salt solutions.
- Equipment: dropper bottles of 0.1 M solutions of  $\text{NaCl}$ ,  $\text{NaCH}_3\text{COO}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHSO}_4$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{ZnSO}_4$ ,  $\text{NH}_4\text{CH}_3\text{COO}$ , *pH* meter and buffers.
- Method:
  1. The *pH* meter probe was calibrated with the buffers supplied. The electrode was carefully rinsed between measurements with distilled water.
  2. The *pH* meter and probe were used to measure the *pH* of each of the solutions. This was done by stirring the probe gently into the solution being tested and waiting at least 30 seconds to ensure the reading was stable.

**2.4.14 Perform a first-hand investigation to determine the concentration of a domestic acidic substance using computer-based technologies**

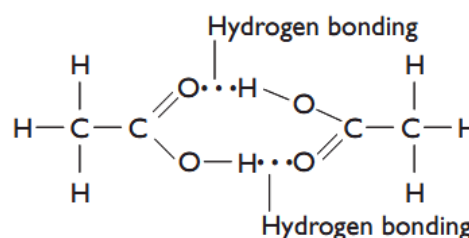
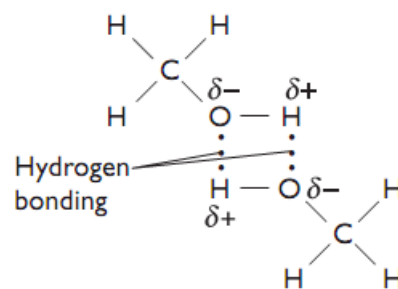
- Aim: To determine the concentration of acetic acid in vinegar using a data logger.
- Method:
  - Dilute 25 mL of vinegar to 250 mL in a volumetric flask.
  - Pipette 25 mL of diluted solution into a 250 mL beaker.
  - Add 50 mL of distilled water.
  - Insert the glass electrode into the solution so that its bulb is immersed.
  - Add a magnetic stirring bar to the beaker.
  - Start the readings on the data logger.
  - Titrate with the  $\text{NaOH}$  solution in increments of 1 mL at the start, recording the *pH* reading each time. Reduce the increment to 0.05 mL near the equivalence point.
  - The equivalence point is marked by a sudden change in *pH* with addition of small quantities of  $\text{NaOH}$ .
  - Graph *pH* against the volume of  $\text{NaOH}$ . The inflexion point in the S-shaped curve represents the equivalence point.
- The *pH* reading at equivalence point can be justified as follows:
$$\begin{aligned}\text{CH}_3\text{COOH} + \text{NaOH} &\rightarrow \text{NaCH}_3\text{COO} + \text{H}_2\text{O} \\ \text{NaCH}_3\text{COO} &\rightarrow \text{Na}^+ + \text{CH}_3\text{COO}^- \\ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} &\rightarrow \text{CH}_3\text{COOH} + \text{OH}^-\end{aligned}$$
  - The  $\text{OH}^-$  produced makes the solution basic (*pH* > 7)
- The **advantage** of using data loggers is that they are **more objective** than using indicators.

**2.5 Esterification****2.5.1 Describe the differences between the alkanol and alkanoic acid functional groups in carbon compounds**

- A **functional group** is a group of atoms attached to a carbon compound which determines its chemical properties. It is the site in the carbon compound where chemical reaction takes place.
- The functional group of *alkanols* is the hydroxyl group ( $-\text{OH}$ ).
- The functional group of *alkanoic acids* is the carboxylic acid group ( $-\text{COOH}$ ).
  - This group is acidic as it can dissociate to form  $\text{H}^+$  ions in solution and behave as a weak acid.

