

Chemical Monitoring and Management

3.1 The Work of Chemists

3.1.1 Outline the role of a chemist employed in a named industry or enterprise, identifying the branch of chemistry undertaken by the chemist and explaining a chemical principle that the chemist uses

- Chemist: Luke Smith
- Named Industry: *Plastics (polymer) industry*
 - Luke is a chemist at a major Australian chemical manufacturing company that makes ethylene from ethane, and then polymerises it into polyethylene.
- Branch of Chemistry: *Industrial/analytical chemistry*
- Role of Chemist:
 - Monitor the quality of the product (polyethylene and ethylene), particularly before the next step in production, such as for impurities.
 - Monitor gaseous emissions and waste water from the plant to ensure that they meet environmental requirements (e.g. *pH*, suspended solids, polluting chemicals, particulates in gaseous emissions) before they are discharged.
 - Collaborate with process engineers at the cracking furnace to adjust operating conditions to optimise product yields.
 - Check equipment works properly, calibrate instruments, train shift workers, carry out analyses to ensure reliability of results, and improve the overall monitoring process.
- Chemical Principles:
 - Gas chromatography is used in many of Luke's analyses, as he is concerned with determining what substances and the amounts of each present in materials.
 - The chemical principles involved are *adsorption* (gas-solid chromatography) and *solubility* (gas-liquid chromatography, GLC). This technique is used to separate components from a mixture out so that the amount of each can be measured. The adsorption and solubility (polarity of molecules) affect the extent to which the chemicals separate.
 - For example, in GLC separation, if the stationary phase is a polar liquid, then the greater the polarity of a component of the mixture to be analysed, the greater is its solubility and so the more slowly it moves through the column.

3.1.2 Identify the need for collaboration between chemists as they collect and analyse data

- Chemistry is a very broad discipline, with different chemists specialising in different fields. However, chemical problems of the world require expertise in more than one field of specialisation, especially in industry.
 - For example, industry can require knowledge of physical (equilibria and reaction rates), organic (reaction mechanisms and optimisation of yield), and analytical, chemical engineering, and environmental specialisations.
- Solving wide-ranging and complex problems requires input from many chemists with different specialities, as they cannot solve these problems in isolation. It is essential for chemists to work collaboratively, regularly interact and exchange different viewpoints about problems as they arise.

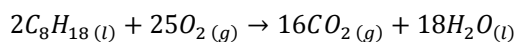
- This need to collaborate means that chemists need to have good communication skills – that they are able to communicate all aspects of their particular disciplines skilfully and concisely.
- Similarly chemists need to work with scientists from other fields collaboratively too in some applications as all science has the potential to impact upon other areas.

3.1.3 Gather, process and present information from secondary sources about the work of practising scientists identifying the variety of chemical occupations and a specific chemical occupation for a more detailed study

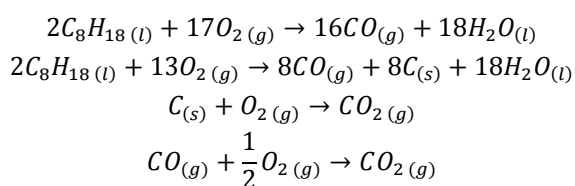
- Analytical chemistry: The determination of what substances are present in samples (qualitative analysis) and how much of each is present (quantitative analysis).
- Physical chemistry: The study and measurement of physical aspects of compounds and reactions (e.g. reaction rates, energy aspects, structures of compounds, nature of chemical bonding).
- Environmental chemistry: The monitoring of concentrations of substances in air, water and soil samples and ensuring they adhere to environmental regulations.
- Industrial chemistry: The chemistry of industrial processes (e.g. manufacture of ammonia, sulfuric and nitric acids) and the many compounds made industrially in modern society.
- Nuclear chemistry: The production and use of radioisotopes in medicine and industry as well as the fundamental nature of nuclear reactions.

3.1.4 Describe an example of a chemical reaction such as combustion, where reactants form different products under different conditions and thus would need monitoring

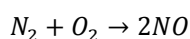
- Combustion reactions:
 - **Complete combustion**: In an abundant supply of oxygen, the fuel can burn completely to form carbon dioxide and water.



- **Incomplete combustion**: With insufficient oxygen, carbon monoxide and/or soot (C) may also be released. The energy released is not the maximum obtainable from the fuel as both C and CO can still be combusted.



- Monitoring:
 - Combustion reactions can produce solely CO_2 or a mixture of CO_2 , CO and C depending on the relative amount of oxygen provided.
 - If the air : fuel ratio is too low (i.e. limited oxygen), C and/or CO are produced as by products, or the fuel may pass into the exhaust stream as volatile organic compounds.
 - If the air : fuel ratio is too high (i.e. excess oxygen), the excess oxygen can react with nitrogen present in the air to yield NO_x .

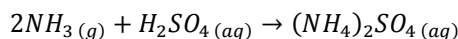


- Therefore, there is a need to *monitor* reactions to ensure:
 - Complete combustion is occurring in order to **minimise pollution** (e.g. CO and NO) and **maximise energy output** and yield of the desired product.
 - The reaction is going to **completion** and not coming into an unfavourable equilibrium.

3.2 Monitoring in Industry – The Haber Process

3.2.1 Identify and describe the industrial uses of ammonia

- Ammonia is used industrially as a feedstock (raw material from which a substance or industrial process is derived) mainly for the manufacture of:
 - **Fertilisers** (*sulfate of ammonia, ammonium nitrate, urea*), which are used to grow plants where soils may be deficient in nitrogen compounds. Ammonia is reacted with sulfuric acid to form ammonium sulfate fertiliser:



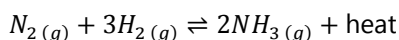
- **Explosives** (derived from nitric acid) such as TNT and nitro-glycerine.
- **Fibres and plastics** (e.g. nylon, rayon).

3.2.2 Identify that ammonia can be synthesised from its component gases, nitrogen and hydrogen

3.2.3 Describe that synthesis of ammonia occurs as a reversible reaction that will reach equilibrium

3.2.4 Identify the reaction of hydrogen with nitrogen as exothermic

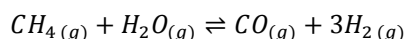
- Haber process:



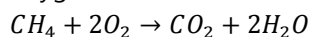
- The forward reaction is **exothermic**: $\Delta H = -92 \text{ kJ/mol}$
- It is a reversible reaction, which will reach equilibrium after some time in a closed system. At standard conditions, equilibrium lies well to the left, so very little NH_3 is present. The conditions in the Haber Process, however, make it commercially viable.

- Feedstock for Haber Process (natural gas, steam, air):

- Nitrogen can be obtained from the atmosphere, so hydrogen is comparatively more difficult to obtain. Industrially, hydrogen is produced by the *steam reforming* of natural gas (mainly methane).

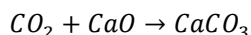


- The mixture of hydrogen and nitrogen in the Haber process **must not contain any oxygen** (which can react explosively with hydrogen).
- Methane is also used to remove oxygen from the air.



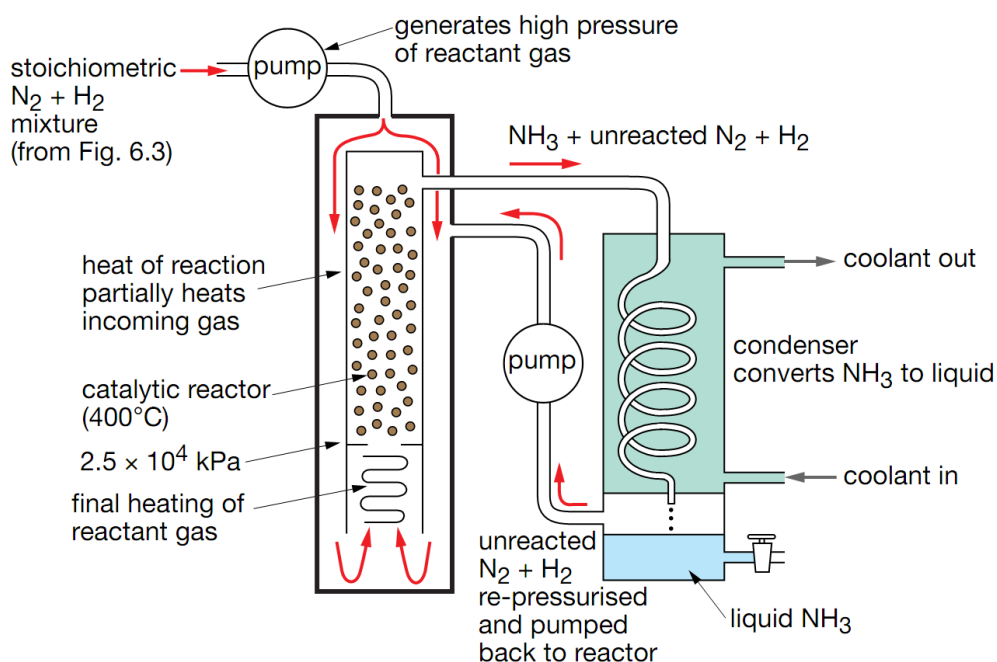
- By adjusting the quantities of methane, steam and air used, this combination of reactions can be made to produce a 3:1 mixture of hydrogen and nitrogen.

- The only unwanted gas in the mixture, carbon dioxide, is removed by reaction with a base.



