9.3 – The Acidic Environment:

Δ. Construct word and balanced formulae equations of all chemical reactions as they are encountered in this module:

- NOTE: In chemistry, [x] means "concentration of x" in moles per litre (mol/L).
- **EG:** [H₃O⁺] means "concentration of H₃O⁺ ions" in mol/L.
- BASIC reactions to remember:
 - Acid reactions:
 - acid + base → salt + water
 - acid + metal → salt + hydrogen gas
 - acid + carbonate ——— carbon dioxide gas + salt + water
 - Formation of hydronium:
 - $\blacksquare \quad H^+ + H_2O \longrightarrow H_3O^+$
- Reactions of various oxides with water:
 - **Non-metal** (acidic) oxides:
 - $CO_{2 (g)} + H_2O_{(1)} \longrightarrow H_2CO_{3 (aq)}$ (carbonic acid)
 - $SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)}$ (sulfurous acid)
 - $= 2NO_{2\,(g)} + H_2O_{\,(l)} \longrightarrow HNO_{3\,(aq)} + HNO_{2\,(aq)} \ (\textit{nitric} \ and \ \textit{nitrous} \ acid)$
 - $P_2O_5_{(g)} + H_2O_{(l)} \longrightarrow 2H_3PO_4_{(aq)}$ (phosphoric acid)
 - Metal (basic) oxides:
 - $\blacksquare \quad K_2O_{(s)} + H_2O_{(l)} \longrightarrow 2KOH_{(aq)} \ (\textit{potassium hydroxide})$
 - $\blacksquare \quad Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} \ (\textit{sodium hydroxide})$
 - $MgO_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2 (aq)} (magnesium hydroxide)$
- Various EQUILIBRIUM reactions:
 - − Formation of **carbonic** acid: $CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$
 - $-\quad Copper \ \textbf{complex-ions} : \ Cu(H_2O)_4{}^{2+}{}_{(aq)} + 4Cl^{^{*}}{}_{(aq)} \Longleftrightarrow \quad CuCl_4{}^{2^{*}}{}_{(aq)} + 4H_2O_{\ (l)}$
 - Decomposition of **dinitrogen tetroxide**: $N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$
- *Non-Arrhenius acid/base reaction:*
 - Gaseous hydrogen chloride and ammonia react:
 - $\blacksquare \quad HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4Cl_{(s)}$

- *IONISATION of strong and weak acids:*
 - **Hydrochloric**: $HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl_{(aq)}$
 - **Nitric**: $HNO_{3 (1)} + H_2O_{(1)} \longrightarrow H_3O^+_{(aq)} + NO_3^-$
 - **Sulfuric**: $H_2SO_{4 (l)} + 2H_2O_{(l)} \longrightarrow 2H_3O^{+}_{(aq)} + SO_4^{2^{-}}$
 - **Ethanoic**: $CH_3COOH_{(s)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$
- Sources of sulfur and nitrogen oxides in the atmosphere:
 - Sulfur Oxides:
 - Organic decomposition: $2H_2S_{(g)} + 3O_{2(g)} \longrightarrow 2SO_{2(g)} + 2H_2O_{(l)}$
 - Burning high-sulfur coals: $S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$
 - Smelting metal sulfides: $2PbS_{(s)} + 3O_{2(g)} \longrightarrow 2PbO_{(s)} + 2SO_2$
 - Nitrogen Oxides:
 - Lightning: $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$
 - Oxidation of nitrogen monoxide: $2NO_{(g)} + O_{2(g)} \longrightarrow NO_{2(g)}$
- Amphiprotic substances:
 - Sodium hydrogen carbonate:
 - $HCO_3^-(aq) + H_3O^+(aq) \longrightarrow H_2CO_3(aq) + H_2O_{(1)}$
 - $\blacksquare \quad HCO_3^-(aq) + OH^-(aq) \quad \longrightarrow \quad CO_3^{2^+}(aq) + H_2O_{(l)}$
- Natural Buffers:
 - The carbonic acid/hydrogen carbonate ion buffer in freshwater lakes:
 - $\begin{tabular}{ll} \blacksquare & $H_2CO_{3\;(aq)} + H_2O_{\;(l)} & \Longrightarrow & $H_3O^+_{\;(aq)} + HCO_3^-_{\;(aq)}$ \\ \end{tabular}$
- Esterification:
 - General **word-formula**:
 - alkanoic acid + alkanol === ester + water
 - Example:
 - butanoic acid + pentanol ==== pentyl butanoate
 - $\blacksquare \quad C_3H_7COOH_{(aq)} + C_5H_{11}OH_{(l)} \\ \Longleftrightarrow \quad C_3H_7COOCH_2C_4H_{9\,(aq)} + H_2O_{(l)} \\$

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

• RECALL:

- General Properties of <u>ACIDS</u>:
 - They taste *sour*.
 - They are corrosive.
 - When in solution, they can conduct electricity.
 - Acids are neutralised by bases.
 - They affect the colour of certain natural and synthetic dyes (**indicators**).
 - pH < 7
 - For LITMUS: **blue** \rightarrow acid \rightarrow **red** (litmus is a dye made from LICHENS).
- General Properties of <u>BASES</u>:
 - They usually taste *bitter*.
 - May be corrosive.
 - Are electrolytes (conduct electricity in solution).
 - Bases are neutralised by acids.
 - They affect the colour of indicators.
 - They feel slippery (bases react with oils on our skin, forming soaps).
 - Are mainly insoluble in water (aqueous bases are called **alkalis**).
 - Bases are usually metal hydroxides (e.g. NaOH) or metal oxides (e.g. MgO).
 - pH > 7
 - For LITMUS: $red \rightarrow base \rightarrow blue$
- Classify common substances as acidic, basic or neutral:
 - Common acids:
 - Vinegar (acetic acid), vitamin C (ascorbic acid), lemon juice (citric acid), aspirin (acetyl salicylic acid), 'fizzy' drinks (carbonic acid), car battery fluid (sulfuric acid).
 - Common bases:
 - Drain cleaners (sodium hydroxide), household cleaners (ammonia), antacid tablets (calcium carbonate), baking powder (sodium bicarbonate), washing powder (sodium carbonate).

- Common **neutral** substances:
 - Pure water, table salt (sodium chloride; <u>but</u> NOT all salts are neutral), milk,
 oils and other fats, sugars.
- 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.
 - Most indicators produce 2 different colours; one when acidic and one when basic.
 - Litmus, phenolphthalein, methyl orange and bromothymol blue are common indicators that change colour over a pH range.
 - Each indicator has its own specific range of pH over which it changes colour.
 - Often, indicators need to be used in combinations to determine the exact pH of a substance, as indicators are usually very limited in their pH range.
- Identify data and choose resources to gather information about the colour changes of a range of indicators:
 - The range of pH range of the common indicators is shown below. LEARN:

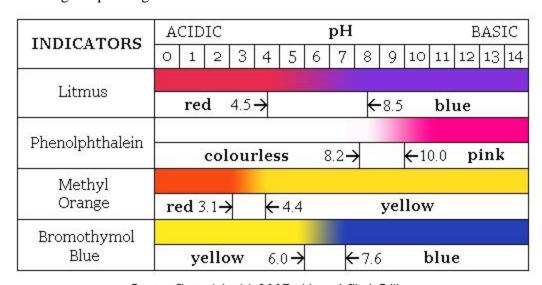


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- As can be seen, the range of pH of an indicator is portrayed in a change of **colour**.

• Identify and describe some everyday uses of indicators including the testing of soil acidity/basicity:

– Testing Soil pH:

- Some plants only grow within narrow pH ranges, so the pH of the soil needs to be regularly tested.
- A neutral white powder (such as talc or barium sulfate) is sprinkled over the damp soil; a few drops of indicator(s) are placed on top.
- The white powder allows the colour change to be seen clearly.

Testing pH of Pools:

- Pool water must be near neutral to avoid health problems.
- A few drops of indicator is placed in a sample of the pool water; alternatively,
 pH paper, already soaked in indicator can be used.

Monitoring pH of Chemical Wastes:

- Wastes that are produced from laboratories or photographic film centres tend to be highly acidic.
- The pH of the wastes must be neutralised before they can be safely disposed.
- Indicators are used to measure the pH, and substances added to neutralise it.
- Solve problems by applying information about the colour changes of indicators to classify some household substances as acidic, neutral or basic:
 - **EG**: Deduce whether the following substances are acidic, neutral or basic:
 - A drain cleaner, composer of mainly **sodium hydroxide** (NaOH), was tested using litmus and phenolphthalein indicator. Litmus turned BLUE and phenolphthalein turned dark PINK.
 - ➤ Since litmus is blue, it is definitely basic. As phenolphthalein turned a dark pink, it must be *strongly* basic.
 - Vinegar, ethanoic acid (CH₃COOH), was tested using methyl orange, and turned RED. Hence, it is an acid.
- **PRACTICAL** Perform a first-hand investigation to prepare and test a natural indicator:
 - Most indicators are derived from natural plant sources.

- In this experiment, an indicator was made from beetroot.
- One large beetroot was peel and chopped; it was then blended thoroughly using a food processor with 100 mL of *distilled* water.
- The mixture was strained into a beaker; this is the indicator.
- In 4 separate test-tubes, 3 mL of distilled water, sodium chloride (NaCl) solution,
 hydrochloric acid (HCl) and sodium hydroxide (NaOH) solution was placed.
- Then using a dropper, 3 drops of beetroot indicator was added to the test-tubes.

- **RESULTS**:

- In the distilled water, it was DARK PURPLE.
- In the NaCl solution, it was DARK RED.
- In the HCl solution, it was PINK.
- In the NaOH solution, it turned YELLOW.

JUSTIFY the method:

- Beetroot was used as it is a very vividly coloured plant; and its pigmentation is very easily extracted.
- A fresh beetroot was used instead of canned beetroot as the canned version may contain preservatives (many of which are weak acids) that may affect the results.
- HCl and NaOH was used as they are on opposite ends of the pH scale; this
 was to show the range of colours the indicator could produce.

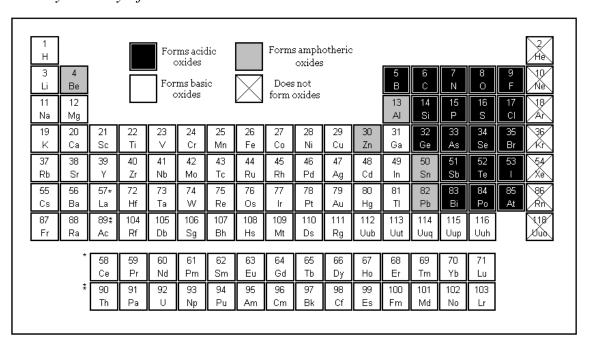
- **LIMITATIONS** of the method:

- Beetroot come in many sizes; this was not controlled.
- The exact pH at which the transition of colours occurred was not determined.
- This could be performed through the use of pH meters or data loggers.