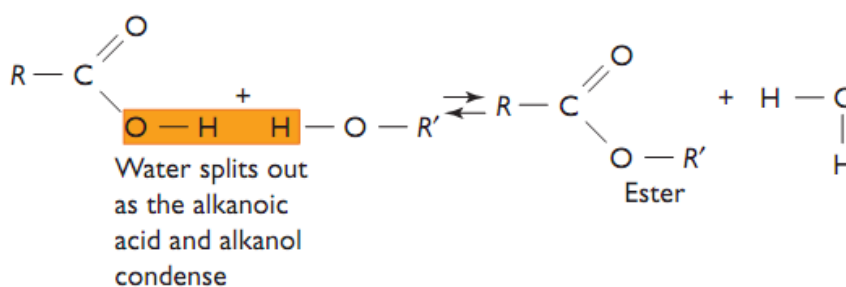
### 2.5.2 Explain the difference in melting point and boiling point caused by straight-chained alkanolic acid and straight-chained primary alkanol structures

- The stronger the **intermolecular forces**, the more energy is required to break the bonds, and hence the higher the melting and boiling points (MP and BP).
- Alkanes have **weak dispersion forces** caused by movement of electrons around the molecule creating dipoles, so MP and BP of alkanes are low.
  - Alkanes have higher MP and BP than corresponding alkenes due to higher molecular weight, which increases electron cloud density and hence distortion, so dispersion forces are greater.
- Alkanols also experience **polar C – O** and **O – H** bonds in addition to dispersion forces, so they have higher MP and BP than alkanes.
  - Hydrogen bonding** exists between molecules, which explains the high water solubility of short-chain alkanols.
  - As chain length increases, however, alkanols become increasingly insoluble.
- Alkanoic acids have stronger intermolecular forces compared with alkanols as they have **more extensive hydrogen bonding** between molecules (due to the extra oxygen atom in their functional group), greatly increasing MP and BP. They also have greater molecular weights than corresponding alkanes or alkanols, so dispersion forces are greater.
  - Alkanoic acids are weak acids, and can be neutralised by strong bases to form salts and water.
- Esters are polar substances due to  $C = O$  and  $C - O$  bonds.
  - However, lack of hydrogen bonding means esters have low MP and BP compared with corresponding acids or alkanols. They are also less soluble in water.



### 2.5.3 Identify esterification as the reaction between an acid and an alkanol and describe, using equations, examples of esterification

- Esters** are compounds formed when alkanolic acids react with alkanols.
- Esterification** is the reaction of an alkanolic acid with an alkanol to produce an alkyl alkanoate (ester). It is a **slow endothermic** reaction that does not go to completion.
 
$$\text{alkanoic acid} + \text{alkanol} + \text{HEAT} \rightleftharpoons \text{alkyl alkanoate (ester)} + \text{water} \quad [\Delta H > 0]$$
- It is classified as a condensation reaction, not an acid-base reaction. The water that is formed comes from the  $OH$  group of the alkanolic acid and the  $H$  of the alkanol functional group.



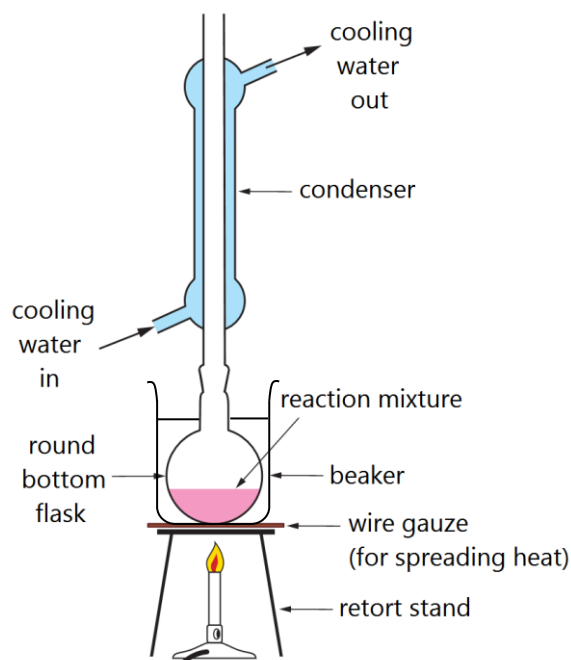
- The reaction is **reversible** and **comparable quantities** of alkanol, acid, ester and water are present at equilibrium.

### 2.5.4 Describe the purpose of using acid in esterification for catalysis

- **Concentrated sulfuric acid** ( $H_2SO_4$ ) is used as a:
  - **Catalyst** to increase the rate of reaction by lowering the activation energy and allowing equilibrium to be reached faster. The catalyst itself does not participate in the reaction.
  - **Dehydrating agent** to increase yield by absorbing the product water to favour the forward reaction, shifting equilibrium to the right (Le Chatelier's principle).

