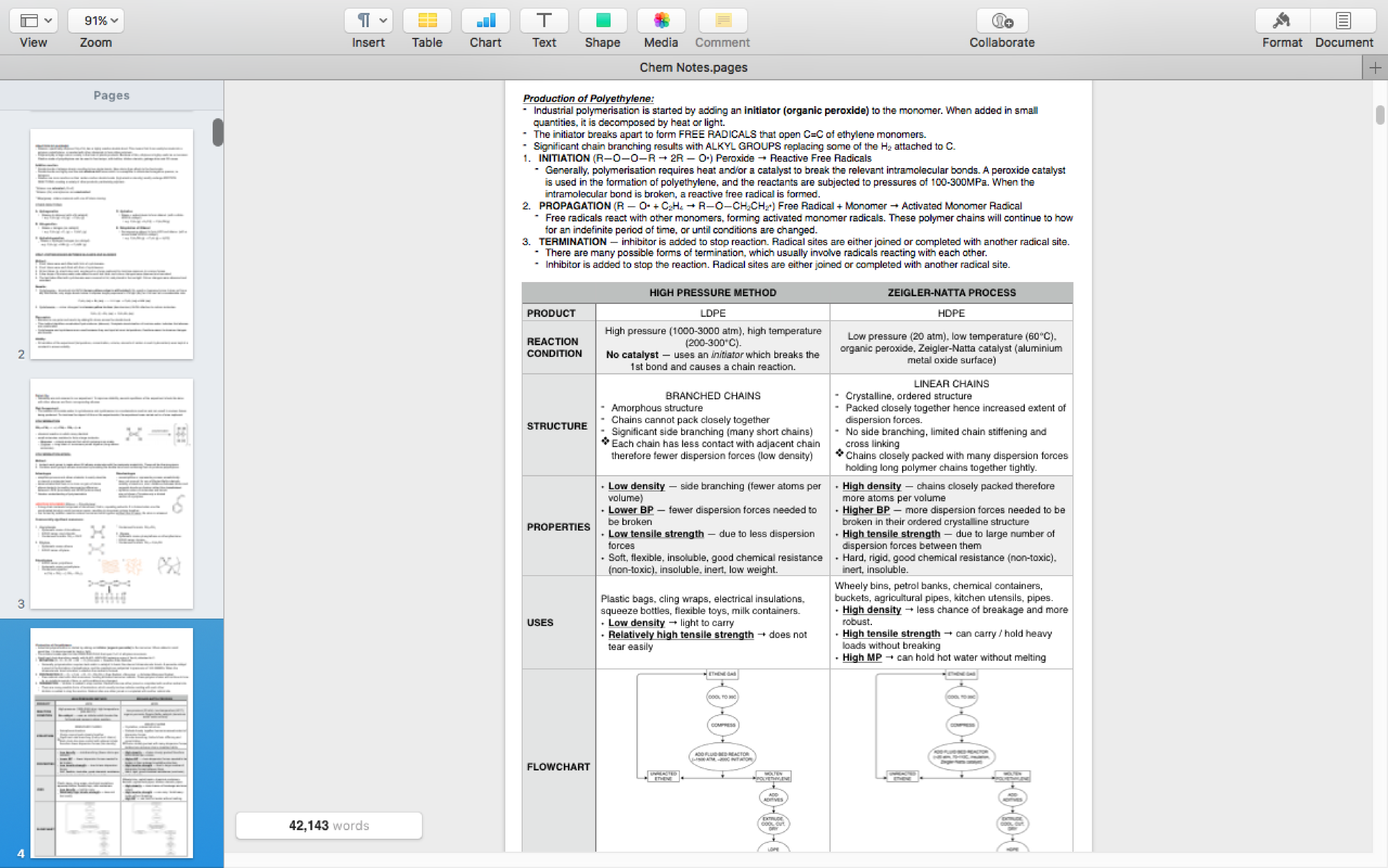