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

- RECALL:
 - The HYDRONIUM ion:
 - When in aqueous solutions, ACIDS disassociate into anions and H⁺ ions.
 - Then this reaction occurs: $H^+ + H_2O \longrightarrow H_3O^+$
 - The H₃O⁺ ion is called the **hydronium** ion, and is more stable than the H⁺ ion.
 - Thus, more correctly, in water, acids form hydronium ions.
- Identify oxides of non-metals which act as acids and describe the conditions under which they act as acids:
 - **Oxides** are compounds that contain OXYGEN.
 - ACIDIC OXIDES:
 - Acidic oxides are oxides that:
 - React with WATER to form acids.
 - React with BASES to form salts.
 - Non-metal oxides behave as ACIDS.
 - E.G. Some non-metal oxides that act as acids are: CO₂ (carbon dioxide), SO₂ (sulfur dioxide), NO₂ (nitrogen dioxide) and P₂O₅ (phosphorus pentoxide).
 - When they are in solution, they become acids:
 - $ightharpoonup CO_{2 (g)} + H_2O_{(l)} \longrightarrow H_2CO_{3 (aq)}$ (carbonic acid)
 - $ightharpoonup SO_{2 (g)} + H_2O_{(l)} \longrightarrow H_2SO_{3 (aq)}$ (sulfurous acid)
 - $ightharpoonup 2NO_{2 (g)} + H_2O_{(l)} \longrightarrow HNO_{3 (aq)} + HNO_{2 (aq)}$ (nitric and nitrous acid)
 - $ightharpoonup P_2O_{5 (g)} + H_2O_{(l)} \longrightarrow 2H_3PO_{4 (aq)} (phosphoric acid)$
 - NOTE: The exceptions are the *neutral* oxides include N2O (dinitrogen oxide),
 CO (carbon monoxide) and NO (nitric oxide), which do not form acids.
 - BASIC OXIDES:
 - Similarly, *basic oxides* are oxides that:
 - React with WATER to form bases.

- React with ACIDS to form salts.
- Metal oxides behave as BASES.
- E.G. Some metal oxides that act as bases are: K₂O (potassium oxide), Na₂O (sodium oxide) and MgO (magnesium oxide).
- In solution, tend to form *basic hydroxides*:
 - $ightharpoonup K_2O_{(s)} + H_2O_{(l)} \longrightarrow 2KOH_{(aq)}$ (potassium hydroxide)
 - $ightharpoonup Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$ (sodium hydroxide)
 - $ightharpoonup MgO_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2 (aq)}$ (magnesium hydroxide)
- AMPHOTERIC OXIDES:
 - Amphoteric oxides are oxides that can act as BOTH acids and bases.
 - Their behaviour depends on the reaction they are put in.
 - The only elements that combine to form amphoteric oxides are *beryllium*, *aluminium*, *zinc*, *tin* and *lead*.
- Analyse the position of these non-metals in the Periodic Table and outline the relationship between position of elements in the Periodic Table and acidity/basicity of oxides:



- The **acidic** oxides are on the RIGHT side of the periodic table (non-metals).
- The **basic** oxides are on the LEFT side of the periodic table (metals).
- The **amphoteric** oxides are in-between; NOBEL gases have no oxides.

- Define Le Chatelier's principle:
 - The Concept of Chemical EQUILIBRIUM:
 - So far, in our brief study of chemistry, we have been concerned mainly with chemical reactions that go to COMPLETION.
 - This means that all the *reactants* are turned into *products*.
 - \triangleright EG: Mg (s) + 2HCl (aq) \longrightarrow MgCl₂ (aq) + H₂ (g)
 - ◆ If 1 mole of magnesium was placed in a solution with 2 moles of HCl, ALL the reactants would be turned into products, and thus the reaction gone to **completion**.
 - ◆ These types of reactions are <u>one-directional</u>; only HCl and Mg will react, the MgCl₂ and H₂ will not react 'backwards'.
 - HOWEVER, many chemical reactions do NOT go to completion.
 - Many reactions are in fact reversible and two-directional; they can go from left to right, or right to left; this is represented using a 2-directional arrow.
 - The reaction from LEFT-to-RIGHT is called the **forward** reaction, and the reaction from RIGHT-to-LEFT is called the **reverse** reaction.
 - Reversible reactions do not go to completion, but rather, they reach a position
 of STABILITY. This is called the point of Chemical EQUILIBRIUM.
 - At this point of **equilibrium**, there is no longer any change in the concentrations of the reactants or products; the reaction has come to a stop.
 - This does NOT mean that all the reactants have become products. At the point of equilibrium, there will be reactants AND products present.
 - For example, the reaction of **carbon dioxide** & **water** is a reversible reaction.
 - \triangleright **EG**: $CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$
 - ◆ The 'double-arrow' symbolises the 2-directional nature of the reaction; water and CO₂ can react to form carbonic acid, and carbonic acid can decompose to form water and CO₂.
 - ♦ At the equilibrium point, no reaction is occurring, and there are species of CO₂, water and carbonic acid, ALL present.
 - The point of chemical equilibrium is **NOT** FIXED. It depends on the conditions of the reaction; this is the basis of Le Chatelier's Principle.

- Le Chatelier's Principle:

- Systems at equilibrium have constant concentrations of reactants and products.
- If conditions change, the system will no longer be at equilibrium.
- Le Chatelier's Principle states that:

"If a chemical system at equilibrium is subjected to a change in conditions, the system will readjust itself to counteract that change."

- A system will *always* seek the point of equilibrium.
- So when a system at equilibrium has a change imposed on in, it will "readjust" to OPPOSE the change to return to a point of equilibrium.
- *Identify factors which can affect the equilibrium in a reversible reaction:*
 - Some factors that affect (or *shift*) the equilibrium position in a reversible reaction
 are a change in **concentration** of a species, a change in **pressure** in the system
 and change in **temperature** of the system.
 - Change in CONCENTRATION:
 - When the *concentration* of a particular substance (species) is:
 - ➤ INCREASED, the equilibrium point will shift towards the **opposite** side of the equation; this opposes the change, as it <u>reduces</u> the concentration of the species by producing more products on the opposite side.
 - ➤ DECREASED, the equilibrium point will shift towards the **same** side of the equation the species is on; this opposes the change, as it <u>increases</u> the concentration of the species by the opposite reaction.
 - Take for example, the *copper complex ion* equilibrium:

$$\textbf{EG: } Cu(H_2O)_4^{2+}{}_{(aq)} + 4Cl^{-}_{(aq)} \Longleftrightarrow CuCl_4^{2-}{}_{(aq)} + 4H_2O_{(l)}$$
 (GREEN)

- **1.** If **Cl** ions are <u>increased</u> the equilibrium will shift to the RIGHT, as more CuCl₄² is formed hence the system will become more green.
- 2. If more water is <u>added</u> the equilibrium will shift to the LEFT, as more $Cu(H_2O)_4^{2+}$ is formed, and the system will become more blue.
- **3.** If **water** is <u>removed</u> the equilibrium will shift to the RIGHT, so that the water lost will be replaced by the forward reaction.

- Change in GAS PRESSURE (or change in VOLUME):
 - For a closed-system composed completely of gases, if the TOTAL pressure on the system is:
 - ➤ INCREASED, the equilibrium will favour the side that reduces pressure, that is, has <u>less</u> moles; thus opposing the change. One way pressure is increased is by **reducing** the volume.
 - ➤ DECREASED, the equilibrium will favour the side that increases pressure, that is, produces <u>more</u> moles; thus opposing the change. One way of pressure is decreased by **increasing** the volume.
 - Take, for example, the equilibrium between dinitrogen tetroxide and nitrogen dioxide:
 - $EG: N_2O_{4 (g)} \Longrightarrow 2NO_{2 (g)}$ $(1 \text{ mole}) \qquad (2 \text{ moles})$
 - **1.** If the TOTAL pressure is **increased**, the equilibrium will shift to the left, to decrease pressure, as there are less moles produce on the left.
 - **2.** If the TOTAL pressure is **decreased**, the equilibrium will shift to the right, to increase the pressure, as more moles are produced on the right.

- Change in TEMPERATURE:

RECALL:

- An <u>exothermic</u> reaction is one that **produces** heat energy. For exothermic reactions, the sign of the *change in heat* (Δ H) is NEGATIVE.
 - ◆ In terms of reversible reactions, exothermic reactions produce heat through the *forward* reaction, but absorb heat in the *reverse* reaction.
- An <u>endothermic</u> reaction is one that **absorbs** heat energy. For endothermic reactions, the sign of the *change in heat* (Δ H) is POSITIVE.
 - ♦ In terms of reversible reactions, endothermic reactions absorb heat through the *forward* reaction, but release heat in the *reverse* reaction.
- If a system is **exothermic**, and the temperature is:
 - ➤ INCREASED, the equilibrium will shift to the left, as the reverse reaction is endothermic, and will cool the system to oppose the heating.

➤ DECREASED, the equilibrium will shift to the right, as the forward reaction is exothermic, and will heat the system to oppose the cooling.

Take for example, the decomposition of calcium carbonate (within a closed system; that is, nothing is allowed to escape). It is an endothermic reaction; the *change in heat* is positive:

- \triangleright EG: CaCO_{3 (s)} \rightleftharpoons CaO_(s) + CO_{2 (g)} Δ H = 178 kJ/mol
 - **1.** If the temperature is INCREASED, the **forward** reaction will increase, with equilibrium lying more on the right, as the endothermic forward cooling opposes the imposed heating.
 - **2.** If the temperature is DECREASED, the **reverse** reaction will increase, with equilibrium lying more on the left, as the exothermic reverse heating opposes the imposed cooling.
- There are many other factors that can affect equilibrium, but these are the most common; simply remember that the system will OPPOSE any change, as stated by Le Chatelier's principle of chemical equilibrium.
- Note: CATALYSTS increase the rate of reaction, as equilibrium is reached faster, but do not affect the point of equilibrium.
- Describe the solubility of carbon dioxide in water under various conditions as an equilibrium process and explain in terms of Le Chatelier's principle:
 - As stated above the reaction of **carbon dioxide** & **water** is a reversible reaction:
 - $CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$ $\Delta H < 0$
 - The equilibrium between carbon dioxide, water & carbonic acid can be examined under different conditions, such as those explored above:
 - Effect of species **concentration**, according to Le Chatelier's Principle:
 - ➤ If the concentration of CO₂ is INCREASED, such as by pumping more CO₂ into the system, the system will dissolve more CO₂ to counteract the change; hence equilibrium shifts to the <u>opposite</u> site; the right.
 - ➤ If the concentration of CO₂ is DECREASED, such as by removing CO₂ from the system, the system will release more CO₂ to oppose this loss; hence equilibrium shifts to the <u>same</u> side; the left.
 - Effect of **pressure**, according to Le Chatelier's Principle:

➤ If pressure is INCREASED, the equilibrium will favour the side that reduces the pressure, and that is the <u>forward</u> reaction; it reduces pressure by dissolving the CO₂ (*solutions* take up less volume than *gases*).

- ➤ If pressure is DECREASED, the equilibrium will favour the side that increases the pressure, and that is the <u>reverse</u> reaction; it increases pressure as the carbonic acid changes back into CO₂ and water.
- Effect of **temperature**, according to Le Chatelier's Principle:
 - ➤ If it is INCREASED, the equilibrium will favour the reverse reaction, as it is endothermic and will oppose the change by cooling the system.
 - ➤ If it is DECREASED, the equilibrium will favour the forward reaction, as it is exothermic and will oppose the change by heating the system.
- Effect of acids (H⁺) and bases (OH⁻), according to Le Chatelier's Principle:
 - $ightharpoonup CO_{2 (g)} + H_2O_{(l)} \Longrightarrow 2H^+_{(aq)} + CO_3^{2^-_{(aq)}}$
 - ➤ If an ACID is added, the concentration of H⁺ will increase, and hence the equilibrium will shift to the left, producing more gas.
 - ➤ If a BASE is added, the OH will react with the H⁺ (creating water) greatly shifting the equilibrium to the right, as more H⁺ is produced to counteract the change. If enough basic substance is added, the reaction could go to completion, and no longer have an equilibrium point.
- Identify natural and industrial sources of sulfur dioxide and oxides of nitrogen:
 - **Sulfur Dioxide** (SO₂):
 - NATURAL <u>sources</u>: Volcanic gases, bushfires, decomposition of organic matter and sulfur-rich geothermal hot springs releasing gases.
 - INDUSTRIAL <u>sources</u>: Processing and burning of fossil fuels and extracting metals from sulfur-rich ores, such as galena (PbS).
 - Nitric Oxide (or nitrogen monoxide, NO):
 - NATURAL <u>sources</u>: The reaction of nitrogen and oxygen in the atmosphere due to high temperatures of lightning.
 - INDUSTRIAL <u>sources</u>: Combustion of fossil fuels, both in cars and in power stations. The nitrogen in the air reacts with oxygen in the hot engines.