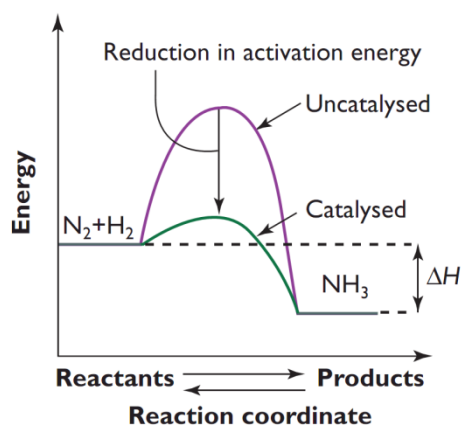
- Very small amounts of methane and argon are present as impurities.

- Process: The reactants pass through the catalytic reactor and the mixture is cooled to condense out the ammonia formed. Unreacted gases are fed back into the catalyst chamber along with fresh reactants. None of the reactant mixture is wasted. The reaction goes to completion, as the reaction product is condensed out.



3.2.5 Explain that the use of a catalyst will lower the reaction temperature required and identify the catalyst(s) used in the Haber process

- A catalyst lowers the activation energy by providing an alternate pathway with lower energy. The catalyst speeds both forward and backward reaction rates equally, such that the equilibrium position is not changed, hence not affecting yields. However, the time taken to reach this equilibrium position is less as reaction rates are faster. Thus, the temperature required to attain a high reaction rate is lower, allowing the equilibrium to favour the products and hence increase yield, whereas using a temperature to attain an equivalent rate of reaction would result in a much lower yield.
- The Haber process uses the catalyst **magnetite** (Fe_3O_4) which increases the rate of reaction by lowering the activation energy of reactants (by offering a surface on which the reaction can occur more favourably). The catalyst is finely ground to expose a high surface area for the reaction to occur.
- Catalysts are useful in industry as there are considerable savings to be made in time and energy as reactions can be conducted (where appropriate) at lower temperatures.

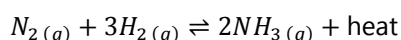


3.2.6 Explain why the rate of reaction is increased by higher temperatures

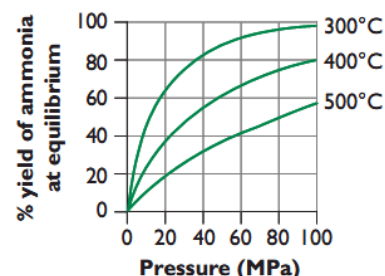
- The kinetic theory of gases predicts that the rate of a reaction increases when more successful collisions occur in the shortest time.
- As temperature increases, particles have **higher kinetic energy**. This increases the **frequency of collisions** between reacting particles exceeding the **activation energy barrier**.
- Hence more reactions occur and the rate of reaction is increased. The rate of both forward and reverse reactions is increased.

3.2.7 Explain why the yield of product in the Haber process is reduced at higher temperatures using Le Chatelier's principle

3.2.8 Analyse the impact of increased pressure on the system involved in the Haber process



- Temperature:
 - Increasing temperature will shift equilibrium to the left as the endothermic reaction is favoured (Le Chatelier's principle), reducing the yield of NH_3 .
 - Conversely, decreasing temperature will shift equilibrium to the right, producing more NH_3 .
- Pressure:
 - Increasing pressure in the system will favour the forward reaction which has fewer molecules (Le Chatelier's principle), so equilibrium will shift to the right, producing more NH_3 .



3.2.9 Explain why the Haber process is based on a delicate balancing act involving reaction energy, reaction rate and equilibrium

- The aim of the Haber process is to maximise yield and reaction rate, and minimise cost in order to gain maximum profit. A delicate balance between these conditions is required to achieve the most profitable yield for the least cost.
- Rate of reaction:
 - Low temperatures produce high yields but cause a slow rate of reaction, so it takes longer to reach equilibrium.
 - High temperatures cause equilibrium to be reached faster, but the equilibrium yield is low.
- Compromise conditions for Haber process:
 - **Temperature: 400°C**
 - A compromise temperature allows reactants to have sufficient kinetic energy to overcome the activation energy barrier while achieving a reasonable yield.
 - **Pressure: 250 atm**
 - Increasing pressure results in a greater yield, however due to economic and safety considerations a lower pressure is used.
 - A high pressure requires thick-walled containers and safety valves which are expensive, and is also unsafe as there is the risk of explosion.
 - **Reactants: 3:1 ratio of H_2 and N_2**
 - As NH_3 is formed and condensed out, left-over reactants can be recycled without any build-up of one reactant.
 - **Catalyst: magnetite (Fe_3O_4)**
 - The catalyst allows lower temperatures and pressures to be used to achieve reasonable reaction rates without a great loss in yield.
- Increasing yield: The **constant removal** of ammonia by **liquefaction** (due to cooling) causes equilibrium to shift to the right and produce more ammonia. Common industrial yield is 30%.
- Energy management: In the Haber process, the heat released can be used to heat up the incoming reactants to minimise energy costs. This also stops the catalyst overheating and losing activity – this is why reactants flow over the outside of the catalyst chamber before entering it.

3.2.10 Explain why monitoring of the reaction vessel used in the Haber process is crucial and discuss the monitoring required

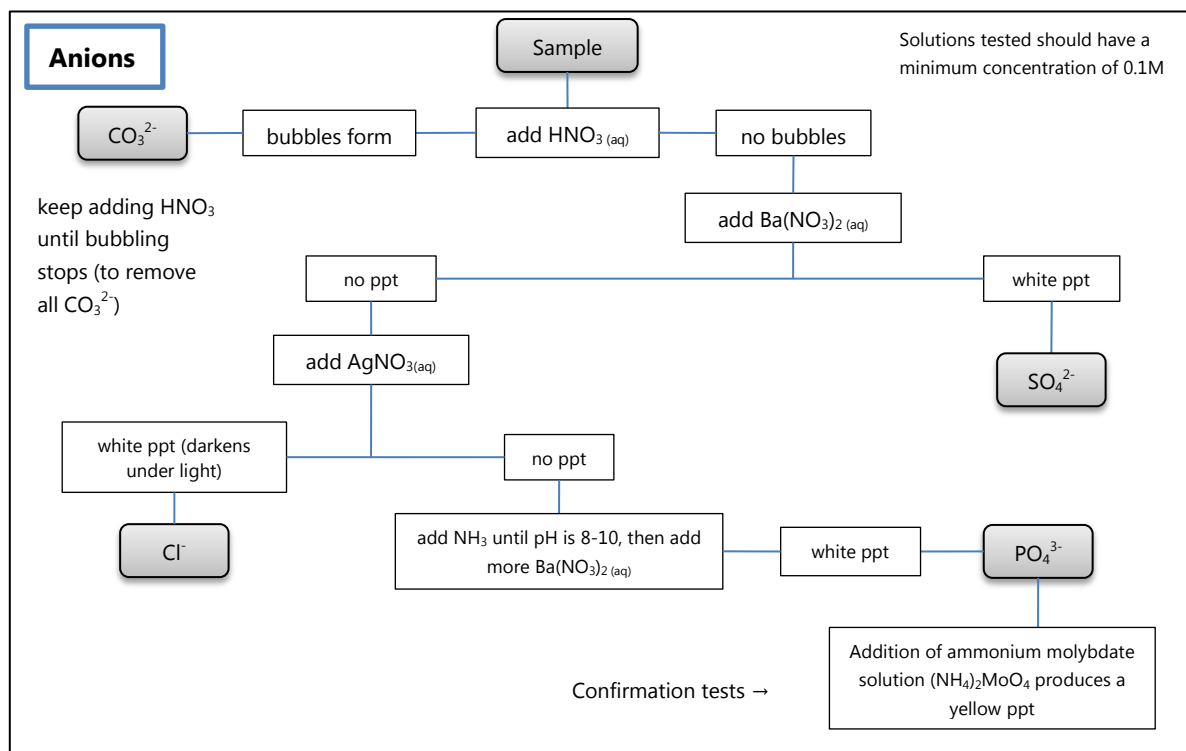
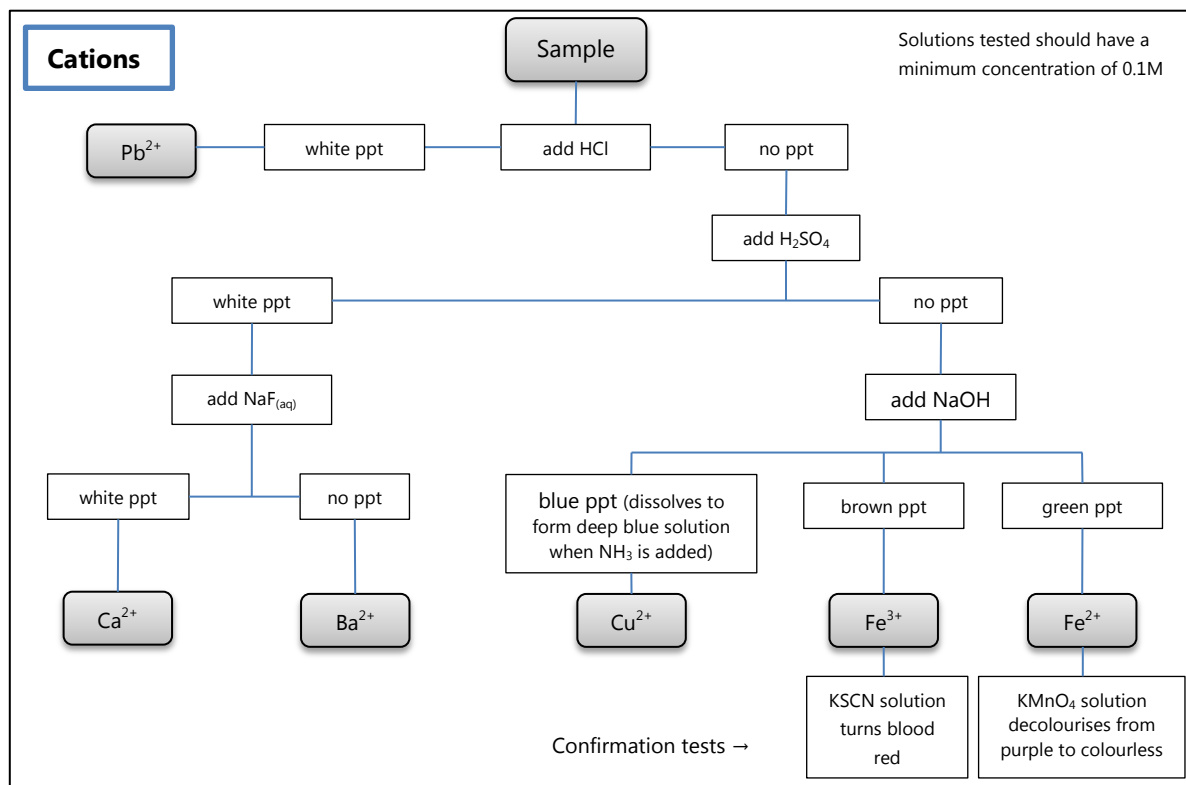
- **Temperature and total pressure** are kept in the range for optimum conversion of reactants to products.
 - Continuous monitoring of the high pressure reaction vessel is required to ensure that the production of ammonia occurs under safe conditions (i.e. pressure not too high) and yield is not compromised (i.e. pressure is too low).
 - If temperature is too high, yield is reduced, and excessive temperature can damage the catalyst.
- **Ratio of H_2 to N_2** feedstocks is kept at 3:1 to avoid a build-up of one reactant.
- **Concentrations of O_2 , CO , CO_2 , sulfur compounds, and argon and methane** are kept low.
 - Oxygen must be absent to avoid risk of explosion.
 - Concentrations of CO , CO_2 and sulfur compounds are kept sufficiently low to prevent poisoning of the catalyst.
 - A build-up of argon and methane lowers the efficiency of the conversion.
- **Catalyst**
 - The particle size of the catalyst must be monitored to ensure it has a high surface area for adsorption of nitrogen and hydrogen gases.
- **Purity of the product NH_3** is monitored to ensure no impurities contaminate the product.