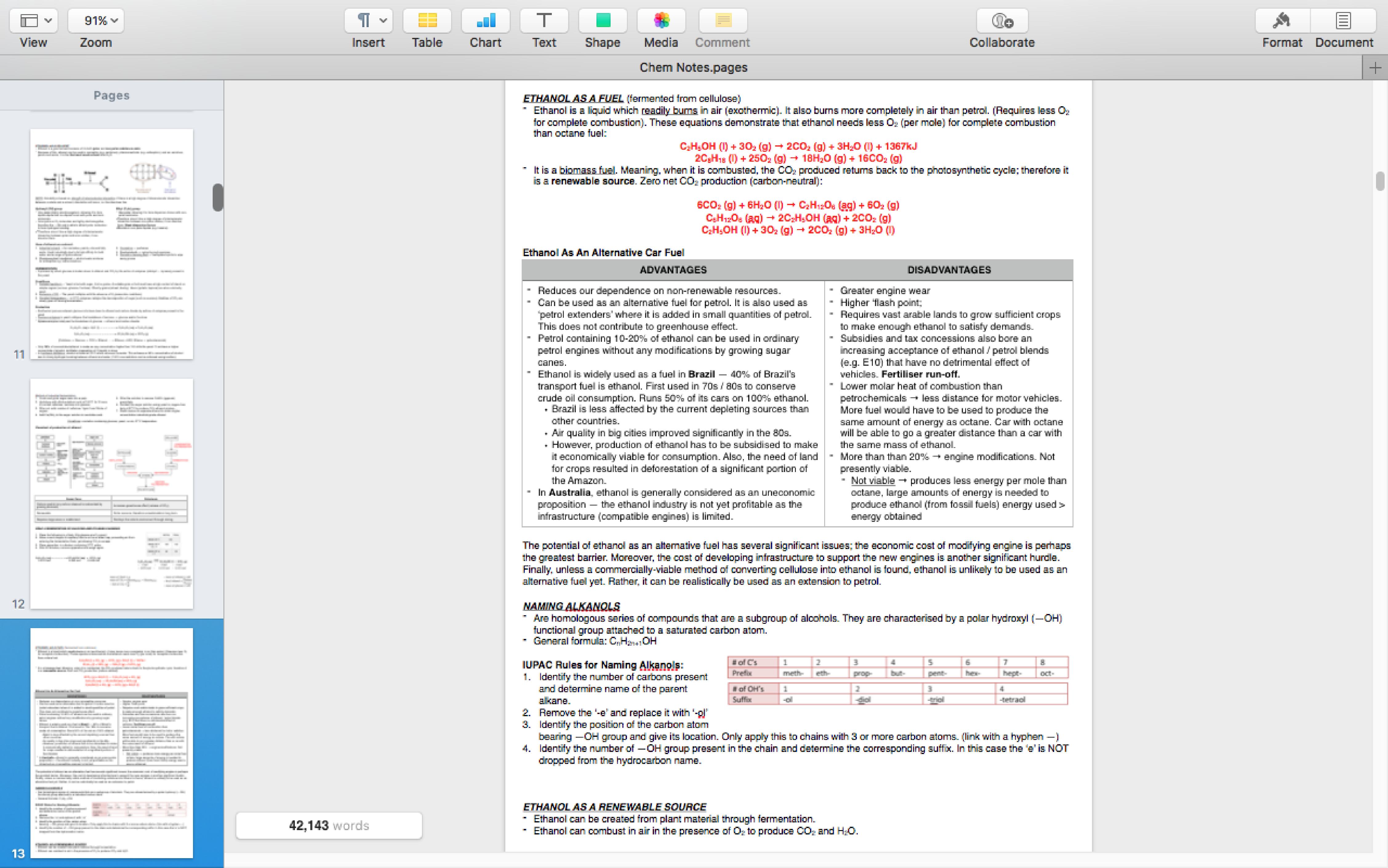