- **Nitrogen Dioxide** (NO₂):

 NATURAL <u>sources</u>: After nitric oxide is produced by lightning, it slowly reacts with oxygen to produce nitrogen dioxide.

- INDUSTRIAL <u>sources</u>: Combustion of fossil fuels, both in cars and in power stations. Power stations release large volumes of NO₂ into the atmosphere.
- Nitrous Oxide (or dinitrogen monoxide, N₂O):
 - NATURAL <u>sources</u>: The action of nitrogen-fixing bacteria (on root nodules of legume plants) on nitrogenous materials in the soil.
 - INDUSTRIAL <u>sources</u>: Agricultural use of nitrogenous fertilizer increases the materials bacterial can act on, increasing levels of nitrous oxide.
- Describe, using equations, examples of chemical reactions which release sulfur dioxide and chemical reactions which release oxides of nitrogen:

– Sulfur Dioxide:

When organic matter decomposes it produces hydrogen sulfide (H₂S), which then oxidises (reacts with oxygen) to produce sulfur dioxide:

$$ightharpoonup$$
 2H₂S (g) + 3O₂ (g) \longrightarrow 2SO₂ (g) + 2H₂O (l)

 The burning of sulfur-rich coal and other fossil fuels directly combines sulfur with oxygen:

$$\triangleright$$
 S_(s) + O_{2(g)} \longrightarrow SO_{2(g)}

The extraction of metals from metal sulfides also releases sulfur dioxide. E.g. smelting of galena for lead:

$$ightharpoonup$$
 2PbO_(s) + 3O_{2 (g)} \longrightarrow 2PbO_(s) + 2SO₂

Oxides of Nitrogen:

 Nitric oxide is produced either when lightning, with its high temperatures combines nitrogen and oxygen:

$$ightharpoonup N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$$

- The same reaction occurs in the high temperatures of engines or power plants, also combining nitrogen and oxygen.
- Nitrogen dioxide is formed when nitric oxide reacts with oxygen in the air:

$$ightharpoonup 2NO_{(g)} + O_{2(g)} \longrightarrow NO_{2(g)}$$

• Assess the evidence which indicates increases in atmospheric concentration of oxides of sulfur and nitrogen:

- The gases NO and NO₂ are collectively referred to as NO_x .
- It is difficult to quantitatively state that oxides of sulfur and nitrogen have been increasing in the atmosphere because these oxides occur in relatively low concentrations, such as 0.01 ppm (parts per million).
- Chemical instruments able to measure very low concentrations, like those for SO₂,
 have only been commercially available since the 1970s, so there is no reliable data for these gases before this time.
- HOWEVER, analysis of gas found in ice-core samples excavated from Antarctica shows that levels of N₂O in the atmosphere has increased by about 10%.
- It can also be stated that the increased burning of fossil fuels after the **Industrial** Revolution did indeed lead to a rise in oxides of sulfur; evidence for this is that
 the air quality of major industrial cities, such as London, deteriorated greatly.
- NO₂ leads to the formation of **photochemical smog**, a direct indicator of excessive levels of nitrogen oxides in the atmosphere.
- In 1952, the so called "Great Smog of December" killed some 4000 people, mainly the frail and elderly, due to the effects of sulfur and nitrogen compounds in the air.
- The increase of the incidence of acid rain also points to the increase in atmospheric concentrations of SO₂ and NO_x compounds.
- Acid rain forms when atmospheric water reacts with these compounds; hence an increase in acid rain points to an increase in these compounds.
- Using chemical instruments in recent times, it has been measured that global atmospheric concentrations of these oxides is not increasing greatly over long periods of time, but simply peaks every now and then.
- 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:
 - See ABOVE for industrial sources of sulfur dioxide and oxides of nitrogen.

- Reasons for CONCERN about these Oxides:
 - Acid Rain: Sulfur dioxide and nitrogen dioxide are acidic oxides that react with water in the atmosphere to form acids:
 - $ightharpoonup SO_{2 (g)} + H_2O_{(l)} \longrightarrow H_2SO_{3 (aq)}$ (sulfurous acid)
 - $ightharpoonup 2NO_{2 (g)} + H_2O_{(1)} \longrightarrow HNO_{3 (aq)} + HNO_{2 (aq)}$ (nitric and nitrous acid)

These acids then combine with rain droplets, forming acid rain. Acid rain is very destructive; it can decimate entire forests, corrode limestone structures and disrupt natural ecosystems by altering natural pH levels.

- Health Problems: Sulfur dioxide is a severe respiratory irritant and can cause breathing difficulties at concentrations as low as 1 ppm. It triggers asthma attacks and aggravates emphysema. Nitrogen dioxide is also a respiratory irritant. At concentrations above 3 ppm, it can begin to destroy tissue, as it forms the strong acid, nitric acid.
- Photochemical Smog: NO₂ causes the formation of smog. This is a form of air pollution in which sunlight reacts nitrogen dioxide, hydrocarbons and oxygen to form ozone, PAN (peroxyacylnitrates) and haze. It greatly affects visibility, while ozone has harmful effects at concentrations as low as 0.1 ppm.
- Explain the formation and effects of acid rain:
 - Pure water has a pH of 7.
 - Rain water collected from non-urbanised, unpolluted sources naturally has a pH
 of about 6-6.5; this is due to the slight dissolving of CO₂ from the atmosphere.
 - Acid rain is any rain that has a pH of <u>less than 5</u>.
 - FORMATION of acid rain:
 - Sulfur dioxide reacts with rain in the atmosphere forming sulfurous acid:

$$ightharpoonup SO_{2 (g)} + H_2O_{(l)} \longrightarrow H_2SO_{3 (aq)}$$

• Sulfurous acid then reacts with oxygen; this is catalysed by air particles:

$$ightharpoonup 2H_2SO_{3 (aq)} + O_{2 (g)} \longrightarrow 2H_2SO_{4 (aq)}$$

• *Nitrogen dioxide* also reacts with rain, making *nitric* and *nitrous* acids:

$$\triangleright$$
 2NO_{2 (g)} + H₂O_(l) \longrightarrow HNO_{3 (aq)} + HNO_{2 (aq)}

• *Nitrous* acid then reacts with *oxygen*, again catalysed by air particles:

$$ightharpoonup 2HNO_{2 (aq)} + O_{2 (g)} \longrightarrow 2HNO_{3 (aq)}$$

• Thus, in industrialised areas, rain can contain relatively high levels of very strong acids; that is nitric and sulfuric acids.

• This reduces the pH to about 3-5, which is grossly unnatural and harmful.

EFFECTS of acid rain:

- Environmental damage includes the <u>destruction</u> of forests (such as the pine forests of Europe and North America), the increasing <u>acidity</u> of lakes, leading to the death of aquatic life (as has been observed in many lakes in Scandinavia) and the ruining of soils, making them unable to support vegetation.
- **Urban** and **structural** damage include the corrosion of marble statues and buildings (marble contains <u>carbonates</u> which acids readily react with).
- Calculate volumes of gases given masses of some substances in reactions, and calculate masses of substances given gaseous volumes, in reactions involving gases at 0°C and 100kPa or 25°C and 100kPa:

!! CALCULATIONS – A Brief Overview of Stoichiometry !!

- Recall:

- A MOLE of any substance is 6.022×10^{23} units of it:
 - The mole is the SI unit for "amount". Just as a *dozen* apples is the same as 12 apples, a *mole* of apples is 'just' 6.022×10^{23} apples.
- This number, 6.022×10^{23} is known as AVOGADRO'S NUMBER.
 - Note: Avogadro's number is derived from the number of carbon atoms in 12 grams of pure carbon-12.
- The RELATIVE ATOMIC MASS (A_r) of an element is the mass of an atom of an element, expressed in *atomic mass units* (**AMU**). This number is found using any Periodic Table; it is the number *under* the element.
- More importantly, the mass of one MOLE of an element (the MOLAR MASS)
 is equal to the relative atomic mass expressed in GRAMS.
 - \triangleright That is, <u>molar mass</u> (in grams) = <u>relative atomic mass</u> (in AMU)
- The short form of 'moles' is 'mol'.

EG: Calculate the mass of 2.5 mol chlorine. From the periodic table, the atomic mass of chlorine is 35.5 AMU. Hence, one mole of chlorine has a mass of 35.5g. Thus, 2.5 mol has a mass of $2.5 \times 35.5 = 88.75g$

- The MOLAR MASS of a compound is simply the SUM of the molar masses of the individual elements.
 - ➤ EG: Calculate the mass of 0.67 mol of ethylene. Ethylene has a chemical formula of C₂H₄. Hence, its molar mass is:

$$2(\text{mass carbon}) + 4(\text{mass hydrogen}) = 2(12) + 4(1) = 28g.$$

Thus, 0.67 moles would have a mass of $0.67 \times 28 = 18.76g$

- The CONCENTRATION of a solution is defined as **moles per litre** or mol/L
- Thus, the list of Chemistry equations so far are:

$$\begin{array}{ll} n = \frac{m}{M} & \longleftrightarrow & moles \, (\text{mol}) = \frac{mass \, (g)}{molar \, mass \, (g)} \\ \\ n = \frac{V}{M_V} & \longleftrightarrow & moles \, (\text{mol}) = \frac{volume \, (L)}{molar \, volume \, (L)} \\ \\ C = \frac{n}{V} & \longleftrightarrow & concentration \, (\text{mol } L^{\text{-1}}) = \frac{moles \, (\text{mol})}{volume \, (L)} \end{array}$$

- **Basic Stoichiometry** (LEARN):
 - *Stoichiometry* is the study of the calculation of quantitative (measurable) relationships of the reactants and products in chemical reactions.
 - One of the *basic* laws of stoichiometry is the 'Law of Definite Proportions':
 - ➤ In chemical reactions, reactants combine in fixed, definite proportions (or RATIOS) to form products. The ratios are determined by the **coefficients** of the species in a BALANCED chemical reaction. The coefficient of a species is the number before the species:
 - ➤ Looking at the coefficients, you can see that in this reaction, S will react with O₂ in the ratio of 1:1, forming 1 SO₂; e.g. if 3 mol of sulfur is burnt, then 3 mol of oxygen is also burnt, and 3 mol of SO₂ is produced.
 - $\bullet \quad EG: \underline{2}H_2S_{(g)} + \underline{3}O_{2(g)} \longrightarrow \underline{2}SO_{2(g)} + \underline{2}H_2O_{(l)}$

➤ In this reaction the ratio of reactants to products is 2:3→2:2. RATIOS are extremely important in determining the masses of reactants and products.