3.2.11 Gather and process information from secondary sources to describe the conditions under which Haber developed the industrial synthesis of ammonia and evaluate its significance at that time in world history

- Haber process:
 - The **Haber Process** was a method for producing ammonia, developed by Germany during WWI.
 - In the early 1900s, there was a shortage of naturally occurring nitrogen sources, especially ammonia and nitrates. The demand for nitrogen compounds for making nitric acid in the chemical industry grew around the same time, as Germany was about to enter WWI.
 - Before the invention of the Haber Process in 1914, the main source of nitrates (for fertilisers and explosives) came from *saltpetre* from Chile. Germany was highly dependent on overseas supplies of nitrate salts for agriculture and manufacture of explosives. During WWI, Germany's supplies of nitrogen compounds were cut off.
 - Fritz Haber first synthesised ammonia from elemental nitrogen and hydrogen. Carl Bosch later converted it into an industrial process for large-scale production of ammonia.
- Evaluation:
 - The Haber process was significant to the German war effort as it insulated German agriculture from any harm caused by interrupted supplies. The industrial synthesis of ammonia facilitated the manufacture of fertilisers for continued food production, and nitric acid, an essential component in the manufacture of explosives and other ammunition.
 - It enabled them to continue their war effort using the Haber process after their supplies of nitrate from Chile were cut off. It has been suggested that without this process, Germany would almost certainly have run out of explosives and fertiliser for food, thereby ending the war.

3.3 Chemical Analysis

3.3.1 Deduce the ions present in a sample from the results of tests



- When identifying **one cation** present in a solution, use a new sample for each test.
- When analysing **mixtures** with several cations:
 - An excess reagent is added until no further precipitate forms.
 - The precipitate is separated from the filtrate (to eliminate interference) using filtration or a centrifuge (quicker) before performing the next test.
 - A centrifuge spins test tubes at high speeds and flings the precipitate to the bottom.
- Sufficient nitric acid ensures all CO_3^{2-} is destroyed and does not interfere with other tests.
 - All carbonates react with dilute acids to form CO_2 gas: $\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

3.3.2 Perform first-hand investigations to carry out a range of tests, including flame tests, to identify the following ions: phosphate, sulfate, carbonate, chloride, barium, calcium, lead, copper, iron

- A **flame test** is used to distinguish some cations by the colour their salts impart to a flame.
- The flame decomposes the ionic compound into its cations and anions, and it is the **cations** that give the **distinctive flame colours**.
 - Chloride salts of various cations work best because they are easily volatilised.
- Procedure for flame tests:
 - A **platinum wire** (mounted on the end of a glass tube) is cleaned by dipping it into concentrated HCl and heating it in the flame to remove impurities.
 - The wire is dipped into the sample to be tested and heated in the flame.
 - The flame colour is characteristic of the cation present, and is independent of the anion.
- Another method is dissolving chloride salts in water and spraying into a Bunsen flame using an **atomiser**.

Cation	Flame colour
Ba^{2+}	yellow-green
Cu^{2+}	blue-green
Ca^{2+}	brick-red
Na^+	yellow
Sr^{2+}	scarlet

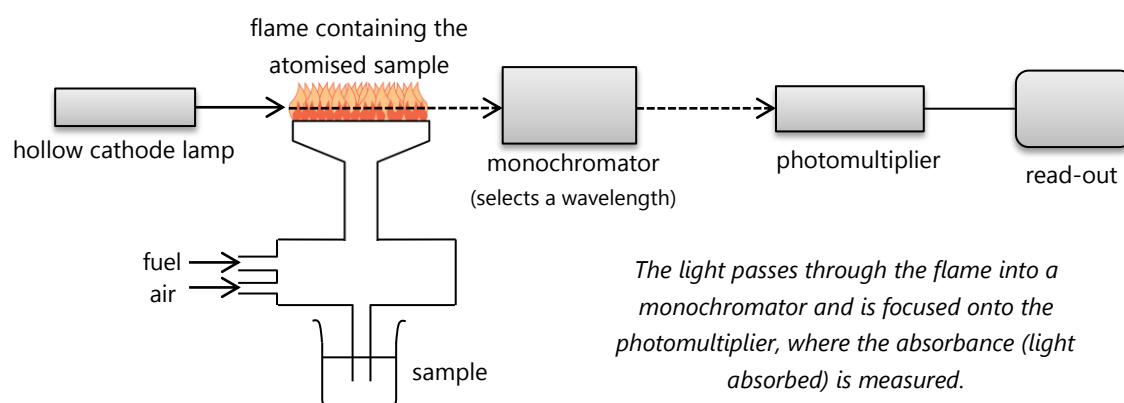
3.3.3 Gather, process and present information to describe and explain evidence for the need to monitor levels of one of the above ions in substances used in society

- **Lead** is a **toxic, heavy metal** which can damage all organs of the body, especially the brain, kidneys and reproductive system, by disrupting enzyme systems.
- Lead is rapidly absorbed by the brain, where it causes **neurological damage** such as impaired hearing and behavioural disorders, especially in children.
- Lead inhibits the formation of haemoglobin in red blood cells, causing anaemia and reducing the ability of blood to transport oxygen.
- Lead **bioaccumulates** (builds up to high levels in living organisms) in the body and is difficult to eliminate. It also **bioconcentrates** (concentration increases as it moves up the food chain) and persists in the environment for long periods of time.
- Therefore, monitoring lead concentrations in the atmosphere, water, food and soil is necessary to ensure people are not exposed to harmful levels. This is especially true for areas providing drinking water and food, in areas of heavy traffic and near industries producing lead.
- Until recently, lead was widely used in **petrol** and so was released to the atmosphere in vehicle exhausts.

- Paints used before 1950 contained a high % of lead, and until the 1980s many government buildings were coated with such paints. Lead in paints is released by deterioration with age or demolition. Today, the maximum allowable concentration of lead in paint is 0.25%.
- Sources of lead include:
 - Lead piping
 - Leaded petrol
 - Paints
 - Smelters
 - Lead manufacturing and recycling industries

3.3.4 Describe the use of atomic absorption spectroscopy (AAS) in detecting concentrations of metal ions in solutions and assess its impact on scientific understanding of the effects of trace elements

- A **spectrophotometer** (or spectrometer) is a device that detects and measures a substance by its absorbance of certain wavelengths of light from the electromagnetic spectrum.
 - The hollow cathode lamp emits radiation of a specific wavelength, which is absorbed by atoms in the sample.
 - The flame provides the heat that is needed to vaporise the sample being analysed.