Production of Polyethylene:

- Industrial polymerisation is started by adding an **initiator (organic peroxide)** to the monomer. When added in small quantities, it is decomposed by heat or light.
- The initiator breaks apart to form FREE RADICALS that open C=C of ethylene monomers.
- Significant chain branching results with ALKYL GROUPS replacing some of the H_2 attached to C.

1. **INITIATION** ($R—O—O—R \rightarrow 2R — O\cdot$) Peroxide → Reactive Free Radicals
   - Generally, polymerisation requires heat and/or a catalyst to break the relevant intramolecular bonds. A peroxide catalyst is used in the formation of polyethylene, and the reactants are subjected to pressures of 100-300MPa. When the intramolecular bond is broken, a reactive free radical is formed.
2. **PROPAGATION** ($R — O\cdot + C_2H_4 \rightarrow R—O—CH_2CH_2\cdot$) Free Radical + Monomer → Activated Monomer Radical
   - Free radicals react with other monomers, forming activated monomer radicals. These polymer chains will continue to how for an indefinite period of time, or until conditions are changed.
3. **TERMINATION** — inhibitor is added to stop reaction. Radical sites are either joined or completed with another radical site.
   - There are many possible forms of termination, which usually involve radicals reacting with each other.
   - Inhibitor is added to stop the reaction. Radical sites are either joined or completed with another radical site.

	HIGH PRESSURE METHOD	**ZEIGLER-NATTA PROCESS**
PRODUCT	LDPE	HDPE
REACTION CONDITION	High pressure (1000-3000 atm), high temperature (200-300°C). **No catalyst** — uses an *initiator* which breaks the 1st bond and causes a chain reaction.	Low pressure (20 atm), low temperature (60°C), organic peroxide, Zeigler-Natta catalyst (aluminium metal oxide surface)
STRUCTURE	BRANCHED CHAINS - Amorphous structure - Chains cannot pack closely together - Significant side branching (many short chains) ❖ Each chain has less contact with adjacent chain therefore fewer dispersion forces (low density)	LINEAR CHAINS - Crystalline, ordered structure - Packed closely together hence increased extent of dispersion forces. - No side branching, limited chain stiffening and cross linking ❖ Chains closely packed with many dispersion forces holding long polymer chains together tightly.
PROPERTIES	• **Low density** — side branching (fewer atoms per volume) • **Lower BP** — fewer dispersion forces needed to be broken • **Low tensile strength** — due to less dispersion forces • Soft, flexible, insoluble, good chemical resistance (non-toxic), insoluble, inert, low weight.	• **High density** — chains closely packed therefore more atoms per volume • **Higher BP** — more dispersion forces needed to be broken in their ordered crystalline structure • **High tensile strength** — due to large number of dispersion forces between them • Hard, rigid, good chemical resistance (non-toxic), inert, insoluble.
USES	Plastic bags, cling wraps, electrical insulations, squeeze bottles, flexible toys, milk containers. • **Low density** → light to carry • **Relatively high tensile strength** → does not tear easily	Wheely bins, petrol banks, chemical containers, buckets, agricultural pipes, kitchen utensils, pipes. • **High density** → less chance of breakage and more robust. • **High tensile strength** → can carry / hold heavy loads without breaking • **High MP** → can hold hot water without melting
FLOWCHART		



ETHANOL AS A FUEL (fermented from cellulose)

- Ethanol is a liquid which readily burns in air (exothermic). It also burns more completely in air than petrol. (Requires less O_2 for complete combustion). These equations demonstrate that ethanol needs less O_2 (per mole) for complete combustion than octane fuel:

$$C_2H_5OH\ (l) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l) + 1367kJ$$
$$2C_8H_{18}\ (l) + 25O_2\ (g) \rightarrow 18H_2O\ (g) + 16CO_2\ (g)$$

- It is a biomass fuel. Meaning, when it is combusted, the CO_2 produced returns back to the photosynthetic cycle; therefore it is a **renewable source**. Zero net CO_2 production (carbon-neutral):

$$6CO_2\ (g) + 6H_2O\ (l) \rightarrow C_6H_{12}O_6\ (aq) + 6O_2\ (g)$$
$$C_6H_{12}O_6\ (aq) \rightarrow 2C_2H_5OH\ (aq) + 2CO_2\ (g)$$
$$C_2H_5OH\ (l) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l)$$