- ➤ EG: Calculate the moles, and the mass, of sulfur dioxide produced when 50g of hydrogen sulfide is oxidised:
 - First, we work how many moles of H_2S is in 50g:

```
n = m/M \text{ (mass/molar mass)} = 50/(2 \times 1 + 32.1); \text{ molar mass of H} = 1, S = 32.1 = 1.466 \text{ mol}
```

- ♦ Since we are only concerned with H₂S and SO₂, we look at the ratio of H₂S:SO₂; the ratio is 2:2, which is the same as 1:1 (simplified). Hence, there were also 1.466 mol of SO₂ produced.
- ♦ To calculate the *mass*:

```
n = m/M 1.466 = m/(32.1 + 2 \times 16); \mbox{ molar mass of } S = 32.1, \mbox{ } O = 16 1.466 = m/64.1 Hence, m = 93.97 grams
```

◆ Therefore, even though there were the same number of moles of both compounds, 50g of H₂S burned to produce 93.97g of SO₂

– Working with Volumes:

- It was discovered that ALL *gaseous* substances, with the same *temperature* and *pressure*, occupied the same VOLUME, no matter how large or massive the molecules that made up the gas were.
- This means that a fixed amount of molecules of *hydrogen gas* (with an atomic weight of **2**) will occupy the same volume as a fixed amount of molecules of *radon gas* (which has an atomic weight of **444**!); theoretically, of course.
- When working with volumes, **mass** is less important than **amount** (moles).
- Thus, it was discovered that:

```
At \, O°C and 100 kPa, the molar volume of all gases is 22.71 L At 25°C and 100 kPa, the molar volume of all gases is 24.79 L
```

• This is a very simple concept that is very easy to apply.

➤ EG: Calculate the volume of sulfur dioxide produced when 50g of hydrogen sulfide is oxidised at 25°C and 100kPa.

◆ From the working produced above, we know that 1.466 mol of sulfur dioxide are produced. Since one mole of gas at 25°C and 100kPa occupies 24.79 L, 1.466 moles of gas will occupy:

```
V = n \times M_V \text{ (moles} \times \text{molar volume)}= 1.466 \times 24.79= 36.34 \text{ L}
```

- **PRACTICAL** 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.
 - A 300mL bottle of soft drink was <u>decarbonated</u> by vigorous *shaking*, and then releasing the gas by opening the cap; no drink was allowed to spill.
 - The bottle was weighed at the beginning, and the end.
 - It was assumed that any mass loss was due to carbon dioxide loss.
 - **RESULTS**:
 - 2.4 g of CO₂ was released. To calculate the volume of gas released at 25°C:

```
n = m/M \text{ (mass/molar mass)}
= 2.4/44; \text{ molar mass of } CO_2 = 44
= 0.0545 \text{ mol}
V = n \times M_V \text{ (moles} \times \text{molar volume)}
= 0.0545 \times 24.79
= 1.35L
```

- **JUSTIFY** the method:
 - The shaking affected the CO₂/H₂CO₃ equilibrium, and this forced the gas out.
 - No liquid was allowed to spill to try to keep a high level of accuracy.
 - Electronic scales were also used for accuracy.
- LIMITATIONS of the method:
 - The accuracy of this method is limited, as there may be loss of water as gas, or there may still be CO₂ dissolved.

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

- Define acids as proton donors and describe the ionisation of acids in water:
 - An acid is a substance that releases **H**⁺ ions.
 - Another name for the H⁺ ion is a 'proton'; this is because a positive hydrogen atom (H⁺) is just a hydrogen nucleus (no electrons) and hence is just a proton.
 - When acids react with other substances, the H⁺ ion is transferred to another species; that is why acids can be defined as **proton-donors**.
 - In water, acids IONISE (separate into its ions).
 - **EG**: Pure hydrogen chloride added to water:
 - $\blacksquare \quad HCl_{\,(g)} \, \longrightarrow \, H^{+}_{\,\,(aq)} + Cl^{\bar{}}_{\,\,(aq)}$
 - However, H⁺ ions are very reactive, and do not really exist in aqueous solutions,
 because they immediately react with water molecules close by.
 - $\blacksquare \quad HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl_{(aq)}^-$
 - So in reality, acids ionise to form **hydronium** ions (H₃O⁺)
- Identify acids including acetic (ethanoic), citric (2-hydroxypropane-1,2,3-tricarboxylic), hydrochloric and sulfuric acid:
 - Acetic Acid:

- Citric Acid:

- 2-hydroxypropane-1,2,3-tricarboxylic acid
- Molecular formula: C₆H₈O₇
- It occurs in citrus fruit.
- Widely used as a preservative.

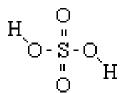
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Hydrochloric Acid:

- Molecular formula: HCl
- It is a very strong acid.
- It is produced in the stomach to aid in digestion.
- It is also industrially made in large quantities, with many uses.

- Sulfuric Acid:
 - Molecular formula: H₂SO₄
 - It is also a strong acid.
 - Most industrially produced chemical.
 - Used to make batteries, fertilizers etc.



- 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.
 - It is numbered from 0 to 14.
 - A pH of 7 is attributed to *neutral* substances (mainly, PURE water).
 - A pH < 7 refers to *acidic* substances; a strong acid is close to 0.
 - A pH > 7 refers to *basic* substances; a strong base is close to 14.
 - Hence, the pH scale allows us to compare acids and bases, and their strengths.
- Describe acids and their solutions with the appropriate use of the terms strong, weak, concentrated and dilute:
 - A strong acid is an acid that releases ALL its H⁺ ions when in solution.
 - Its molecules are completely *disassociated* in solution.
 - Its ionisation reaction goes to completion:
 - **EG**: $HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl_{(aq)}$
 - A weak acid is an acid that does NOT completely release all its H⁺ ions; hence it is 'weaker' than a strong acid of the same concentration.
 - Some of its molecules remain intact in solution
 - Its <u>ionisation</u> reaction with water is a reversible reaction that reaches equilibrium when a certain number of H⁺ ions are released:
 - EG: $CH_3COOH_{(s)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$
 - The terms concentrated and dilute refer ONLY to the <u>amount</u> of acid molecules present in the solution; they have nothing to do with ionisation.
 - A CONCENTRATED acid has approximately more than 5 mol/L of solute.
 - A DILUTE acid has less that 2 mol/L of solute.
 - Hence, strong acids can be both concentrated and dilute, and weak acids can also be both concentrated and dilute.

 Identify pH as -log₁₀[H+] and explain that a change in pH of 1 means a tenfold change in [H+]:

- The way \mathbf{pH} is calculated is through an equation related to \mathbf{H}^+ concentration
- This equation is:
 - $pH = -log_{10}[H^+]$ OR $pH = -log_{10}[H_3O^+]$
- A change in pH of 1 means a <u>10-fold</u> change in [H⁺]:
 - **EG**: pH of 4; $[H^+] = 10^{-4}$ while a pH of 3; $[H^+] = 10^{-3}$. $10^{-3} / 10^{-4} = 10$.
 - A more rigorous algebraic proof can be easily produced.
- SIMILARLY, there is another scale of acidity and basicity: it is the **pOH** scale.
- It is almost the same as pH, except that is uses OH concentration as a measure, instead of H⁺ concentration:
 - $pOH = -log_{10}[OH^-]$
- The RELATIONSHIPS between pH and pOH are:
 - PH + pOH = 14
 - $[H^+][OH^-] = 10^{-14}$
- Water undergoes self-ionisation in ALL solutions: H₂O = H⁺ + OH⁻
- In pure water, the $[H^+] = [OH^-] = 10^{-7}$; pH = pOH = 7. Thus it is **neutral**.
- But for acids, $[H^+] > [OH^-]$, and for bases $[OH^-] > [H^+]$
- Process information from secondary sources to calculate pH of strong acids given appropriate hydrogen ion concentrations:
 - The pH of a *strong* acid is easily calculated, given the molar concentration, as we know ALL its protons are released into solution.
 - However, an acid may be able to release MORE than one proton. These acids are called polyprotic acids.
 - CALCULATING pH of a strong, monoprotic acid:
 - Monoprotic acids release only one proton, e.g. HCl:
 - $ightharpoonup HC1 \longrightarrow H^+ + C1^-$
 - **EG**: Calculate the pH of 0.01 M hydrochloric acid.
 - ➤ M means mol/L; hence this is 0.01 mol/L, or 10⁻² mol/L
 - ightharpoonup Then pH = $-\log_{10}(10^{-2}) = 2$
 - CALCULATING pH of a strong, **diprotic** acid:

- Diprotic acids release 2 protons, e.g. H₂SO₄.
 - $ightharpoonup H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$
- Hence, for every mole of acid, it releases 2 protons.
- **EG**: Calculate the pH of 0.1 M sulfuric acid:
 - \blacktriangleright It has 0.1 mol/L; therefore its [H⁺] = 2 × 0.1 = 0.2 mol/L
 - \triangleright So, pH = $-\log_{10}(0.2) = 0.7$
- CALCULATING pH of a strong, triprotic acid:
 - Triprotic acids release 3 protons, e.g. H₃PO₄.
 - $ightharpoonup H_3PO_4 \longrightarrow 3H^+ + PO_4^{3-}$
 - **EG**: Calculate the pH of 0.05 M of phosphoric acid:
 - \triangleright So, pH = $-\log_{10}(3 \times 0.05) = 0.82$
- Extra: CALCULATING pH of a **WEAK** acid:
 - Recall that weak acids do not fully ionise; if the degree of ionisation is given, usually as a percentage, than the pH can be determined.
 - **EG**: Calculate the pH of 0.1 mol/L ethanoic acid if only 1.3% ionises:
 - \rightarrow [H⁺] = 1.3% of 0.1 = 0.0013
 - \rightarrow pH = -log₁₀(0.0013) = 2.9
- Extra: CALCULATING pH of a strong **BASE**:
 - Just as acids can be *polyprotic*, bases can release more than one OH⁻ ion.
 - This must be taken into consideration when calculating the pH.
 - **EG**: Calculate the pH 0.1 M of Ca(OH)₂ if it fully ionises:
 - ightharpoonup Ca(OH)₂ \longrightarrow 2OH + Ca²⁺
 - \rightarrow [OH⁻] = 2 × 0.1 = 0.2
 - \rightarrow pOH = $-\log_{10}(0.2) = 0.69$
 - \rightarrow pH = 14 pOH = 14 0.69 = 13.3
- Extra: CALCULATING the pH of a solution after **DILUTION**: $c_1v_1 = c_2v_2$
 - In this case, the dilution formula is used; $c_1v_1 = c_2v_2$.
 - **EG**: Find the pH of the solution formed when 10 mL of 0.1 M sulfuric acid is diluted to 250 mL (it is *diprotic*):
 - In this case, $c_1 = [H^+] = 2 \times 0.1 = 0.2$, $v_1 = 0.01$ L and $v_2 = 0.25$ L
 - ightharpoonup Hence: $\mathbf{c_2} = \mathbf{c_1} \times \mathbf{v_1} \div \mathbf{v_2} = 0.2 \times 0.01 \div 0.25 = 0.008 \,\mathrm{M}$

- ightharpoonup The original pH would be $-\log_{10}(0.1 \times 2) = 0.69$
- ightharpoonup The new pH is $-\log_{10}(0.008) = 2.1$
- Extra: CALCULATING the pH of a solution after **NEUTRALISATION**:
 - The partial neutralisation of a acid and a base can leave a solution that is slightly acidic or basic; the volumes and concentrations of solutions used determines the pH of the final product.
 - The solution will only be neutral when there are exactly the same number of moles of H⁺ and OH⁻ reacted.
 - EG: 10 mL of 0.5 M hydrochloric acid is mixed with 25 mL of 0.35 M sodium hydroxide. Find the pH of the final product, assuming salt is neutral:
 - Firstly, a balanced chemical equation <u>must</u> be written:
 - \bullet HCl_(aq) + NaOH_(aq) \longrightarrow NaCl_(aq) + H₂O_(l)
 - As can be seen, the molar ratio of reaction for the acid and base is 1:1.
 - \triangleright Calculating the number of moles of acid and base, using $n = c \times v$:
 - Acid: $n = 0.5 \times 0.01 = 0.005$
 - \bullet Base: n = $0.35 \times 0.025 = 0.00875$
 - ➤ There are more moles of base than there are acid; hence there will be an excess of base after neutralisation completes.
 - \triangleright Moles of base remaining = 0.00875 0.005 = 0.00375
 - As NaOH only releases one OH $^{-}$ ion, [OH $^{-}$] = 0.00375
 - \bullet pOH = $-\log_{10}(0.00375) = 2.426$
 - Hence pH = 14 pOH = 11.6
- 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:
 - Recall that **strong** acids completely ionise in solution, while **weak** acids only partially ionise in solution.
 - Equal concentrations (1 mol/L) of *citric*, *acetic* and *hydrochloric* acid were made,
 and their pH was measured using a pH probe.
 - The resultant pH's were: HCl = 1, $CH_3COOH = 2.9$ and $C_6H_8O_7 = 2.1$