- **AAS is a quantitative form of analysis that uses the absorption of light to measure the concentration of metal ions in solution.**
- Theory:
 - AAS uses the principle of selective light absorption by metal ions. Elements absorb or emit radiation of specific frequencies that are characteristic of the element, and so individual elements can be analysed even in the presence of other elements.
 - Ground state atoms of an element are irradiated with light of a wavelength in that element's emission spectrum (so that those atoms will absorb some of the light). By measuring the fraction of the light at that wavelength that is absorbed, the concentration of the element can be determined ($A = kc$).
- Procedure:
 - A lamp is chosen that emits light of a wavelength which is absorbed by the element to be measured (e.g. lead lamp for determining concentration of lead in a sample).
 - A standard solution of the metal to be analysed is prepared and diluted to obtain a series of standards with accurately known concentrations.

- The standard solutions are aspirated into the flame and the absorbance of each is determined.
- The variation of the absorbance with concentration is plotted to give a calibration graph.
- The unknown solution is passed through the system and the absorbance measured.
- The concentration of the unknown sample is determined by interpolation on the graph.
- Uses of AAS:
 - Monitoring small concentrations of micro-nutrients in soils and heavy metals in the environment (e.g. mercury in fish).
 - Measuring small amounts of contaminants in food, medicines and manufactured goods.
 - Analysing metal content in mineral samples to determine their economic viability.
 - Determining concentrations of trace elements in living organisms.

Advantages of AAS	Disadvantages of AAS
<i>Sensitive and accurate</i> as it can easily measure ppm concentrations on small samples	<i>Expensive</i>
<i>Selective</i> as a specific lamp is used, corresponding to the metal ion being investigated (the metal ion does not have to be isolated from the mixture)	<i>Not onsite</i>
<i>Automated and rapid analysis</i> is possible once equipment is set-up (multiple measurements are conducted in batches)	Requires that the <i>presence</i> of the metal ion be confirmed first
<i>Reliable</i> as repetitions of measurements can be easily made	

- Impact of AAS on understanding of trace elements:
 - Trace elements (e.g. *Cu, Zn, Co*) are required by living organisms in small concentrations (1-100 ppm) for proper functioning of physiological processes.
 - Before the invention of AAS, analytical methods were not sensitive enough to measure the low concentrations of trace elements. The presence of trace elements was unnoticed, and the causes of deficiency diseases were unknown.
 - AAS was very sensitive and could be used to detect trace elements in soils and plants even in the presence of other metals. AAS showed that trace elements existed in living organisms and were essential for their well-being.
 - AAS has allowed chemists to investigate the role of trace elements in various situations:
 - Iron is required for the production of haemoglobin in the blood.
 - The analysis of blood and urine samples in humans by AAS can lead to diagnosis of medical conditions.
 - Using AAS, soil analysis can identify levels of essential trace elements (e.g. zinc, copper). Soils deficient in trace elements will not produce good crops or provide animals with mineral requirements, so dietary supplements or fertilisers can be added as necessary.
 - Thus, AAS had a great impact upon scientific understanding of trace elements.
- Example of trace element: Lead
 - Prior to the development of AAS it was not uncommon for lead to go undetected in the environment as there was no known analytical technique that could accurately determine such low concentrations. Precipitation reactions required concentrations much greater than 1 ppm.

- By monitoring lead levels using AAS and the symptoms of those exposed to lead, new information has been obtained with regards to the very low levels of lead responsible for minor symptoms (e.g. irritability, tiredness and headaches) and the higher levels responsible for major symptoms (e.g. neurological problems, seizures and coma).
- It was discovered that the safe level of exposure was 0 – no amount of lead is safe for humans. It is essential to avoid or limit exposure and to assess the level of lead in those exposed. Legislation could then be introduced to prevent the inclusion of lead in products such as paints, and public awareness of lead exposure and its symptoms has increased.
- *Assessment:* Thus, AAS has had a significant impact on scientific understanding of the effects of lead and how its use should be regulated. The gains in terms of better public health have been significant.

3.3.5 Gather, process and present information to interpret secondary data from AAS measurements and evaluate the effectiveness of this in pollution control

- AAS is extremely effective in monitoring pollution (esp. water and soil pollution) as it can measure very low concentrations of elements. It can detect small amounts of heavy metals (e.g. *Pb*, *Hg*, *Cd*) before they become concentrated enough to cause damage to the environment.
 - Gravimetric or volumetric techniques are not suitable as they are not sensitive enough to detect low levels of metal pollutants.
- AAS is cost effective, scientifically valid, highly sensitive, easy to use and readily available. It can be used to detect low concentrations of mercury in fish, copper and aluminium in waterways, zinc in oysters and lead fallout beside highways.
- Thus, AAS is extremely effective in pollution control as it enables the detection of small concentrations of pollutants in the environment, which could not be previously detected.

3.3.6 Identify data, plan, select equipment and perform first-hand investigations to measure the sulfate content of lawn fertiliser and explain the chemistry involved

- Aim: To determine the sulfate content of ammonium sulfate by gravimetric analysis.
- Method:
 1. Accurately weigh about 0.2 g of ammonium sulfate and record the mass.
 2. Dissolve the ammonium sulfate in about 100 mL of distilled water in a 500 mL beaker.
 3. Add 1-2 mL of 1 mol L⁻¹ HCl to ensure there is no carbonate in the sample. Dilute this solution to about 200 mL with distilled water and heat until almost boiling (> 80°C).
 4. Allow the solution to cool slightly then add 10 mL of BaCl₂ solution dropwise with stirring until no further white precipitate is formed.
 - Test for complete precipitation by adding a few more drops of BaCl₂ solution.
 5. Add dropwise with stirring 10 mL of 0.1% agar-agar solution, which will coagulate the BaSO₄ precipitate.
 6. Place a pre-weighed filter paper cone in a funnel supported by a ring clamp and retort stand, and filter the mixture.
 - If the filtrate is not clear, test for complete precipitation by adding one drop of BaCl₂.
 7. Wash the precipitate with distilled water to remove any Cl⁻ from the precipitate.
 - Add one drop of AgNO₃ to a sample of the filtrate. If a precipitate appears then repeat the washing until the filtrate no longer precipitates with AgNO₃.
 8. Dry the precipitate in an oven to a constant mass, then weigh.

3.3.7 Analyse information to evaluate the reliability of the results of the above investigation and to propose solutions to problems encountered in the procedure

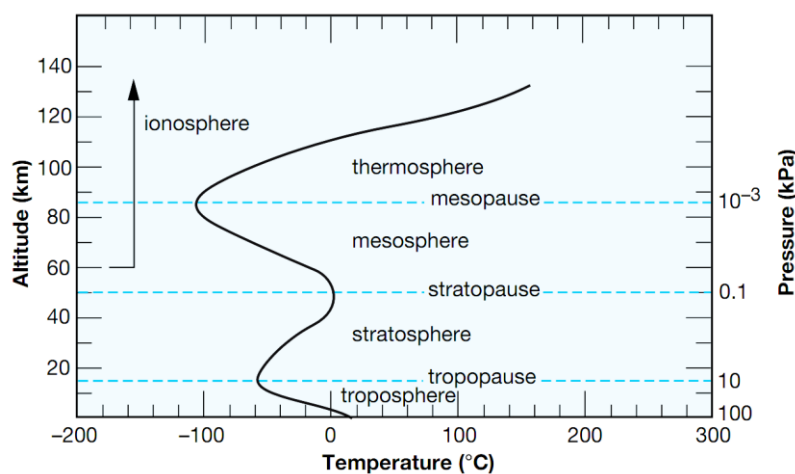
- **Gravimetric analysis** is a quantitative technique to determine the percentage by weight of a specific element or ion in a substance
- Main problems encountered:
 - **Ensuring no CO_3^{2-} is present:** CO_3^{2-} may precipitate with Ba^{2+} , so HCl was added to acidify the solution and remove any carbonate ions that could be present.
 - **Incomplete precipitation of SO_4^{2-} :** The complete precipitation of sulfate was ensured by adding *excess* $BaCl_2$.
 - **Filtering the very fine $BaSO_4$ precipitate:** This was overcome by adding agar-agar solution, which offers a surface on which the $BaSO_4$ can be adsorbed, so that the precipitate is coagulated, forming larger particles.
 - **Ensuring the $BaSO_4$ is free of water:** This was ensured by placing the precipitate in an oven and drying to constant mass.
 - **Final mass of SO_4^{2-} :** Adding agar-agar solution and excess $BaCl_2$ would contribute to the final mass of the SO_4^{2-} . Thus, only very little (10 mL) of agar-agar solution was added and the precipitate was washed with distilled water to remove chloride ions.
- Improving validity:
 - Use a more accurate electronic balance that measures up to at least 5 significant figures.
 - Use a sintered glass filtering crucible instead of fine filter paper, to prevent very fine particles passing through as part of the filtrate.
 - This would mean that agar-agar solution would not be needed, thus increasing validity.
 - Use a greater mass of solid, so that weight of $BaSO_4$ collected is greater, reducing the % error.

3.4 Atmospheric chemistry and ozone

3.4.1 Describe the composition and layered structure of the atmosphere

- The atmosphere is a layer of gas (200-300 km thick) that surrounds the Earth.
- Composition of atmosphere:
 - Major constituents: 78% nitrogen, 21% oxygen, 0.9% argon.
 - Minor constituents (in ppm): carbon dioxide, oxides of nitrogen (NO_x), sulfur compounds (SO_2 and H_2S), carbon monoxide, neon, helium, hydrogen, ammonia, ozone (O_3) and volatile organic compounds, such as methane.
- Structure of atmosphere:
 - The **troposphere** is the layer closest to the ground (0-15 km altitude).
 - Temperature decreases as altitude increases (due to thinning of gases).
 - Gases are well mixed due to convection currents (hot air near ground level rises, causing cooler air at higher altitudes to fall) - 'weather' is experienced.
 - The **stratosphere** contains the main zone of the ozone layer (15-50 km altitude).
 - Due to this layer of ozone, temperature increases as altitude increases (as UV radiation is absorbed and heat is released), preventing convection currents so there is very little vertical mixing of gases (cold air at bottom and hot air at top simply stay there).
 - Air is dry and stable so minimal 'weather' is experienced.
 - Most ozone occurs above the equator, where solar radiation is strongest and most direct.