Ethanol As An Alternative Car Fuel

ADVANTAGES	DISADVANTAGES
- Reduces our dependence on non-renewable resources. - Can be used as an alternative fuel for petrol. It is also used as 'petrol extenders' where it is added in small quantities of petrol. This does not contribute to greenhouse effect. - Petrol containing 10-20% of ethanol can be used in ordinary petrol engines without any modifications by growing sugar canes. - Ethanol is widely used as a fuel in **Brazil** — 40% of Brazil's transport fuel is ethanol. First used in 70s / 80s to conserve crude oil consumption. Runs 50% of its cars on 100% ethanol. • Brazil is less affected by the current depleting sources than other countries. • Air quality in big cities improved significantly in the 80s. • However, production of ethanol has to be subsidised to make it economically viable for consumption. Also, the need of land for crops resulted in deforestation of a significant portion of the Amazon. - In **Australia**, ethanol is generally considered as an uneconomic proposition — the ethanol industry is not yet profitable as the infrastructure (compatible engines) is limited.	- Greater engine wear - Higher 'flash point; - Requires vast arable lands to grow sufficient crops to make enough ethanol to satisfy demands. - Subsidies and tax concessions also bore an increasing acceptance of ethanol / petrol blends (e.g. E10) that have no detrimental effect of vehicles. **Fertiliser run-off.** - Lower molar heat of combustion than petrochemicals → less distance for motor vehicles. More fuel would have to be used to produce the same amount of energy as octane. Car with octane will be able to go a greater distance than a car with the same mass of ethanol. - More than than 20% → engine modifications. Not presently viable. - Not viable → produces less energy per mole than octane, large amounts of energy is needed to produce ethanol (from fossil fuels) energy used > energy obtained

The potential of ethanol as an alternative fuel has several significant issues; the economic cost of modifying engine is perhaps the greatest barrier. Moreover, the cost of developing infrastructure to support the new engines is another significant hurdle. Finally, unless a commercially-viable method of converting cellulose into ethanol is found, ethanol is unlikely to be used as an alternative fuel yet. Rather, it can be realistically be used as an extension to petrol.

NAMING ALKANOLS

- Are homologous series of compounds that are a subgroup of alcohols. They are characterised by a polar hydroxyl (—OH) functional group attached to a saturated carbon atom.
- General formula: $C_nH_{2n+1}OH$

IUPAC Rules for Naming Alkanols:

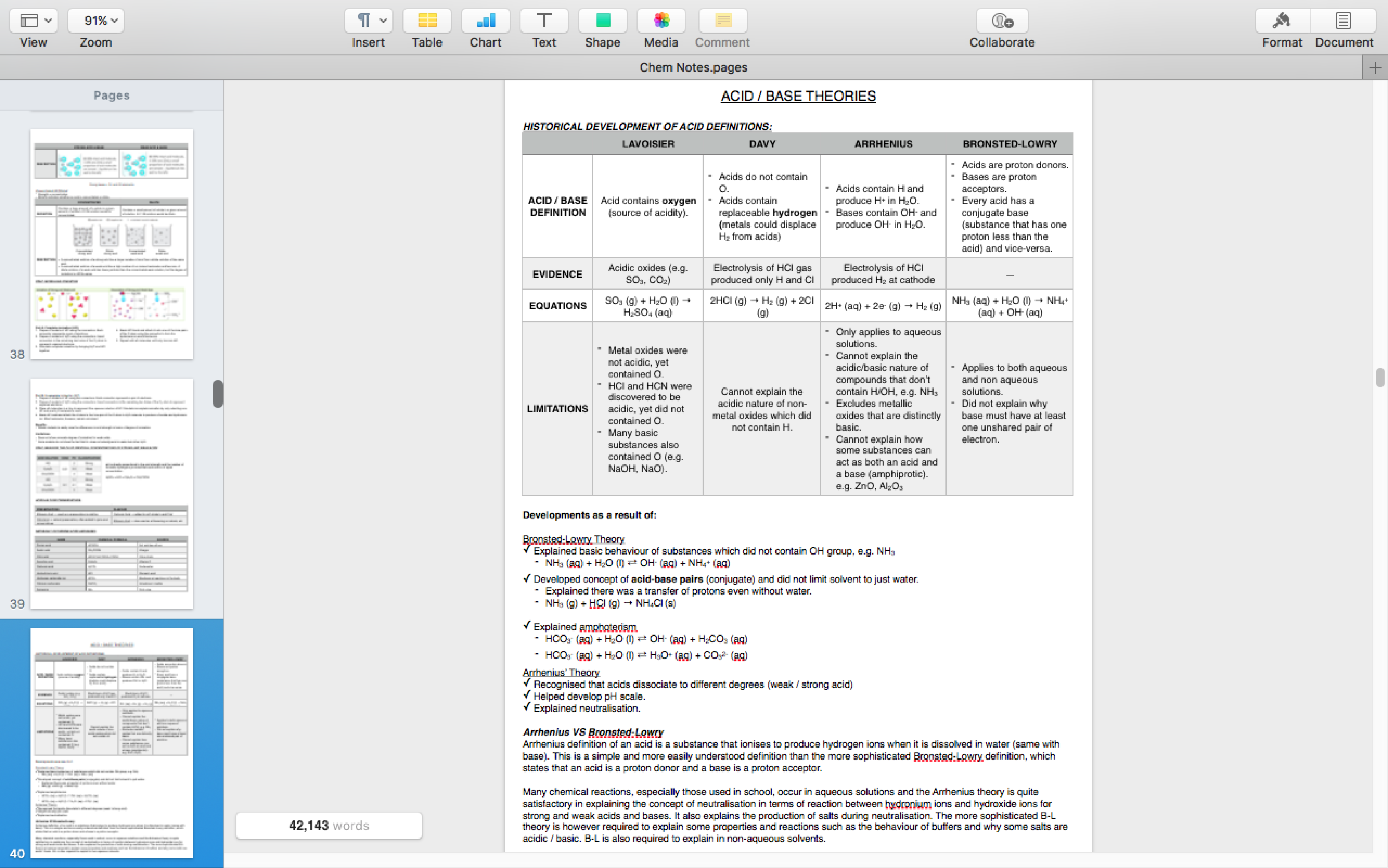
1. Identify the number of carbons present and determine name of the parent alkane.
2. Remove the '-e' and replace it with '-ol'
3. Identify the position of the carbon atom bearing —OH group and give its location. Only apply this to chains with 3 or more carbon atoms. (link with a hyphen —)
4. Identify the number of —OH group present in the chain and determine the corresponding suffix. In this case the 'e' is NOT dropped from the hydrocarbon name.