- Using the formula, $[H^+] = 10^{-pH}$ (derived from the pH formula), we can find out the concentrations of hydrogen ions released by each acid:

- **HCl**: $[H^+] = 10^{-1} = 0.1 \text{ mol/L}$
- **CH₃COOH**: $[H^+] = 10^{-2.9} = 0.00126 \text{ mol/L}$
- $C_6H_8O_7$: $[H^+] = 10^{-2.1} = 0.0079$
- The DEGREE of IONISATION of an acid refers to the percentage of H⁺ ions that have been released; it is calculated by expressing the actual [H⁺] over the number of molecules of the acid.
 - HCl: $0.1/0.1 \times 100 = 100\%$ ionisation (as expected from a strong acid)
 - **CH₃COOH**: $0.00126/0.1 \times 100 = 1.26\%$ ionisation (a very weak acid)
 - $C_6H_8O_7$: 0.0079/0.1 × 100 = 7.9% ionisation (a moderately weak acid)
- Hence, looking at the degrees of ionisation, the strongest acid is hydrochloric acid,
 followed by citric acid, and then ethanoic acid.
- Gather and process information from secondary sources to write ionic equations to represent the ionisation of acids:
 - **Hydrochloric**: $HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl_{(aq)}$
 - Nitric: $HNO_{3 (l)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + NO_3^-$
 - **Sulfuric**: $H_2SO_{4 (1)} + 2H_2O_{(1)} \longrightarrow 2H_3O^{+}_{(aq)} + SO_4^{2^{-}}$
 - **Ethanoic**: $CH_3COOH_{(s)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$
- 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 an acid that releases ALL its H⁺ ions when in solution.
 - Its molecules are completely *disassociated* in solution.
 - Its ionisation reaction goes to <u>completion</u>:
 - **EG**: $HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl_{(aq)}$
 - Conversely, a weak acid is an acid that does NOT completely release all its H⁺ ions; hence it is 'weaker' than a strong acid of the same concentration.
 - Some of its molecules remain intact in solution.
 - Its <u>ionisation</u> reaction with water is a reversible reaction that reaches equilibrium when a certain number of H⁺ ions are released:
 - **EG**: $CH_3COOH_{(s)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

- Hence the pH can be affected by factors that shift its equilibrium.
- Use available evidence to model the molecular nature of acids and simulate the ionisation of strong and weak acids:

- Take these two beakers as a model of the molecular nature of acids, and the level of ionisation of different acids.
- In the LEFT beaker, there is a solution of sulfuric acid. All the molecules have completely ionised, as it is a strong acids. Each H₂SO₄ molecule has released 2 protons, as it is a diprotic acid.
- However, in the RIGHT beaker, there is a solution of **ethanoic** acid, of equal concentration. Only half of the acid molecules have ionised (in reality the percentage is much lower, 1.26% ionisation). The unionised molecules remain as intact molecules, holding on to their hydrogens.
- Gather and process information from secondary sources to explain the use of acids as food additives:
 - Acids are added to food for 2 reasons: as preservatives, and to add flavour.
 - PRESERVATIVES:
 - Ethanoic acid (in the form of *vinegar*) is used as a preservative in 'pickling'.
 - *Propanoic* acid is often used as a preservative in bread.
 - Sulfur dioxide is added to food as a preservative, as it forms sulfurous acid, which kills bacteria in food.

• *Citric* acid is a natural preservative, often added to jams and conserves.

– FLAVOURINGS:

- *Carbonic* acid is added to soft drinks to add 'fizz'.
- *Phosphoric* acid is also added to soft drinks to add 'tartness' of flavour.
- Ethanoic acid, as vinegar, is also used as a flavouring.
- 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; it is produced naturally by the lining of our stomachs. It aids in the digestion of food.
- Citric acid: C₆H₈O₇; occurs naturally in large quantities in citrus fruits.
- *Ethanoic acid*: CH₃COOH; it is found naturally in vinegar, which is produced by the natural oxidation of ethanol.
- *Lactic acid*: C₃H₆O₃; it is formed in the body during strenuous exercise.

NATURAL BASES:

- *Ammonia*: NH₃; it is present in the stale urine of animals. It 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*: CaCO₃; it is found naturally as limestone.
- **PRACTICAL** Solve problems and perform a first-hand investigation to use pH meters/probes and indicators to distinguish between acidic, basic and neutral chemicals:
 - Part A Testing Substances With Methyl Orange:
 - 10 test-tubes were set up with 5 mL of acidified solution (0.1 M HCl).
 - 2 drops of methyl orange were placed in each test-tube.
 - A range of substances was dropped in each test-tube, from various carbonates, metal oxides, sulfates, and common household substances.
 - Any change, such as indicator colour change or bubbles, was recorded.

- **RESULTS**:

 It is known that methyl orange is red in strongly acidic solutions, and yellow in slightly acidic to highly alkaline solutions.

- Any substance that caused the acidified solution to turn yellow was classified as a base. This included:
 - ➤ Carbonates: Calcium carbonate and sodium hydrogen carbonate caused the solution to turn yellow and formed bubbles.
 - ➤ *Metal Oxides*: Calcium oxide and zinc(II) oxide turned the solution yellow, without any bubbles.
 - > Hydroxides: Magnesium hydroxide rapidly turned the solution yellow.
- The other substances caused no change in the solution; these were labelled acidic or neutral. These included sucrose, salt (NaCl), lemon juice, vinegar and magnesium sulfate.

Part B – Testing Common Substances Using a pH Meter:

- 5g of the substance was dissolved in 20 mL of water and the pH tested.
- They were then classified as acids, bases or neutral.
- *Neutral*: Both table salt and milk were neutral.
- *Bases*: Washing powder, the antacid tablet and toothpaste.
- *Acids*: Soil, vitamin C tablet and aspirin.

– JUSTIFY the method:

- Methyl orange is only red in strongly acidic solutions, so even a very weak base would have been able to elicit a colour change.
- A wide range of substances was used to portray the wide range of possible bases. This showed that bases are not only limited to metal hydroxides.
- A pH meter gave instantaneous accurate results.
- Equal amounts of each substance, dissolved in 20 mL of water made for a fair test of the substance's pH.

– LIMITATIONS of the method:

• The methyl orange test was not able to distinguish acidic and neutral substances, as both caused no colour change from the red.

• **PRACTICAL** – Plan and perform a first-hand investigation to measure the pH of identical concentrations of strong and weak acids:

- 20 mL of 0.1 M solutions of ethanoic, citric, hydrochloric and sulfuric acid were placed in four separate beakers.
- A pH meter was used to measure the pH's of the solutions.
- **RESULTS**:
 - Sulfuric acid; pH = 0.7
 - Hydrochloric acid; pH = 1.2
 - Citric acid; pH = 2.9
 - Ethanoic acid; pH = 3.3
- Sulfuric acid has the lowest pH of all the solutions as it is a diprotic strong acid, where was hydrochloric acid is a monoprotic strong acid. Citric and ethanoic acid are weak acids.

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

- Outline the historical development of ideas about acids including those of Lavoisier, Davy and Arrhenius:
 - **Lavoisier**; stated that ACIDS contain OXYGEN:
 - Proposed that acids were corrosive substances that all contained oxygen.
 - He hypothesised that since many of the common acids contain oxygen (such as *acetic acid*, C₂H₃COOH, *carbonic acid*, H₂CO₃, *sulfuric acid*, H₂SO₄), all acids must contain oxygen.
 - He thought that oxygen was the source of the acidity.
 - **Davy**; stated that ACIDS contain HYDROGEN:
 - He showed that hydrochloric acid (HCl) did not contain oxygen, disproving Lavoisier's hypothesis.
 - Many other non-oxygen containing acids had been discovered, such as hydrofluoric acid (HF), hydrobromic acid (HBr) and hydrocyanic acid (HCN).
 - Thus he hypothesised that all acids contain hydrogen.
 - Arrhenius; stated that ACIDS produced H⁺ IONS when in WATER:
 - He proposed the idea that acids <u>disassociate</u> into their ions when they are dissolved in water.
 - Thus, he hypothesised that acids release a H⁺ when in an aqueous solution.
 - He also said that bases release OH ions in aqueous solutions.
- Gather and process information from secondary sources to trace developments in understanding and describing acid/base reactions:
 - The chemical theory behind the reactions of acids and bases is a topic that has been studied for many centuries.
 - As seen above, many hypotheses have been made about these substances.
 - In modern times, the theories of Lavoisier and Davy have been deemed redundant,
 or insufficient, while Arrhenius acid/base theory is still used as a simple model.
 - The 2 most recent theories are the Brönsted-Lowry and the Lewis acid/base model:

Scientist(s)	Acid Definition	Base Definition	History
Lavoisier	Corrosive	No definition	Worked with metal oxides that
	substances that		form the common oxyacids
	contain oxygen		with water.
Davy	Corrosive	No definition	Worked with hydrohalic acids
	substances with		such as HCl and HBr,
	hydrogen		disproving Lavoisier.
Arrhenius	Substances	Substances that	Made theories of acid/base
	disassociate into	disassociate into	ionisation. Only aqueous
	H ⁺ ions in	OH ⁻ ions in	(water) solutions were
	solution	solution	considered.
Brönsted-	Proton (H ⁺)	Proton (H ⁺)	Extended acid/base reactions
Lowry	donor	acceptor	to those without water. Acids
			must contain hydrogen; no
			solution required
Lewis	Electron pair	Electron pair	No hydrogen required. Not
	acceptor	donator	required for HSC course.

- Outline the Brönsted-Lowry theory of acids and bases:
 - The **Arrhenius** definition of acids and bases is LIMITED in that it:
 - Only applies to aqueous (water) solutions.
 - Does not explain why some salts that do not contain hydrogen can sometimes acts as acids and bases (e.g. KCN, pH of 11.3).
 - Cannot explain how some substances can act as BOTH an acid and a base.
 - The Brönsted-Lowry theory of acids and bases extended the Arrhenius theory to explain the behaviour of a much wider range of substances, with not only water as the solvent.
 - It states that:
 - An acid is a PROTON donor (is gives protons to a base)
 - A base is a PROTON <u>acceptor</u> (is accepts protons from an *acid*)
 - NOTE: A proton is just an H⁺ ion; it is a hydrogen's *nucleus*, hence a **proton**.
 - This is different from *Arrhenius* theory as acids and bases no longer have to be aqueous solutions; by Brönsted-Lowry definition they can be solids, gases, cations, anions, non-water solutions; even water can be an acid, or a base.
 - EG: Reacting hydrogen chloride gas and ammonia:
 - $HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4Cl_{(s)}$

According to Arrhenius theory, this is not an acid/base reaction, as there is no water present, and no free H⁺ ions; HCl and NH₃ are *gases* in this reaction, so they are not Arrhenius acids and bases.