- 99% of Earth's atmosphere is present in the troposphere and stratosphere.
- The slow transfer of gases across the tropopause is a key factor of the ozone hole problem.
 - Ozone in the stratosphere does not migrate into troposphere where it would poison living organisms.
 - Pollutants released at ground level are rapidly dispersed throughout the troposphere but diffuse very slowly into the stratosphere.
- In the **mesosphere**, temperature decreases as altitude increases as few molecules in this region absorb radiation, so it is very cold.
- In the **thermosphere**, temperature increases as altitude increases due to the absorption of high frequency radiation (solar radiation).
- Even though the % of O_2 in air stays constant from 0-50 km altitude, the concentration of O_2 decreases as altitude increases, because the amount of air also decreases with altitude.



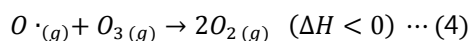
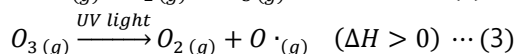
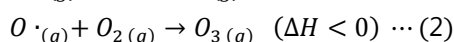
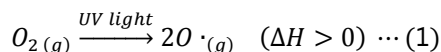
3.4.2 Identify the main pollutants found in the lower atmosphere and their sources

Pollutant	Sources
carbon monoxide	motor cars, incomplete combustion of fossil fuels
oxides of nitrogen (NO , NO_2)	combustion at high temperatures in vehicles and power stations
sulfur dioxide	combustion and metal extraction (from sulfide ores)
hydrocarbons	unburnt fuels and industrial solvents
particulates (e.g. soot)	combustion, mining, bushfires

3.4.3 Describe ozone as a molecule able to act both as an upper atmosphere UV radiation shield and a lower atmosphere pollutant

- Ozone in the upper atmosphere (stratosphere):
 - Ozone forms the 'ozone layer' which protects all life forms by acting as a **radiation shield** (filtering out UV light which damages living tissue).
 - There are 3 forms of UV radiation:
 - UV-A is beneficial as it facilitates photosynthesis and helps form Vitamin D in humans.
 - UV-B and UV-C are harmful as they cause skin cancer (melanoma), eye cataracts, severe sunburn and reduce plant growth in some crops, harming vegetation.
 - Oxygen absorbs almost all of the UV-C and ozone absorbs most of the UV-B while allowing useful UV-A to pass through.

- Formation and decomposition of ozone:



- Reactions (1) and (3) absorb UV radiation and reactions (2) and (4) release the energy as heat, warming up the air.
- The net result of the formation and decomposition cycle of ozone is that solar energy is converted to heat energy.
- Thus, temperature in the stratosphere is higher than at the tropopause.
- Effects of UV Radiation:
 - Damage to DNA in living cells.
 - Increased incidence of sunburn and skin cancer, and greater risk of eye cataracts.
 - Lowering of immune response, causing increased risk of disease and illness.
 - Reduced growth in some plants due to UV interference with photosynthesis mechanisms.
 - Degradation of synthetic plastic polymers used as structural materials.
- Ozone in the lower atmosphere (troposphere):
 - Ozone is a **major toxic air pollutant** that causes health and environmental problems.
 - Health issues:**
 - Ozone poisonous to humans as it is strong oxidant that reacts with sensitive mucous membranes when breathed in.
 - It has many harmful effects:
 - » Causes irritation of the eyes and airways and breathing difficulties.
 - » Aggravates respiratory problems (such as asthma).
 - » Produces headaches and premature fatigue.
 - Photochemical smog** is a type of air pollution that is produced when sunlight reacts with vehicle exhaust gases to form ozone and other harmful substances.
 - Ozone forms in the troposphere when sunlight is intense and concentrations of nitrogen dioxide are high:

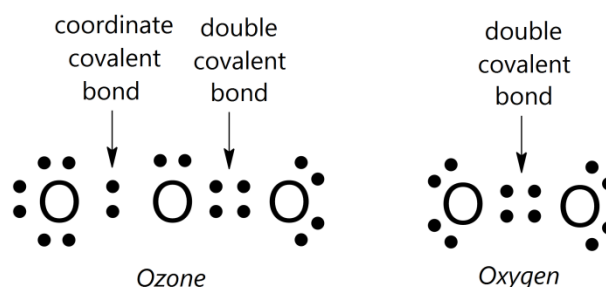
$$NO_{2(g)} \xrightarrow{sunlight} NO_{(g)} + O \cdot_{(g)}$$

$$O \cdot_{(g)} + O_{2(g)} \rightarrow O_{3(g)}$$
 - The chemical reactions of photochemical smog also form particulates, which because of their ability to scatter light cause the brown haze associated with such smog.

3.4.4 Describe the formation of a coordinate covalent bond

3.4.5 Demonstrate the formation of coordinate covalent bonds using Lewis electron dot structures

- A **coordinate covalent bond** is one in which both of the shared electrons come from the one atom. Once it is formed, it is the same as a normal covalent bond.
- The symbol used to designate a coordinate bond is an arrow (\rightarrow).



- **Ozone** consists of 3 O atoms. A lone pair of electrons on one of the O atoms of an O_2 molecule forms a coordinate covalent bond with the third O atom.

3.4.6 Compare the properties of the oxygen allotropes O_2 and O_3 and account for them on the basis of molecular structure and bonding

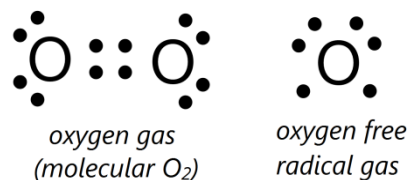
- *Intramolecular* forces (e.g. covalent bonds) hold a molecule together and are considered in chemical reactions.
- *Intermolecular* forces (e.g. dispersion forces, dipole-dipole forces or hydrogen bonds) are forces between molecules and are considered when a substance changes state (e.g. boils, melts, etc.).
- **Allotropes** are different structural forms of the same element (in the same physical state). They have different physical properties (e.g. colour, density, hardness, electrical conductivity) which can be explained by their molecular structure and bonding.
- Oxygen has 2 allotropes:
 - *Oxygen gas* (O_2) is a colourless, odourless gas (formed by photosynthesis).
 - *Ozone* (O_3) is a pale blue, toxic gas with a sharp, pungent odour (formed by UV radiation and electric discharge on oxygen).
- **Density:** Ozone is denser than oxygen as ozone has 3 O atoms compared with 2 for oxygen.
- **Boiling point:** (O_2 is -183°C , O_3 is -111°C)
 - Ozone has a higher boiling point than diatomic oxygen.
 - Ozone has a higher molecular mass, which increases electron cloud density and hence distortion, so dispersion forces are greater and more energy is required in the boiling process.
 - Ozone is also slightly polar so it has stronger intermolecular forces (dipole-dipole).
 - Separating a mixture of oxygen and ozone involves cooling to liquefy and then carrying out fractional distillation (as boiling points are different).
- **Solubility:**
 - Oxygen has low solubility compared with ozone.
 - Non-polar O_2 does not form strong intermolecular forces in polar water.
 - The polarity of ozone allows it to have intermolecular interactions with water.
- **Reactivity/Stability:**
 - Ozone is much less stable than oxygen.
 - Oxygen is very stable as considerable energy is required to break its double bond (which has a high bond energy).
 - The single coordinate covalent bond in ozone requires much less energy to be broken, so ozone readily decomposes to a stable O_2 molecule.
- **Oxidation ability:**
 - Oxygen is a moderately strong oxidant, while ozone is a very strong oxidant.
 - Oxygen reacts with metals to form only oxides, whereas ozone reacts more readily to form metal oxides with the release of oxygen gas.
- **Shape:**
 - Oxygen is linear (non-polar), while ozone is bent (polar).
 - Ozone is bent in shape as this minimises repulsion between the bonding and non-bonding valence electrons. This bent shape means that ozone is a polar molecule, so there is an uneven distribution of electron clouds, causing one end to be slightly more negative than the other.

- Note: Do not explain the bent shape of ozone in terms of certain atoms being more electronegative. The atoms in ozone are all oxygen and so have no differences in electronegativity.

3.4.7 Compare the properties of the gaseous forms of oxygen and the oxygen free radical

- A **free radical** is a neutral species with an unpaired electron.
The oxygen free radical is an oxygen atom with 2 electron pairs and 2 unpaired electrons.
- It is formed by the absorption of UV light in the stratosphere:

$$O_2(g) \xrightarrow{\text{UV light}} 2O^{\cdot}(g)$$
- The stability of O_2 and O_3 relative to oxygen atoms is because they have completed valence shells.
- The presence of unpaired electrons in the oxygen free radical makes it more reactive than oxygen gas (as unpaired electrons exist in higher energy states than the ground state).
 - Thus, oxygen free radicals exist only briefly in the lower atmosphere.