### 2.5.5 Explain the need for refluxing during esterification

- **Refluxing** is the process of heating a liquid mixture with a condenser attached vertically above the reaction vessel, in order to prevent the loss of volatile reactants or products. It allows the reaction to be brought about at a *higher temperature* than would otherwise be possible.
- Esterification is a slow reaction so heat is required to increase the rate of reaction (by increasing the *kinetic energy* of molecules).
- However, the reactants and products are organic compounds which are volatile, and readily vaporise on heating.
- To avoid loss of material from the reaction vessel, a **condenser** is attached to the flask.
- Cold water circulates to cool the vapours, which condense back into liquid and fall back into the reaction mixture.
- A **water bath** ensures even heating and safety (as organic compounds are volatile and flammable and must be kept away from naked flames).
- **Boiling chips** encourage the mixing of reactants to distribute heat. They prevent 'bumping' as they provide a large surface area on which vaporisation can occur without the risks of sudden superheating of liquids and explosive ejection of vapours.



### 2.5.6 Outline some examples of the occurrence, production and uses of esters

#### 2.5.7 Process information from secondary sources to identify and describe the uses of esters as flavours and perfumes in processed foods and cosmetics

- Esters occur naturally in living things. They have strong flavours and odours, so they are produced for use as flavours and perfumes in processed foods and in cosmetics.
- Uses of esters:
  - **Flavourings:** Many esters are used as **flavourings** and **perfumes** due to their pleasant, fruity odours (e.g. pineapple - *butyl butanoate*; apple – *ethyl pentanoate*).
  - **Solvents:** Domestic uses of esters include *ethyl ethanoate* for **nail polish remover** and scents for **perfumes**.



- *Emulsifiers*: Esters (e.g. *glycerol*) that have high molecular weight are used as **emulsifying agents** to prevent oils and water separating into layers in cosmetics and food products.

### 2.5.8 Identify data, plan, select equipment and perform a first-hand investigation to prepare an ester using reflux

- Aim: To prepare ethyl ethanoate from ethanoic acid and ethanol using reflux.
- Theory: Esters are prepared by the reaction of an alkanoic acid and alkanol in the presence of concentrated  $H_2SO_4$  which acts as a dehydrating agent and removes water formed. Refluxing improves the safety of the operation, as the volatile components are flammable.
- Equipment: absolute ethanol (solid), glacial acetic acid (solid), concentrated 18 M  $H_2SO_4$ , reflux condenser with hoses, water bath and Bunsen burner, boiling chips, beaker.
- Method:
  - 12 mL ethanol and 15 mL ethanoic acid were mixed together in a round-bottom flask.
  - 3 mL of concentrated  $H_2SO_4$  was added, and a few boiling chips were added.
  - A reflux condenser was attached above the flask, with cold water flowing into the base of the condenser jacket and out the top.
  - The flask was placed in a water bath.
  - The mixture was heated on a Bunsen flame for 30 min. and then allowed to cool.
  - The reaction mixture was poured into a beaker containing water, and then shaken to allow the layers to separate (the ester is immiscible with water, so 2 separate layers will form). The ester layer is less dense than the aqueous layer so it will float on top of the water.
  - The ester was separated from the reaction mixture using a separating funnel.
  - The ester was allowed to cool and its odour was noted.
- Discussion:
  - The application of heat to the reaction speeds up the rate of reaction (as the reaction is endothermic), allowing it to reach equilibrium faster.
  - Adding sodium carbonate to the ester layer removes excess acid:
 
$$Na_2CO_3 + 2H^+ \rightarrow 2Na^+ + H_2O + CO_2$$
  - Adding calcium chloride dries the ester layer (as  $CaCl_2$  is a dehydrating agent, which absorbs moisture).
  - Differences in boiling points are used to purify the ester through fractional distillation.
- Risk Assessment:
  - $H_2SO_4$  is a concentrated strong acid which is corrosive.
  - Organic compounds are volatile and flammable, so they must be kept in a well-ventilated area, away from naked flames.
  - Long hair should be tied back and ties should be removed to prevent fire hazard and accidental collision with any equipment in the experiment.
  - Safety glasses were worn throughout the experiment as it involves boiling highly volatile reactants.