# of C's	1	2	3	4	5	6	7	8
Prefix	meth-	eth-	prop-	but-	pent-	hex-	hept-	oct-

# of OH's	1	2	3	4
Suffix	-ol	-diol	-triol	-tetraol

ETHANOL AS A RENEWABLE SOURCE

- Ethanol can be created from plant material through fermentation.
- Ethanol can combust in air in the presence of O_2 to produce CO_2 and H_2O.



ACID / BASE THEORIES

HISTORICAL DEVELOPMENT OF ACID DEFINITIONS:

	LAVOISIER	DAVY	ARRHENIUS	BRONSTED-LOWRY
ACID / BASE DEFINITION	Acid contains **oxygen** (source of acidity).	- Acids do not contain O. - Acids contain replaceable **hydrogen** (metals could displace H_2 from acids)	- Acids contain H and produce H^+ in H_2O. - Bases contain OH^- and produce OH^- in H_2O.	- Acids are proton donors. - Bases are proton acceptors. - Every acid has a conjugate base (substance that has one proton less than the acid) and vice-versa.
EVIDENCE	Acidic oxides (e.g. SO_3, CO_2)	Electrolysis of HCl gas produced only H and Cl	Electrolysis of HCl produced H_2 at cathode	–
EQUATIONS	$SO_3\ (g) + H_2O\ (l) \rightarrow H_2SO_4\ (aq)$	$2HCl\ (g) \rightarrow H_2\ (g) + 2Cl\ (g)$	$2H^+\ (aq) + 2e^-\ (g) \rightarrow H_2\ (g)$	$NH_3\ (aq) + H_2O\ (l) \rightarrow NH_4^+\ (aq) + OH^-\ (aq)$
LIMITATIONS	- Metal oxides were not acidic, yet contained O. - HCl and HCN were discovered to be acidic, yet did not contained O. - Many basic substances also contained O (e.g. NaOH, NaO).	Cannot explain the acidic nature of non-metal oxides which did not contain H.	- Only applies to aqueous solutions. - Cannot explain the acidic/basic nature of compounds that don't contain H/OH, e.g. NH_3 - Excludes metallic oxides that are distinctly basic. - Cannot explain how some substances can act as both an acid and a base (amphiprotic). e.g. ZnO, Al_2O_3	- Applies to both aqueous and non aqueous solutions. - Did not explain why base must have at least one unshared pair of electron.