- However, if one looks closer, a proton **donation** and **acceptance** has occurred:
 - $HCl + NH_3 \longrightarrow NH_4^+ + Cl^-$
- HCl has donated a proton to NH₃ OR NH₃ has accepted a proton from HCl.
- Hence, by Brönsted-Lowry definition, HCl gas is an acid, and NH₃ gas is a base.
- Describe the relationship between an acid and its conjugate base and a base and its conjugate acid:
 - Because an acid is a proton-donor, and a base is a proton-acceptor, the concept of conjugate acids and bases can be introduced:
 - A CONJUGATE BASE is the original *acid* with a proton removed
 - A CONJUGATE ACID is the original base with a proton added
 - EG: Reaction between hydrochloric acid and water:
 - $\blacksquare \quad HCl_{(aq)} + H_2O_{(l)} \longrightarrow H_3O_{(aq)} + Cl_{(aq)}$
 - The original acid is HCl; its *conjugate* base is Cl (acid *minus* proton).
 - The original base is H_2O ; its *conjugate* acid is H_3O^+ (base *plus* proton).
 - The RELATIONSHIP between acid/bases and their conjugates:

Acid/Base	Conjugate
STRONG acid (e.g. HCl)	Extremely WEAK base (e.g. Cl ⁻)
STRONG base (e.g. OH ⁻)	Extremely WEAK acid (e.g. H ₂ O)
WEAK acid (e.g. CH ₃ COOH)	WEAK base (e.g. CH ₃ COO ⁻)
WEAK base (e.g. NO ₂ -)	WEAK acid (e.g. HNO ₂)
Extremely WEAK acid (e.g. H ₂ O)	STRONG base (e.g. OH ⁻)
Extremely WEAK base (e.g. H ₂ O)	STRONG acid (e.g. H ₃ O ⁺)

- *Identify conjugate acid/base pairs:*
 - Conjugate acid/base pairs are easily identified in chemical reactions by applying the conjugate rules seen above.
 - Conjugate base is <u>acid</u> without a proton; conjugate acid is <u>base</u> with a proton.
 - **EG**: $HCl_{(aq)} + H_2O_{(1)} \longrightarrow H_3O_{(aq)} + Cl_{(aq)}$

- Acid/base pairs are HCl/Cl and H₃O⁺/H₂O
- **EG**: $NH_{3 (aq)} + H_{2}O_{(1)} \rightleftharpoons NH_{4}^{+}_{(aq)} + OH_{(aq)}^{-}$
 - Acid/base pairs are H₂O/OH and NH₄+/NH₃
- **EG**: What is the conjugate acid of NH_2 ?
 - It is the base plus a proton; hence it is NH₃
- Identify a range of salts which form acidic, basic or neutral solutions and explain their acidic, neutral or basic nature:
 - A **salt** is defined as a compound that forms when an *acid* is <u>neutralised</u> by a *base*.
 - Acids are NOT all neutral however; there are many acidic and basic salts.
 - The reason why many salts solutions are NOT neutral (pH \neq 7.0) is that many ions can act as Brönsted-Lowry acids/bases.
 - The acidity or alkalinity of a salt solution depends on the *reactants* of the neutralisation reaction:
 - A strong acid and a strong base will make a neutral salt
 - A weak acid and a weak base will make a neutral salt
 - A strong acid and a weak base will make a slightly ACIDIC salt
 - A weak acid and a strong base will make a *slightly* BASIC salt
 - These are the general rules for neutralisation reactions, but the acidity or alkalinity
 of a salt must be proved by reacting the salt's ions with water:
 - Reaction between a STRONG acid and a WEAK base:
 - \triangleright Theoretically the salt will be *slightly* acidic; pH < 7.
 - EG: $HNO_{3 (aq)} + NH_{3 (aq)} \longrightarrow NH_4NO_{3 (aq)}$
 - Nitric acid is a strong acid, and ammonia is weak base; hence ammonium nitrate will be a slightly acidic salt.
 - ➤ HOWEVER you must prove it. React the salt's ions with water:
 - \bullet NH₄⁺ + H₂O \longrightarrow NH₃ + H₃O⁺
 - \bullet Cl⁻ + H₂O \longrightarrow No Reaction
 - The presence of *hydronium* ions proves it is an acidic solution.
 - Reaction between a WEAK acid and a STRONG base:
 - \triangleright The salt will be *slightly* basic; pH > 7.
 - $\bullet \quad EG: NaOH_{(aq)} + CH_3COOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$

➤ Sodium hydroxide is a **strong** base, and ethanoic acid is a **weak** acid; hence sodium ethanoate will be a slightly basic salt.

- To prove it:
 - $Na^+ + H_2O \longrightarrow No Reaction$
 - \bullet CH₃COO⁻ + H₂O \longrightarrow CH₃COOH + OH⁻
- The presence of hydroxide ions proves it is a basic solution.
- Reaction between a STRONG acid and a STRONG base:
 - ➤ This salt will be neutral; pH close to 7.
 - EG: $KOH_{(aq)} + HCl_{(aq)} \longrightarrow KCl_{(aq)} + H_2O_{(l)}$
 - ➤ Neither of the ions in the product reacts with water; hence it is neutral.
- Identify amphiprotic substances and construct equations to describe their behaviour in acidic and basic solutions:
 - An **amphiprotic** substance is one that can act as BOTH an <u>acid</u> and a <u>base</u>.
 - Their behaviour depends on the environment they are placed in.
 - **EG**: The *hydrogen carbonate* ion (bicarbonate ion) HCO₃ is amphiprotic:
 - $\blacksquare \quad HCO_3^-{}_{(aq)} + H_3O^+{}_{(aq)} \quad \longrightarrow \quad H_2CO_3{}_{(aq)} + H_2O{}_{(l)}$
 - $\blacksquare \quad HCO_3^-{}_{(aq)} + OH^-{}_{(aq)} \ \longrightarrow \ CO_3^{2^-}{}_{(aq)} + H_2O_{\ (l)}$
 - Other amphiprotic species include the *hydrogen sulfite* ion (HSO₃) and water.
- *Identify neutralisation as a proton transfer reaction which is exothermic:*
 - Neutralisation reactions are reactions between acids and bases.
 - The junior-science definition of neutralisation as "acid + base = salt and water"
 is extended and neutralisation is described as simply any proton-transfer reaction.
 - As acids are proton-donors & bases are proton-acceptors, neutralisation reactions between acids and bases are clearly PROTON-TRANSFER reactions.
 - Protons (H⁺) are transferred from the acid to the base.
 - **EG**: $HCl_{(aq)} + KOH_{(aq)} \longrightarrow KCl_{(aq)} + H_2O_{(l)}$
 - If we remove all the *spectator ions*, the basic underlying proton-transfer reaction is easily seen:
 - $\blacksquare \quad H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$
 - Hence, the proton is transferred to the hydroxide ion, forming water.
 - $-\quad \textbf{EG:} \ H^{\scriptscriptstyle +}{}_{(aq)} + NH_{3}{}_{(aq)} \ \longrightarrow \ NH_{4}{}^{\scriptscriptstyle +}{}_{(aq)}$

• In this reaction, the proton is transferred to the ammonia, forming ammonium.

- As can be seen, no water is produced; it is still considered neutralisation.
- ALL neutralisation reactions are *exothermic*; they all liberate heat energy.
- The $\Delta H \approx -56$ kJ/mol, depending on the strength of the reactants.
 - **Recall**: Exothermic reactions <u>release</u> energy as more energy is released in bond formation than is absorbed in bond breaking; negative ΔH value.
- 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:
 - It is important to immediately neutralise any chemical spills involving strong acids and bases, as they are corrosive and can be extremely dangerous.
 - Neutralisation reactions are widely used as safety measures in cleaning up after such incidents.
 - When neutralising an acid or a base the following procedure is followed:
 - The most preferred agents of neutralisation has the properties of being *stable*, *easily transported*, *solid* (powdered), *cheap* and **amphiprotic** (so it can act as a WEAK acid or a WEAK base).
 - This is the safest material, as it can neutralise both acids and bases; even if an excess is used, it is very weak, and so does not pose any safety risks.
 - The neutralised product is then absorbed using paper towels and disposed.
 - The most common substance used to neutralise spills in laboratories is powdered sodium hydrogen carbonate; this is because the hydrogen carbonate ion (HCO₃⁻) is an amphiprotic species, and it is cheap and readily available substance.
 - Strong acids and bases must <u>never</u> be used to neutralise spills; if an excess is used,
 the spill will become dangerous again.
- Describe the correct technique for conducting titrations and preparation of standard solutions:
 - Titration is a chemical technique used to experimentally determine the unknown concentration of a solution through a chemical reaction.
 - Acid/base titration uses a neutralisation reaction to determine this concentration.

- The Chemical Theory of Acid/Base Titration:

- Titration is also known as *volumetric analysis*.
- The point of *acid/base titration* is to determine the concentration of an <u>unknown</u> solution by slowly reacting a certain volume of this solution with another solution of <u>known</u> concentration, until the *endpoint* is reached.
- The ENDPOINT of a chemical reaction occurs when all available molecules have reacted, and the reaction comes to an end.
- The *volumes* of the reactants at the endpoint are carefully measured; using the knowledge of these volumes, and the original concentration of the standard solution, the concentration of the unknown solution can be calculated.

- **EG:** Nitric Acid & Sodium Carbonate:

- Take for example, the titration of a solution of *nitric acid* (HNO₃) of UNKNOWN concentration with a known solution of alkaline, 0.05 M *sodium carbonate* (Na₂CO₃).
- The solution of known concentration is called the **standard** solution.
- The *first step* in any acid/base titration is to identify the chemical reaction that is going to occur, by writing a balanced chemical equation. In this case:
 - ightharpoonup 2HNO_{3 (aq)} + Na₂CO_{3 (aq)} \longrightarrow 2NaNO_{3 (aq)} + CO_{2 (g)} + H₂O (l)
- 20 mL of the 0.05 M sodium carbonate was titrated with the nitric acid and the endpoint was reached after 22.2 mL of nitric was used.
 - NOTE: The method for conducting titrations, as well as the ways to determine the location of the endpoint, will be discussed below...
- Looking at the chemical equation, the molar ratio of reaction is 2:1
- Hence, 22.2 mL of nitric acid contains TWICE as many moles as 20 mL of sodium carbonate. Calculating:
 - ho n₁ = c₁ × v₁ = 0.05 x 0.02 = 0.001 mol of sodium carbonate.
 - $ightharpoonup n_2 = 2 \times n_1 = 0.002$ mol of nitric acid.
 - ho $c_2 = n_2 / v_2 = 0.002 / 0.0222 = 0.09 M$
- From this titration, the concentration of nitric acid was calculated to be 0.09 M
- Many rules must be adhered to for an accurate titration.
- Most important is the preparation of an extremely precise standard solution.

Primary Standards:

There are certain criteria chemicals need to satisfy before they can be used to create standard solutions; these suitable chemicals, called *primary standards*, must have the following properties:

➤ VERY HIGH PURITY:

♦ This is to produce accurate results, untainted by chemical impurities.

> CHEMICAL STABILITY (low reactivity):

◆ Standards must be chemically stable so they do not react violently with the water solvent, or with gases in the atmosphere (e.g. CO₂).

➤ NON-HYGROSOPIC AND NON-EFFLORESCENT:

Hygroscopic substances absorb water from their surroundings, while efflorescent substances release water into their surroundings. Both these processes change the concentration of solutions, resulting in imprecise primary standards.

➤ HIGH SOLUBILITY:

• Primary standards need to dissolve completely into their solutions.