3.4.8 Identify and name examples of isomers (excluding geometrical and optical) of haloalkanes up to eight carbon atoms

- A **haloalkane** is a compound in which one or more *H* atoms of an alkane are replaced by halogen atoms (e.g. *F*, *Cl*, *Br*, *I*).
- An **isomer** is a compound with the same molecular formula but different structural formula.
- Rules:
 1. *Prefixes*: bromo-, chloro-, fluoro-, iodo-
 2. The position of a halogen atom is denoted by a number; double bond takes preference.
 3. Number the chain from the end that produces the smallest sum of numbered positions.
 4. Name halogen atoms alphabetically, ignoring any di-, tri-, tetra- in this ordering.
 5. If rules 1-4 lead to more than one possible name, give the lowest numbers to the most electronegative halogen; order of electronegativity: $F > Cl > Br > I$

3.4.9 Identify the origins of chlorofluorocarbons (CFCs) and halons in the atmosphere

- **CFCs** (chlorofluorocarbons) are compounds containing *Cl*, *F* and *C* only (no *H* atoms).
 - CFCs were introduced (under trade name 'freons') as replacements for ammonia in refrigeration.
 - CFCs are odourless, non-flammable, non-toxic, unreactive and readily liquefied on compression, making them more attractive than the ammonia they replaced.
 - They were also later used as aerosol propellants, foaming agents for polymer materials and cleaning agents in electronic circuitry.
 - However, after discovering that they play a major role in ozone depletion (and to a small extent in greenhouse effect), they were phased out.
- **Halons** (bromofluorocarbons) are compounds of *C*, *Br* and other halogens (no *H* atoms).
 - Halons are very stable, dense and non-flammable liquids that were widely used in fire extinguishers (e.g. $CBrClF_2$), where water would be ineffective and dangerous (e.g. involving live electrical circuits).
 - These halons were released directly into the atmosphere, where they slowly diffused into the stratosphere, so their use in fire extinguishers has been phased out.

- Halons are even more ozone-depleting than CFCs as they release bromine radicals ($Br\cdot$), which cause much greater ozone depletion than chlorine radicals.

3.4.10 Analyse the information available that indicates changes in atmospheric ozone concentrations, describe the changes observed and explain how this information was obtained

- Ozone levels are measured in Dobson Units (DU).
- Stratospheric ozone is monitored from ground-based instruments, instruments in satellites and instruments on weather balloons.
 - Ground-based
 - Ground based instruments are **UV spectrophotometers** pointing vertically upwards through the atmosphere.
 - The light intensity at wavelengths at which ozone absorbs and at wavelengths on either side (at which ozone does not absorb) are measured and compared to determine the total ozone in the atmosphere per unit area of Earth surface.
 - Satellite-based
 - The **TOMS (total ozone mapping spectrophotometers)** have been placed on US satellites.
 - Since the satellites have been in orbit, the instruments scan the entire globe and measure ozone concentration as a function of altitude and geographical location.
 - Balloon-based
 - UV spectrophotometers can be placed in **weather balloons** above the stratosphere.
 - These instruments are pointed downwards and measure ozone from above.
- The changes observed:
 - The main depletion of ozone has occurred over the Antarctic, due to the polar region's favourable conditions for ozone-destroying reactions.
 - Scientists identified that a dramatic decline in springtime ozone occurred from the late 1970s over the entire Antarctic. The decline reached approximately 30% by 1985.
 - The ozone depletion which appears each spring is still worsening (at times exceeding 50%), but its size fluctuates yearly and between spring and the rest of the year.
 - The above evidence was determined by scientific and government organisations and so can be considered to be valid indications of changing ozone concentrations.

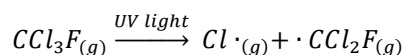
3.4.11 Present information from secondary sources to write the equations to show the reactions involving CFCs and ozone to demonstrate the removal of ozone from the atmosphere

3.4.12 Discuss the problems associated with the use of CFCs and assess the effectiveness of steps taken to alleviate these problems

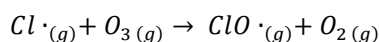
- The main problem with the use of CFCs is the destruction of ozone in the stratosphere – i.e. depletion of the ozone layer.
- CFCs are inert (so they are not destroyed by sunlight and oxygen) and insoluble in water (so they are not washed out by rain).
- Hence, CFCs remain in the troposphere for long periods of time, and diffuse slowly into the stratosphere, where they deplete the ozone layer.

- How CFCs destroy the ozone layer:

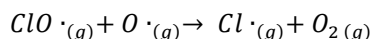
- CFCs undergo photodissociation to form reactive chlorine radicals:



- Destruction of ozone:

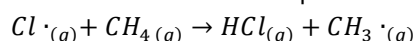


- Regeneration of chlorine radical:

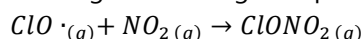


- The net result is that ozone and an oxygen radical are converted into 2 oxygen molecules, and the chlorine radical has not been used up. This causes a chain reaction, where the chlorine radical is able to attack another ozone molecule and repeat the process thousands of times. Hence a small amount of CFC in the stratosphere can cause significant ozone destruction.
- The $Cl \cdot$ radical acts as a catalyst in these reactions, as it is both reactant and product in the overall process: $O_3_{(g)} + O \cdot_{(g)} \rightarrow 2O_2_{(g)}$
- Note: Theoretically, a single chlorine radical could destroy the entire ozone-layer, however other reactions occur which remove this radical.

- A chlorine atom reacts with methane in the stratosphere to end the chain reaction:



- The $ClO \cdot$ species can react with nitrogen dioxide gas to produce chlorine nitrate:

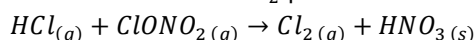


- These reactions remove $Cl \cdot$ and $ClO \cdot$ from the chain reaction and so are methods of stopping ozone depletion.

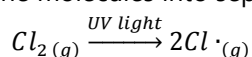
- The Antarctic Spring Ozone Hole:

- The periodic ozone depletion in the stratosphere over Antarctica can be explained in terms of a catalytic surface process occurring on ice crystals formed in the cold air of the polar vortex in winter.

- In this vortex, a reaction between HCl and $ClONO_2$ produces molecular chlorine:



- This has no effect on ozone levels during winter, however when the Sun comes up in early spring, sunlight is able to split chlorine molecules into separate chlorine atoms:



- Hence, in spring, there is another source of chlorine radicals, greatly increasing ozone depletion over the Antarctic and causing the 'ozone hole' (where ozone layer is thin).
- By early summer, the polar vortex breaks up and the finite amount of Cl_2 formed during winter is used up, so the rate of ozone destruction returns to its normal level.

- Dealing with the Ozone-Hole problem:

- The only way to stop ozone destruction is to stop releasing CFCs of any form.

- *The Montreal Protocol:*

- The **Montreal Protocol** (1987) is an international treaty to protect the ozone layer by phasing out ozone-depleting chemicals, such as CFCs and halons, and replacing them with less-damaging molecules.
- It required the phasing out of ozone-depleting chemicals according to a timetable, with different phasing out periods for developed and developing countries. Developed countries provide financial assistance to help developing countries to phase out CFCs.
- It provides incentives and trade sanctions to ensure its targets are achieved.

- Australia is well ahead in phasing out the use of ozone-depleting chemicals – CFCs, HCFCs, halons and tetrachloromethane are all phased out.
- Evaluation of the Montreal Protocol:
 - The Montreal Protocol has been successful as progress in reducing emissions of CFCs worldwide appears to be quite significant, and most countries are meeting the required targets. This has been largely due to the availability of acceptable alternative compounds such as HFCs to replace CFCs.
 - Overall, reduction in atmospheric concentrations of CFCs has not been major, but at least the ozone thinning has not become worse.
- Dealing with increased UV Radiation:
 - The CFCs already in the stratosphere cannot be removed so measures are needed to reduce the effects of problems caused by CFCs (e.g. high levels of UV radiation).
 - These include using sunscreens with high sun protection ratings (at least SPF 30+) and the use of UV stabilisers in polymers to reduce breakdown by UV radiation.

3.4.13 Present information from secondary sources to identify alternative chemicals used to replace CFCs and evaluate the effectiveness of their use as a replacement for CFCs

- Alternatives to CFCs:
 - **HCFCs** (*hydrochlorofluorocarbons*) were the first replacements for CFCs. They are only **moderately effective** in minimising ozone depletion.
 - HCFCs are broken down in the troposphere due to the high reactivity of their $C-H$ bonds, which are susceptible to attack by reactive radicals and atoms.
 - Only a small % of HCFCs reach the stratosphere, but once they do, ozone destruction rapidly occurs.
 - Hence their ozone depletion potential, although significant, is much less than that of CFCs. Their long-term toxicity to humans is yet to be determined.
 - HCFCs replaced CFCs in refrigeration and as foaming agents, but they were only a temporary solution.
 - **HFCs** (*hydrofluorocarbons*) are widely used as replacements for CFCs and HCFCs. They are **very effective** in minimising ozone depletion.
 - HFCs contain reactive C-H bonds (so they degrade in the troposphere) and have no chlorine (so they do not form $Cl\cdot$ radicals and hence have no ozone depletion potential).
 - The most widely used HFC is HFC-134a, which is used in refrigeration and air conditioning.
 - While HFC-134a is non-flammable and has suitable properties, it is more expensive and less efficient than the CFCs it replaces, but this is a small price to pay for protecting stratospheric ozone.
- Evaluation:
 - Neither alternative class of chemicals for ozone replacement has been totally successful, but HFCs have been shown to be very promising so far.
 - Further research is still required to develop effective alternative chemicals to CFCs.