Developments as a result of:

Bronsted-Lowry Theory

✓ Explained basic behaviour of substances which did not contain OH group, e.g. NH_3
  - $NH_3\ (aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + NH_4^+\ (aq)$

✓ Developed concept of **acid-base pairs** (conjugate) and did not limit solvent to just water.
  - Explained there was a transfer of protons even without water.
  - $NH_3\ (g) + HCl\ (g) \rightarrow NH_4Cl\ (s)$

✓ Explained amphoterism.
  - $HCO_3^-\ (aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + H_2CO_3\ (aq)$
  - $HCO_3^-\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CO_3^{2-}\ (aq)$

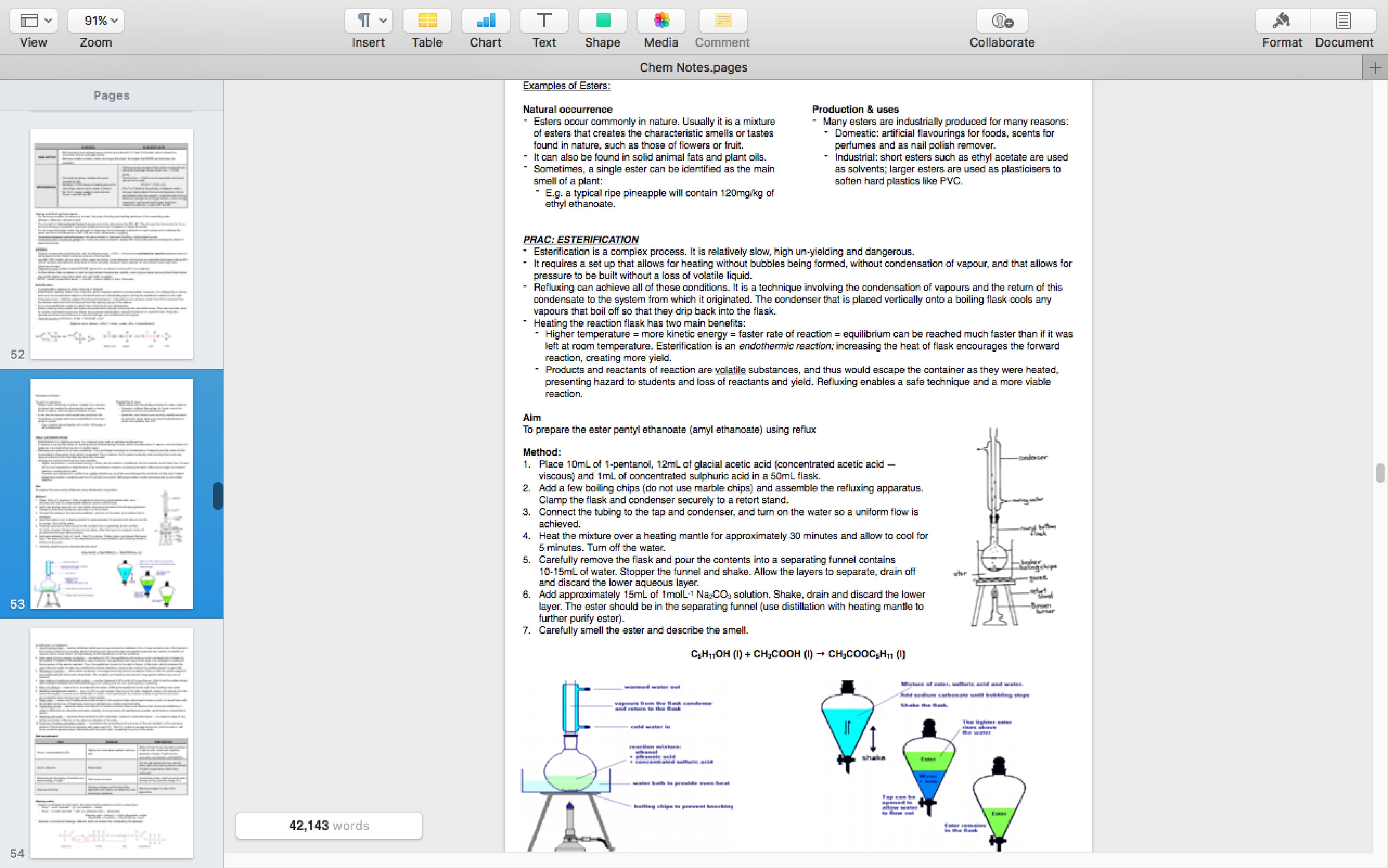
Arrhenius' Theory

✓ Recognised that acids dissociate to different degrees (weak / strong acid)
✓ Helped develop pH scale.
✓ Explained neutralisation.

Arrhenius VS Bronsted-Lowry

Arrhenius definition of an acid is a substance that ionises to produce hydrogen ions when it is dissolved in water (same with base). This is a simple and more easily understood definition than the more sophisticated Bronsted-Lowry definition, which states that an acid is a proton donor and a base is a proton acceptor.

Many chemical reactions, especially those used in school, occur in aqueous solutions and the Arrhenius theory is quite satisfactory in explaining the concept of neutralisation in terms of reaction between hydronium ions and hydroxide ions for strong and weak acids and bases. It also explains the production of salts during neutralisation. The more sophisticated B-L theory is however required to explain some properties and reactions such as the behaviour of buffers and why some salts are acidic / basic. B-L is also required to explain in non-aqueous solvents.