➤ HIGH MOLECULAR WEIGHT:

- ◆ The high molecular weight of primary standards sets off any errors in measurement that may have occurred.
- Hence, from the above example, we can see that sodium carbonate is indeed a suitable primary standard; it can easily be obtained at extremely high purities, in a solid powdered form, and when it forms solutions, they are stable.
- Unsuitable chemicals to use as primary standards include sodium hydroxide, which in solution will react with gases in the air, hydrochloric acid, which is efflorescent, and sulfuric acid, which is severely hygroscopic.

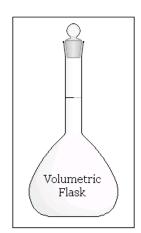
Preparing Standard Solutions:

- The typical laboratory glassware in which standard solutions are made are called *volumetric flasks*; 250 mL flasks are most commonly used.
- Using the above example, we will determine the amount of primary standard needed to create 250 mL of the 0.05 M standard solution of sodium carbonate.
- CALCULATIONS:

- Arr $M_R(Na_2CO_3) = 2(22.990) + (12.011) + 3(15.999) = 105.987$
- \rightarrow n = c × v = 0.05 x 0.25 = 0.0125 mol
- \rightarrow m = n x M_R = 0.125 x 105.987 = 1.325 g
- Hence, to make up 250 mL of 0.5 M solution, 1.325 g are needed.

- METHOD:

- 1. Firstly, the primary standard *must* be as pure as possible, as this means it must free of moisture. The primary standard must be placed in an oven, and cooled in a dessicator to remove all traces of moisture.
- 2. Thoroughly rinse a 250 mL volumetric flask, a small beaker and a glass funnel with *distilled water*. Place the funnel in the neck of the volumetric flask, and place the beaker on an electronic scale.



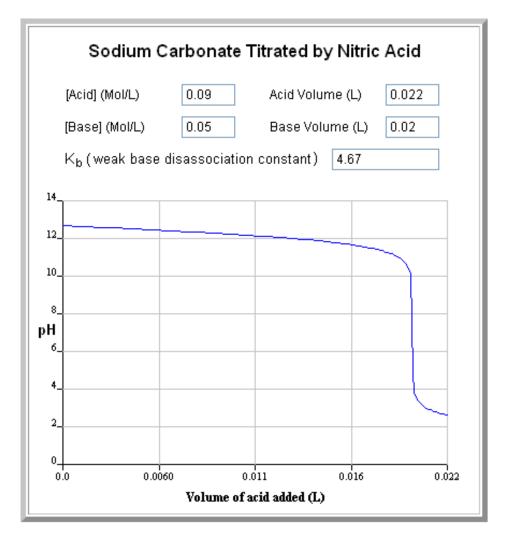
- 3. Zero the scale, and using a very clean spatula, transfer as accurately as possible, 1.325 g of sodium carbonate into the beaker.
- 4. Using a wash-bottle of distilled water, transfer the powder into the flask by 'washing' it into the funnel. Ensure that the entire beaker is washed, and all water that touches the beaker flows into the funnel, to ensure all solute is transferred. Wash the funnel, allowing the water to flow into the flask, and then remove it.
- 5. Fill the flask half-way up to the 250 mL graduation mark, and gently swirl the flask until all the solute has dissolved. Set the flask on the bench.
- 6. Using the wash-bottle, fill the flask with water until it is just under the graduation mark. Using a Pasteur pipette, add distilled water until the meniscus sits exactly on the 250 mL mark.
- 7. Cover the flask with its glass stopper and invert the entire flask three times. If the meniscus has lowered, add a few more drops. If not, the standard solution is complete.

Determining The Location of the Endpoint:

The endpoint of a chemical reaction is the point where the reaction STOPS, because all the species (of at least one reactant) have reacted.

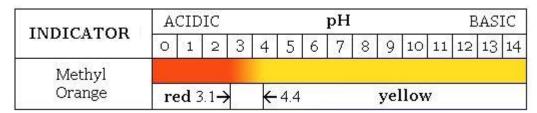
• In acid/base titration, the reaction is a <u>neutralisation</u> reaction and hence we use our knowledge of pH to determine when the endpoint has been reached.

- At the endpoint, all the species have reacted, and there is only the aqueous salt left; *however*, this does NOT mean that the pH at the endpoint is 7.
- The pH at the endpoint depends on the acid and base being used.
- **EG**: For the titration above, nitric acid is titrated into the sodium carbonate:
 - ▶ Before titration occurs, for sodium carbonate, pH is much greater than 7.
 - As nitric acid is slowly added, the pH decreases steadily, until the endpoint is reached, at 22.2 mL of acid.
 - ➤ BUT the salt formed between a strong acid and a weak base is slightly acidic; hence at the endpoint, the solution in the flask is slightly acidic.
- This is the titration curve of the above reaction:



- INDICATORS:

- To determine the pH, to determine the endpoint, we use indicators.
- However, a suitable indicator must be used.
- For strong-acid/weak-base titrations, as above, *methyl orange* is the most suitable indicator. This is because it changes from yellow to pale orange/pink within the slightly acidic range, corresponding with the endpoint of pH = 2.5:



• For strong-base/weak-acid titrations, phenolphthalein is suitable.

The Correct Technique for Conducting Titrations:

- There is a very precise and specific technique to titration, which uses a variety of calibrated glassware. These include:
 - ➤ *Volumetric Flask*: This is used to prepare and hold standard solutions.
 - Conical Flask: This is used to hold the reactants during titration. Its shape prevents the reactants from spilling as they are swirled together.
 - \blacktriangleright Burette: The burette is a piece of cylindrical glassware, held vertically, with volumetric divisions on its full length and a precision tap (stopcock), on the bottom. It is used to dispense precise amounts of a liquid reagent in titration. Burettes are extremely precise and accurate to ± 0.05 mL.
 - ➤ Pipette: The pipette is a glass tube used to transfer precise volumes of liquid reagents. Pipettes are usually designed to transfer one measurement of volume, such as only 25 mL. The reagent is drawn up the pipette using a pipette filler (e.g. a rubber bulb).
- Before titration can begin, all glassware must be RINSED appropriately. The proper rinsing technique for the different glassware is:
 - ➤ Volumetric flasks (including glass stoppers) are rinsed thoroughly with *distilled water*, preferably multiple times. Close the flask with the stopper until it is going to be used; it is left wet.
 - ➤ Conical flasks are rinsed thoroughly with distilled water and left wet.

➤ Burettes are rinsed with a specific technique; first the distilled water is filled into the burette and the tap opened. Water is allowed to flow out and thoroughly rinse the tip. More water is then added, and the entire glass tube is swirled in your hands to wash the sides of the burette. The water is then poured out from the top. Burettes MUST be rinsed THREE TIMES with distilled water and then ONCE more with the solution it is going to contain. *No, it's not insane, it's standard laboratory procedure.*

- ➤ Pipettes are also rinsed THREE times with distilled water, and then ONCE with the solution it is going to contain.
- After everything is rinsed appropriately, the glassware is filled.
- Usually, the acid is placed in the burette, and the base in the conical flask, but it really doesn't matter much. Using the above example again:
 - ➤ Using a funnel, the nitric acid is poured into the burette until ABOVE the zero mark. Hold a white card behind the zero mark, and open the tap slowly until the meniscus sits JUST on top of the mark. The white card makes the meniscus clearer.
 - ➤ Using the pipette, a fixed volume of sodium carbonate (say 25 mL) is drawn from the volumetric flask and deposited into the conical flask.
- A few drops of methyl orange indicator are added to the conical flask, and the solution turns a clear yellow colour.

– THE TITRATION:

- *Finally*, the titration can be performed.
- The conical flask is placed on a white tile (to make the solution's colour clear) under the burette, which is held in a retort stand.
- The tap is slowly opened, and the conical flask is continuously swirled.
- When the first colour change is noticed, the tap is immediately closed. A swirl of the conical flask will likely return the solution back to its original colour.
- Very slowly open the tap so that solution flows out in drops, and stop when the endpoint is reached, as shown by the colour of the indicator:
 - ➤ In the case of the above example, the endpoint is *pale pink*.

The first titration performed is a rough draft and often overshoots the endpoint.
 This first titration is rejected.

Titration is performed multiple times to achieve the accurate results.

- The Calculations Involved With Titration:

- All the calculations required are detailed above; all titration concentrations can be calculation using the equation $n = c \times v$.
- But for those too lazy to calculate the concentration by this method, there is a formula for a quick answer:

For the balanced equation of an acid/base reaction of the following form:

$$A \times (acid) + B \times (base) \longrightarrow Products$$

The following equation holds:

$$\boxed{\frac{A}{C_aV_a} = \frac{B}{C_bV_b}}$$

Where:

A,B are the coefficients of the acid and the base.

 $C_{\boldsymbol{a}}\,, C_{\boldsymbol{b}}$ —are the concentrations of the acid and the base.

 $V_{\mathbf{a}}$, $V_{\mathbf{b}}$ are the volumes of the acid and the base.

- Qualitatively describe the effect of buffers with reference to a specific example in a natural system:
 - A buffer is a solution that is able to maintain a constant pH; even the addition of a strong acid or base does not change its pH.
 - The buffer solution contains approximately equal amounts of a *weak* acid and its *conjugate* base. The equilibrium involved can be represented as:
 - $HA + H_2O \rightleftharpoons H_3O^+ + A^-$
 - 'HA' is the weak acid, which protonates water, forming its conjugate base, 'A-'
 - Using Le Chatelier's principle, we can deduce why the pH remains constant:
 - Addition of any acid (regardless of its strength) increases [H₃O⁺]. However, this does not decrease the pH; the additional acid simply reacts with the conjugate base and forces the equilibrium to the left, forming more of the weak acid, and the pH returns to its original value.

■ Addition of any base (that is OH⁻ ions) does not increase the pH as expected; as the base reacts with the hydronium, [H₃O⁺] decreases. This shifts the equilibrium to the right, and more H₃O⁺ is produced through the forward reaction. The pH returns to its original value.

- An example of a NATURAL buffer system is the carbonic acid system:
 - This system occurs naturally in freshwater lakes and rivers, and it maintains the constant neutral pH needed for life to exist.
 - Carbon dioxide from the air dissolves in the water, forming carbonic acid, while its conjugate base, hydrogen carbonate, is present as ions leeched out of rocks and minerals of the lake. Because there are comparable amounts of the acid and its conjugate base, it is considered a buffer:
 - \rightarrow H₂CO_{3 (aq)} + H₂O (l) \rightleftharpoons H₃O⁺ (aq) + HCO₃ (aq)
 - This natural system protects many water systems from the effects of acid rain.
- **PRACTICAL** 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:
 - See ABOVE for a very extensive coverage of acid/base titration.
 - Another titration performed was between potassium hydrogen phthalate (a weak acid) and sodium hydroxide (a strong base), using phenolphthalein indicator.
- **PRACTICAL** Choose equipment and perform a first-hand investigation to identify the pH of a range of salt solutions:
 - In this practical, the pH of a range of salt solutions was estimated by examining the parent acids and bases.
 - The actual pH was then measured using a pH meter.
 - <u>Salts</u>:
 - Sodium acetate CH₃COONa:
 - Parent acid is CH₃COOH (weak) and parent base is NaOH (strong).
 - > Predicted pH is slightly basic.
 - ightharpoonup True pH = 8.9

- Sodium nitrate NaNO₃:
 - ➤ Parent acid is HNO₃ (**strong**) and parent base is NaOH (**strong**)
 - > Predicted pH is neutral.
 - ightharpoonup True pH = 7
- Other salts:
 - ightharpoonup NaHCO₃ pH = 8
 - $ightharpoonup MgCl_2 pH = 3$
- PRACTICAL Perform a first-hand investigation to determine the concentration of a domestic acidic substance using computer-based technologies:
 - 50 mL of household vinegar was placed in a small beaker.
 - A pH probe was attached to the laboratory computer; the probe was rinsed with distilled water, and then rinsed with left-over solution.
 - The probe was then placed in the solution, and the pH measured.
 - The probe was rinsed again, and pH was measured twice more.
 - The average pH was calculated, and using this, the concentration of H⁺ ions found
 - Given the fact that food-grade ethanoic acid only has about 0.4% ionisation, the concentration of ethanoic acid was then calculated.