3.5 Monitoring the Water Supply

3.5.1 Identify that water quality can be determined by considering concentrations of common ions, total dissolved solids, hardness, turbidity, acidity, dissolved oxygen and biochemical oxygen demand

3.5.2 Perform first-hand investigations to use qualitative and quantitative tests to analyse and compare the quality of water samples

- **Concentrations of common ions:**

- Concentrations of Na^+ and Cl^- indicate the *salinity* of the water, which affects aquatic life.
- Measuring concentrations of common ions:
 - Cation concentrations in ppm and even ppb can be measured using AAS.
 - The chlorine ion is the most common ion in most natural water, and its concentration can be measured gravimetrically or by titration with $AgNO_3$.
- Note: If $pH < 6.5$, then carbonate is unlikely to be present in high concentrations.

- **Total dissolved solids (TDS):**

- **TDS** is the mass of solids dissolved in unit volume of water (measured in mg/L or *ppm*). TDS includes mainly *ionic compounds* and smaller amounts of *organic molecules*.
- TDS fluctuates over time due to the influx of rainwater and floodwater.
- Measuring TDS:
 - **By evaporation:**
 - » The water sample is filtered into a previously weighed large evaporating basin to remove suspended solids and then evaporated to dryness with a Bunsen burner.
 - » The evaporating basin is allowed to cool and the remaining solids are weighed.
 - » This method must be carried out carefully, because by heating the solution to dryness there is a tendency of the solute being “spitted” out of the solution. The best method is to reduce the volume of water to a small amount, then dry in an oven.
 - » Also, this method is not very accurate as dissolved solids are usually presence in concentrations of $< 1\text{ g/L}$. This would require a large amount of water to be evaporated for accurate results to be obtained.
 - **By conductivity:**
 - » TDS can be measured by a conductivity meter (which is calibrated with a conductivity standard solution before use), as almost all the solid dissolved in natural water is ionic and so contributes to the total conductivity.
 - » Although conductivity tests give a measure of total dissolved *salts*, this is a fair approximation for total dissolved *solids*.

- **Hardness:**

- **Hardness** is a measure of the total concentration of calcium and magnesium ions in the water. It is expressed as mg of $CaCO_3$ / L of the sample of water.
- Ca^{2+} and Mg^{2+} form insoluble salts with soap, and appear as scum precipitates on the surface of the water and often stick to the enamel of baths and hand basins.
- Measuring hardness:
 - **Qualitative test:** Equal volumes of soap solution are added to 5 mL of distilled water and 5 mL of sample water. The extent of lathering is compared to determine the hardness.

- **Volumetric analysis** (quantitative test):
 - » Volumetric titration with EDTA reagent, which reacts with Ca^{2+} and Mg^{2+} in a 1:1 ratio. The indicator used is Eriochrome Black-T.

$$Ca^{2+} + EDTA^{4-} \rightarrow CaEDTA^{2-}$$

$$n(Ca^{2+}) = n(EDTA^{4-})$$
- **AAS:** Concentrations of Ca^{2+} and Mg^{2+} can be measured using AAS.
- **Turbidity:**
 - **Turbidity** is a measure of cloudiness or lack of transparency (measured in NTU), caused by the presence of *undissolved* solids and suspended solids. It is a measure of the degree to which light travelling through the water is scattered by the suspended particles.
 - High turbidity can interfere with light penetration through the water, which reduces the rate of photosynthesis and hence reduces dissolved oxygen. Photosynthetic activity of phytoplankton is suppressed, leading to less oxygen and death of aquatic life. Turbid water destroys feeding and spawning grounds of fish and clogs up reservoir and stream channels.
 - Measuring turbidity:
 - **Turbidity tube:** Turbidity can be assessed by measuring the depth of water needed to render invisible a mark (X) on the flat bottom of a turbidity tube (long measuring cylinder). Turbidity is read off engraved marks at different depths.
- **Acidity:**
 - **Acidity** is a measure of the concentration of hydrogen ions, in water ($pH = -\log_{10}[H^+]$).
 - A *pH* outside the normal range of 6.5-8.5 indicates a polluted system, caused by the discharge of chemicals into the water (e.g. fertiliser run-off, industrial waste, acid drainage). This may cause a reduction in species diversity, as more sensitive species of aquatic life will disappear.
 - Measuring pH: The pH of water is measured using a *calibrated pH meter* or **probe**, pH strips or **indicators**.
- **Dissolved oxygen (DO):**
 - **DO** is a measure of the concentration of oxygen (O_2) in the water (measured in *ppm*).
 - Oxygen has a very low solubility in water, however dissolved oxygen is vital for aquatic life.
 - Measuring dissolved oxygen:
 - **Electronic oxygen sensor:**
 - » This relies on the fact that the rate of electrolysis of a substance is proportional to its concentration, with all other variables kept constant.
 - » Oxygen is electrolysed and the current is measured and converted to an oxygen concentration.
 - **Winkler method:** This involves the volumetric analysis of dissolved oxygen. 1 mole of $S_2O_3^{2-}$ is equal to $\frac{1}{2}$ mole of I_2 which is equal to $\frac{1}{4}$ mole of O_2 .
- **Biochemical oxygen demand (BOD):**
 - **BOD** is a measure of the concentration of dissolved oxygen that is needed for the complete breakdown of the organic matter in the water by aerobic bacteria over a 5-day period.
 - High BOD levels indicate large amounts of organic matter in the water, which drains the water of oxygen, causing a low DO level (i.e. BOD and DO are inversely related).
 - A high DO level and low BOD is preferable.

- Measuring BOD:
 - **5-day BOD test**:
 - » Two water samples are taken.
 - » One sample is measured for DO immediately while the other sample is placed in a dark sealed container and incubated for 5 days before its DO level is measured.
 - » The difference between the DO readings is the BOD (measured in mg/L).
$$BOD = DO_{initial} - DO_{after\ 5\ days}$$
 - » The five day sample will have a lower DO level as organic compounds in the water will react with oxygen over the five days.

3.5.3 Identify factors that affect the concentrations of a range of ions in solution in natural bodies of water such as rivers and oceans

- **Heavy rain or flooding**:
 - Sustained heavy rain picks up ions and solids from the soil and carries the water into rivers and oceans.
- **pH of the rain**:
 - Water from acid rain ($pH < 5$) leaches cations (e.g. Ca^{2+} and Mg^{2+}) from the soil.
- **Agricultural activity**:
 - Fertiliser run-off from agricultural land contains nitrates and phosphates and is washed away by rain into waterways.
 - Leaching of animal faeces on grazing pastures will result in increased concentrations of nitrogen and phosphorus in waterways.
- **Land clearing**:
 - Deforestation destroys plant roots and causes soil to become easily eroded.
 - Rain flowing over cleared land carries sediment loads into the water body, increasing turbidity and TDS due to high levels of mineral ions in the soil.
- **Effluent discharge**:
 - Discharges of raw sewage directly into the water will greatly increase the concentrations of many ions, especially phosphate and nitrate, which will cause eutrophication.
 - The decomposition of organic matter converts phosphorus to phosphate and nitrogen to nitrate, increasing the nutrient load of the water body.
 - Stormwater run-off in urban areas can also carry high levels of ions.
 - Industrial effluents and leaching from rubbish dumps can increase the levels of dangerous heavy metal ions in water (e.g. Pb^{2+} and Zn^{2+}).

3.5.4 Gather, process and present information on the range and chemistry of the tests used to identify heavy metal pollution of water and monitor possible eutrophication of waterways

- **Heavy metals**:
 - **Heavy metals are the transition metals in addition to lead and arsenic.**
 - The heavy metals of the most concern are mercury, lead, cadmium, chromium and arsenic.
 - Qualitative test (sulfide test):
 - A water sample is acidified, then a few drops of sodium sulfide (Na_2S) is added.
 - If a precipitate forms, then one of the following ions is present:
 - » Lead, silver, mercury, copper, cadmium or arsenic

- If no precipitate forms with acid present, the sample is made slightly alkaline. If this then produces a precipitate, one of the following is present:
 - » Chromium, zinc, iron, nickel, cobalt, manganese or aluminium
- Chemistry: The sulfide test is based on the equilibrium:

$$S^{2-}_{(aq)} + 2H_3O^{+}_{(aq)} \rightleftharpoons H_2S_{(aq)} + 2H_2O_{(l)}$$
 - In acid solution, the equilibrium lies to the right.
 - » There is only a small amount of sulfide, but it is sufficient to precipitate *extremely insoluble* sulfides (e.g. Pb^{2+} and Cu^{2+}).

$$Pb^{2+}_{(aq)} + S^{2-}_{(aq)} \rightleftharpoons PbS_{(s)}$$
 - In alkaline conditions, the equilibrium lies to the left.
 - » There is a large amount of sulfide, so it precipitates with cations that form *less insoluble* sulfides (e.g. Zn^{2+} and Fe^{2+}).