Examples 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.
- It can also be found in solid animal fats and plant oils.
- Sometimes, a single ester can be identified as the main smell of a plant:
  - E.g. a typical ripe pineapple will contain 120mg/kg of ethyl ethanoate.

Production & uses

- Many esters are industrially produced for many reasons:
  - Domestic: artificial flavourings for foods, scents for perfumes and as nail polish remover.
  - Industrial: short esters such as ethyl acetate are used as solvents; larger esters are used as plasticisers to soften hard plastics like PVC.

PRAC: ESTERIFICATION

- Esterification is a complex process. It is relatively slow, high un-yielding and dangerous.
- It requires a set up that allows for heating without bubbles being formed, without condensation of vapour, and that allows for pressure to be built without a loss of volatile liquid.
- Refluxing can achieve all of these conditions. It is a technique involving the condensation of vapours and the return of this condensate to the system from which it originated. The condenser that is placed vertically onto a boiling flask cools any vapours that boil off so that they drip back into the flask.
- Heating the reaction flask has two main benefits:
  - Higher temperature = more kinetic energy = faster rate of reaction = equilibrium can be reached much faster than if it was left at room temperature. Esterification is an *endothermic reaction;* increasing the heat of flask encourages the forward reaction, creating more yield.
  - Products and reactants of reaction are volatile substances, and thus would escape the container as they were heated, presenting hazard to students and loss of reactants and yield. Refluxing enables a safe technique and a more viable reaction.