- **RESULTS**:

- The average pH measured was 2.5
- $[H^+] = 10^{-pH} = 10^{-2.5} = 0.00316 \text{ mol/L}$
- But $[H^+] = 0.4\% \times c$; (where c = concentration of ethanoic acid)
- Hence $c = 0.00316 \div 0.004 = 0.79$
- Therefore vinegar is 0.79 M ethanoic acid.

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

• RECALL:

- A functional group is a specific group of atoms within a molecule that is responsible for the characteristic chemical properties of that molecule.
- Polarity occurs within a bond when one of the atoms is more electronegative than
 the other; the bond has a slight charge.
- Describe the differences between the alkanol and alkanoic acid functional groups in carbon compounds:
 - The functional group of alkanols is the **hydroxyl group** (–OH):
 - *Structure*: An oxygen and a hydrogen molecule covalently bonded.
 - Extra: It is a highly polar group due to the polar C-O and O-H bonds
 - The functional group of alkanoic acids is the **carboxyl group** (-COOH).
 - Structure: An oxygen is double-bonded to a central carbon, and an –OH group is single-bonded to the same carbon. The –OH is not called a hydroxyl group when within a carboxyl group.



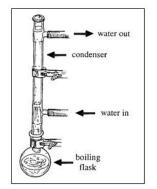
- *Extra*: This group is acidic because some of the hydrogen can disassociate, to form H^+ ions in solution. That is, $COOH \rightarrow COO^- + H^+$. Also, it is more polar group than the hydroxyl group due to its polar C-O, O-H and C=O bonds.
- Explain the difference in melting point and boiling point caused by straightchained alkanoic acid and straight-chained primary alkanol structures:
 - For the same number of carbons in a straight carbon-chain, the highest boiling points and melting points belong to the *alkanoic acids*, then the *alkanols*, and then the parent *alkanes*.
 - The intermolecular forces between a collection of molecules determines what physical state they will exist in (solid, liquid or gas) for a given pressure and temperature.
 - The stronger the intermolecular forces, the more 'tightly bound' the molecules are
 to each other, and hence more energy needs to be forced into the system to
 overcome these forces (i.e. higher melting or boiling point).

For ALKANES, the only intermolecular forces between molecules are <u>dispersion</u> forces. These forces are caused by the movement of electrons around the molecule, which create instantaneous moments of charge (a "dipole"). These dipoles attract each other, creating these dispersion forces, or dipole-dipole forces. They are *very* weak, and hence the boiling and melting points of alkanes are low.

- ALKANOLS also experience dispersion forces, as well as electromagnetic interactions between <u>polar bonds</u>. Alkanols contain the polar C-O and O-H bonds. As they have a partial charge, they attract each other. Also, hydrogen bonding occurs between molecules. Their intermolecular interactions are stronger than those of alkanes, and hence they have higher melting and boiling points.
- ALKANOIC ACIDS have the strongest intermolecular interactions, as they have three polar bonds in each molecule: C-O, C=O and O-H bonds. In addition, hydrogen bonding occurs. This greatly increases the melting and boiling points of alkanoic acids.
- Identify esterification as the reaction between an acid and an alkanol and describe, using equations, examples of esterification:
 - Esters are sweet-smelling, volatile organic compounds that contain the ester *functional* group: "-COOC-". The structure of this functional group is shown at right.

- In the diagram, \underline{R} and $\underline{R'}$ represent a hydrogen, or carbon chains. Hence the simplest ester is HCOOCH₃; this is called methyl methanoate.
- Esterification is the process which forms esters. In the most general sense it is the reaction between an acid and an alcohol.
 - However, for the HSC course, we limit our knowledge of esterification as the reaction between straight-chained primary ALKANOIC acids, and straightchained primary ALKANOLs. This forms <u>carboxylate</u> esters.
 - Keep in mind that many other types of acids (such as phosphoric acid) and alcohols (such as tri-alcohols) can react to form non-carboxylate esters.
- Carboxylate esters are formed when a carboxyl functional group (-COOH) of an alkanoic acid reacts with the hydroxyl functional group (-OH) of an alkanol.
- Esterification is a **condensation** reaction; a water molecule is generated.

- Esterification is a reversible reaction in which equilibrium lies much to the left at room temperature. It is a moderately slow endothermic reaction:
 - alkanoic acid + alkanol \rightleftharpoons ester + water $\Delta H > 0$
- Describe the purpose of using acid in esterification for catalysis:
 - Concentrated sulfuric acid is often added during the process of esterification; this serves 2 purposes:
 - Sulfuric acid acts as a catalyst. It speeds up the rate of reaction, allowing the point of equilibrium to be reached faster.
 - Sulfuric acid increases the **yield** of the reaction. It does this by acting as a dehydrating agent; it absorbs the water, encouraging the forward reaction, shifting equilibrium to the right according to Le Chatelier's principle.
- Explain the need for refluxing during esterification:
 - Heating the reaction flask has 2 main benefits:
 - The higher the temperature, the faster the rate of reaction; equilibrium can be reached much faster than if it was left at room temperature.
 - Also, esterification is an endothermic reaction; increasing the heat of the flask encourages the forward reaction, creating more ester.



- However, the ester, alkanol and alkanoic acid are all highly volatile substances;
 any open heating will cause the reactants as well as products to evaporate away.
- A refluxing apparatus is basically a condenser placed vertically onto a boiling flask; it cools any vapours that boil off so that they drip back into the flask.
- Refluxing allows the mixture to react at high temperatures without fear that the reactants or products will evaporate away.

• Identify the IUPAC nomenclature for describing the esters produced by reactions of straight-chained alkanoic acids from C1 to C8 and straight-chained primary alkanols from C1 to C8:

 Straight-chained alkanoic acids only have one carboxyl functional group, located on one of the end-carbons.

Naming alkanoic acids:

- Count the number of carbons; taking the name of the parent alkane with the same number of carbons, drop the 'e' and add on '-oic acid'.
 - **EG**: The 3-C alkane is propane. Hence 3-C alkanoic acid is propanoic acid.
- There are 2 exceptions to the rule; the IUPAC-preferred name for the alkanoic acids for 1-C and 2-C are not methanoic or ethanoic acids, but rather formic acid and acetic acid respectively.

Naming alkanols:

- Similarly, count the number of carbons, take the parent alkane name, drop the
 'e' and add on an '-ol'.
- In this case, there are no exceptions. The IUPAC names coincide with all the systematic names; methanol and ethanol are considered correct.

Naming esters:

- An ester is always in the following order: <u>alkanol</u> then <u>alkanoic acid</u>.
- There are two different situations when esters would have to be named.
- Given the alkanol and the alkanoic acid, name the ester:
 - Firstly, take the alkanol and replace '-anol' with '-yl'. Secondly, take the alkanoic acid and replace '-oic acid' with '-oate'. Finally, place the 2 words together, alkanol then alkanoic acid, and you have named the ester.
 - **EG**: Name the ester formed by reacting propanol and acetic acid.
 - ◆ Propanol → Propyl; Acetic acid → Acetate.
 - ♦ Therefore the ester is propyl acetate.
- Given the ester structural formula, name the ester:
 - Firstly, you have to identify how many carbons were in the alkanol and the alkanoic acid; split the ester along the C-O-C bond. The side with the C=O bond is the acid, as only the carboxyl group has a double bond.

Now that the acid and alkanol has been identified, the steps above are easily followed.

EG: Name the following ester:

- Using an imaginary line, split the molecule across the C-O-C bond.
- ◆ To the left, there is the C=O bond, and 4 carbons (counting the C=O); hence, the alkanoic acid used had 4 carbons. It was butanoic acid.
- ♦ It follows then that the right side is the alkanol, which has 3 carbons.

 Therefore propanol was used.
- ♦ Therefore the ester is propyl butanoate.
- *Outline some examples of the occurrence, production and uses of esters:*
 - Natural Occurrence:
 - Esters occur commonly in nature.
 - Usually, it is a mixture of esters that creates the characteristic smells or tastes found in nature, such as those of flowers or fruit.
 - Sometimes, a single ester can be identified as the main smell of a plant:
 - **EG**: A typical ripe pineapple with contain 120 mg/Kg of ethyl ethanoate.

- <u>Production & Uses</u>:

- Many esters are industrially produced for many reasons.
- Domestic uses of esters include artificial flavourings for foods, scents for perfumes and as nail polish remover.
- Short esters such as ethyl acetate are used as industrial solvents, where as larger esters are used as plasticisers to soften hard plastics (like PVC).
- Process information from secondary sources to identify and describe the uses of esters as flavours and perfumes in processed foods and cosmetics:
 - Esters are industrially produced to mimic flavours and scents found in nature
 - These are for use in processed foods, or mixed to produce unique perfumes.
 - Domestic food flavourings are often esters dissolved in a solvent such as ethanol

 Many processed foods are flavoured artificially, e.g. banana-flavoured milk is flavoured with the ester iso-pentyl acetate.

- Cosmetics contain esters as scents, such as perfumes, with are comprised almost exclusively of a mixture of esters in a solvent, or to give soaps, hand-lotions or other cosmetics a pleasant smell.
- Other cosmetic uses of esters include as solvents for other products, such as nail polish removers.
- **PRACTICAL** Identify data, plan, select equipment and perform a firsthand investigation to prepare an ester using reflux:
 - The ester prepared was ethyl ethanoate.
 - Ethanol and ethanoic acid were used as the reactants.
 - ethanol + ethanoic acid === ethyl ethanoate + water
 - In a round-bottom flask, 40 mL of ethanol, 30 mL of ethanoic acid and 10 drops of concentrated sulfuric acid were placed.
 - Boiling chips were also dropped into the flask.
 - The condenser attachment of the reflux apparatus was attached to the flask, and secured onto a retort stand; water was passed into the condenser.
 - The flask was placed in a *water-bath* in a large beaker.
 - A Bunsen-burner was used to bring the water to a gentle boil, which brought the reflux apparatus to a temperature of 100°C; it was left to reflux for 30 minutes.
 - Heating was stopped and the entire apparatus was left to cool, with the water still flowing.
 - Disassemble the apparatus, carefully holding on to the flask.
 - The refluxed contents were poured into a *separating funnel*; the mixture was washed with 50 mL of distilled water and shaken. The lower aqueous layer was drained off, and this washing was repeated twice more.
 - Finally 15 mL of saturated NaHCO₃ solution and 35 mL of distilled water was added, the mixture shaken, and the aqueous layer drained off.
 - The final product is relatively pure ethyl ethanoate.
 - JUSTIFY the method:
 - See ABOVE for the justification for refluxing.

• See ABOVE for the justification of the addition of sulfuric acid.

- Boiling chips were added to facilitate a slow and gentle heating.
- A water bath was also used to allow for gentle heating
- The use of the separating funnel for extracting the ester was justified because all the reactants and products except the ester are water soluble; ethanol, ethanoic acid, and of course water, are all water soluble. Hence they are all immiscible with the ester.
- The ester also is less dense and floated on top, allowing the aqueous reactants to be drained off.
- Washing with distilled water was used to remove as much ethanol, ethanoic acid and sulfuric acid from the ester as possible; multiple washings increased the purity of the ester.
- Finally, the sodium hydrogen carbonate was used to neutralise any remaining sulfuric acid in the mixture.