$$Zn^{2+}_{(aq)} + S^{2-}_{(aq)} \rightleftharpoons ZnS_{(s)}$$
- Other qualitative tests include **flame tests** (e.g. for Cu^{2+}) and other **precipitation tests** (e.g. $NaOH$ forms a precipitate with mercury, cadmium, zinc, chromium and aluminium ions).
- Quantitative tests:
 - **Gravimetric** and **volumetric** analysis can be used, but this is limited due to the low concentrations involved in environmental water samples.
 - **Atomic emission spectroscopy** is widely used for monitoring water quality as it is able to analyse several metals in one measurement.
 - » It is used for *qualitatively* identifying elements in a sample.
 - **Atomic absorption spectroscopy** is also used but metals must be measured one at a time as each requires a separate lamp.
 - » It is used for *quantitatively* identifying elements in a sample
- Eutrophication:
 - ***Eutrophication is the process in which a water body becomes enriched with nutrients (e.g. phosphate and nitrate) to such an extent that algal blooms become likely.***
 - Effects of algal blooms:
 - Sunlight is blocked by excessive plant growth at the water surface, so photosynthesis is disrupted.
 - Algal blooms interfere with diffusion of oxygen from the air into the water.
 - When algae die, their decomposition leads to severe oxygen depletion in the waterway that threatens the survival of aquatic life.
 - Blue-green algae (cyanobacteria) in algal blooms produce poisons that can kill livestock and cause serious illness in humans. Water becomes unsuitable for normal uses, as it is clogged up with algae and has an unpleasant taste.
 - The effects of eutrophication are measured by assessing dissolved oxygen levels and BOD, and observing for any unprecedented presence of algae.
 - Generally, phosphate is the growth-limiting nutrient (present in the least amount), so it is the best one to monitor to check for eutrophication.
 - Phosphate:
 - *Qualitative*: The presence of phosphate ions is indicated by a (pale) yellow **precipitate** with ammonium molybdate.
 - *Quantitative*: Phosphate concentrations are measured using a sensitive **colorimetric** method, which relies on the quantitative measurement of the absorption of light by a

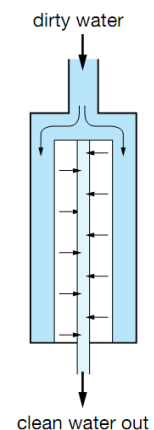
coloured solution. A measured quantity of a solution of ammonium molybdate is added, followed by a measured quantity of ascorbic acid (vitamin C). This produces an intense blue colour. By comparing the absorbance of this solution with known standard solutions, the concentration of phosphate can be calculated colorimetrically.

– Nitrate:

- *Qualitative:* The **brown ring test** is used, where a test tube is filled with a water sample, and $FeSO_4$ and concentrated H_2SO_4 are added. The formation of a brown ring at the junction indicates the presence of nitrate ions.
- *Quantitative:* Nitrate concentrations are measured instrumentally using a **colorimeter**. The nitrate ions are reacted with a reductant to convert them to nitrite ions. The nitrite reacts with a colour reagent to produce a pink-purple dye that is measured colorimetrically against known standards.

3.5.5 Describe the design and composition of microscopic membrane filters and explain how they purify contaminated water

- **Microscopic membrane filters consist of a thin film of a synthetic polymer through which small uniform pores filter out solutes, colloidal particles and microorganisms from solution.**
- Membrane filters use gravity, vacuum or pressure pumps to force the liquid through the membrane so that clean water is collected from inside the tube.
- Types of membrane filters:
 - The simplest type of membrane filter is a sheet of porous polymer that is folded around a hollow core and surrounded by a casing.
 - Water passes *across* the surface of the membrane (not through it) to reduce blockage, and particles larger than the pore sizes are filtered off.
 - Clean water exits via the hollow core.
 - Another type of membrane filter involves forming the membranes into hollow capillaries (tiny tubes) – these are called *hollow fibre* membrane filters.
 - Large numbers of these capillaries are bound together to form a filtering unit with a very large surface area.
 - Raw water runs along the outside of the capillary fibres and clean water penetrates the pores to the inside of each capillary.
- Microscopic membrane filters have microscopic pores and the use of appropriate sized filters can avoid the need to chemically treat the water.
- The filters can be classified as microfiltration, ultrafiltration, nanofiltration and reverse osmosis membranes depending on the size of the pore. The finer the pore size, the smaller the particles trapped and the more expensive the membrane.
- Although membrane filters can remove small suspended particles, they cannot remove ions (e.g. nitrate or phosphate or heavy metal ions) and dissolved solids. In this case, reverse osmosis is used, which involves applying pressure to a solution to push water molecules through a membrane, leaving impurities behind.
- The filters can be cleaned by back-flushing, and can then be reused.



3.5.6 Describe and assess the effectiveness of methods used to purify and sanitise mass water supplies

- Monitoring catchment:
 - The **catchment** is the area of land from which all the streams and rainfall drain into a city's water storage dam.
 - The first step in ensuring good quality water is to protect the catchment by keeping it clean.
 - This involves preventing land-clearing, industry or agriculture in the entire catchment area to ensure that the water that flows into the dam is free of sediments and animal wastes.
- Screening:
 - Before the water from catchment areas is treated or stored, it is passed through **metal screens** that remove large debris (e.g. sticks, leaves, trash) which may interfere with subsequent purification steps.
- Clarification and Flocculation:
 - **Clarification** involves removing any turbidity or colour so that the water is clear and colourless.
 - Coagulants such as iron (III) chloride are added to cause **flocculation**, where fine, suspended particles clump together to form flocs (aggregations of particles) so they are more easily filtered.

$$Fe^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow Fe(OH)_3(s) + 3H^+_{(aq)}$$
 - As the production of H^+ can corrode water pipes, $Ca(OH)_2$ is often added at this stage to raise the pH back to ~ 7 and allow the flocs to remain stable.
 - The coagulated precipitate takes most of the suspended matter out of the water.
- Sedimentation and Filtration:
 - Flocculated water is allowed to settle, causing dirt and other particles to fall to the bottom as a **sludge** where it is removed.
 - The clear water is then filtered through **layers of sand and gravel**, removing the rest of the particulate matter.
 - The water is also passed through an **anthracite filter** (carbon-containing mineral coal) to remove organic molecules.
- Chlorination:
 - Water is **sanitised** during the final stage of the process by adding *gaseous chlorine* which forms hypochlorite ions (ClO^-) to destroy pathogens such as bacteria (e.g. *E. coli*), microbes and other disease-causing agents.
- Assessment of effectiveness:
 - These methods are effective when used together to purify water as the process is fast and reliable. None of the methods are effective on its own as they remove different particles from the water.
 - **Sand filtration** removes a high proportion of the particulate matter in the water after flocculation, but not extremely small particles. It is sufficiently fast to produce the volume of treated water required by cities, without the expense of using finer filters such as membrane filters.
 - While **chlorination** is a cost-effective way of removing most disease-causing agents, it is not as effective at killing viruses and protozoans (e.g. *Giardia* is not removed). Excessive chlorine may impart an unpleasant odour to the water.

- A **membrane filter** is more effective at removing fine suspended particles than a sand filter, but is more costly and impractical for purifying a town's water supply as it slows down the rate of water flow and purification.
 - In fact, due to the relatively high quality of Sydney's raw water, membrane filtration is currently considered too expensive for the relatively small improvement in water quality that it provides.
- **Ozone sterilisation** would be effective at removing harmful organisms that chlorination cannot destroy, however again this would occur at substantially increased costs.

3.5.7 Gather, process and present information on the features of the local town water supply in terms of catchment area, possible sources of contamination in this catchment, chemical tests available to determine levels and types of contaminants, physical and chemical processes used to purify water chemical additives in the water and the reasons for the presence of these additives

- **Catchment area:**
 - Warragamba Dam is Sydney's main water storage dam, accounting for 80% of Sydney's water with its catchment area of about 9000 km².
- **Sources of contamination:**
 - Land Clearing
 - Land-clearing and deforestation activities lead to increased turbidity and TDS in the water flowing into the dam.
 - Agriculture
 - Run-off from agricultural land contains high levels of phosphates and nitrates as a result of leeching fertilisers from the soil and crops.
 - Cattle graze extensively along the creeks and rivers in the catchment. Water that runs over pasture-land can carry with it animal faeces. This contamination can lead to the growth of bacteria and a high BOD.
 - Mining
 - Rainwater can leach out minerals (iron and manganese) from the natural soil and rock strata around the catchment area.
 - Sewage
 - Sewage treatment plants along some of the catchment rivers discharge treated sewage into the river.
 - During floods, sewage treatment plants cannot handle the heavy input of stormwater flows, so raw untreated sewage is allowed to flow into the water body.
 - This leads to contamination of water with bacteria and excess ions.
- **Testing for contaminants:**
 - Test for *common ions*: electrical conductivity
 - Test for *heavy metal ions*: sulfide-test (qualitative) and AAS (quantitative)
 - Test for *nitrates and phosphates*: colourimetry
 - Test for *BOD*: Winkler method
- **Water purification:**
 - Water is first screened to remove large debris.
 - Flocculation occurs using $FeCl_3$, followed by stirring to encourage precipitate formation.

- The water is left in a sedimentation tank to settle. The sludge is removed and the water is filtered through layers of sand and gravel.
- The water is finally sanitised by chlorination.
- **Chemical additives:**
 - Chlorine (Cl_2) is added as a disinfecting agent to sanitise water
 - Gaseous chlorine is dissolved in the water, forming hypochlorite ions (ClO^-) which kill bacteria and some viruses.
$$Cl_{2(aq)} + H_2O_{(l)} \rightarrow HOCl_{(aq)} + HCl_{(aq)}$$
 - Fluoride (F^-) is added in the form of NaF to strengthen tooth enamel, decreasing the likelihood of tooth decay (but it does not improve the safety of the water).
 - pH readjustment occurs using limewater, $Ca(OH)_2$, to prevent corrosion of pipes.