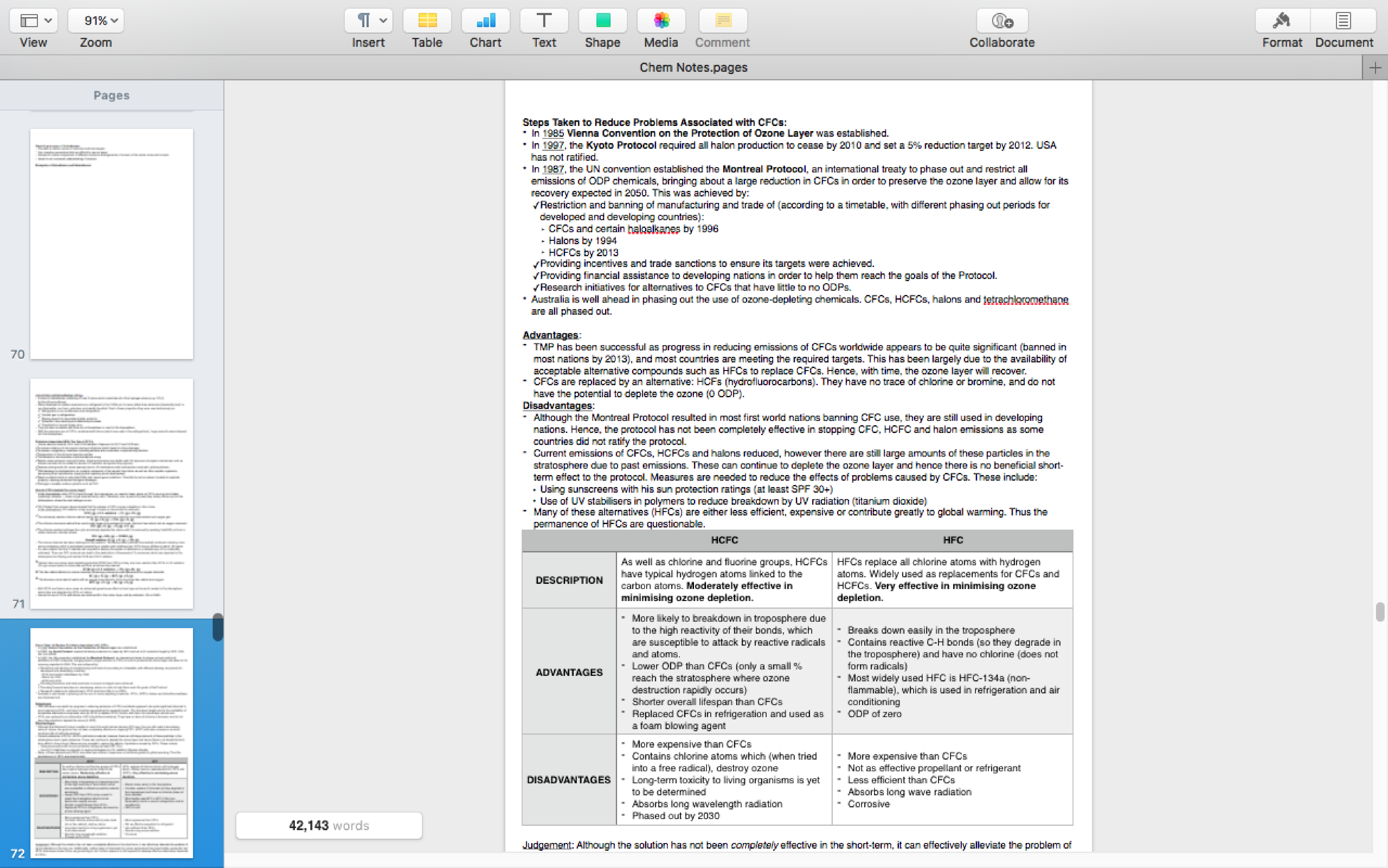
Aim

To prepare the ester pentyl ethanoate (amyl ethanoate) using reflux

Method:

1. Place 10mL of 1-pentanol, 12mL of glacial acetic acid (concentrated acetic acid — viscous) and 1mL of concentrated sulphuric acid in a 50mL flask.
2. Add a few boiling chips (do not use marble chips) and assemble the refluxing apparatus. Clamp the flask and condenser securely to a retort stand.
3. Connect the tubing to the tap and condenser, and turn on the water so a uniform flow is achieved.
4. Heat the mixture over a heating mantle for approximately 30 minutes and allow to cool for 5 minutes. Turn off the water.
5. Carefully remove the flask and pour the contents into a separating funnel contains 10-15mL of water. Stopper the funnel and shake. Allow the layers to separate, drain off and discard the lower aqueous layer.
6. Add approximately 15mL of 1molL^{-1} Na_2CO_3 solution. Shake, drain and discard the lower layer. The ester should be in the separating funnel (use distillation with heating mantle to further purify ester).
7. Carefully smell the ester and describe the smell.

$$C_5H_{11}OH\ (l) + CH_3COOH\ (l) \rightarrow CH_3COOC_5H_{11}\ (l)$$



Steps Taken to Reduce Problems Associated with CFCs:

- In 1985 **Vienna Convention on the Protection of Ozone Layer** was established.
- In 1997, the **Kyoto Protocol** required all halon production to cease by 2010 and set a 5% reduction target by 2012. USA has not ratified.
- In 1987, the UN convention established the **Montreal Protocol**, an international treaty to phase out and restrict all emissions of ODP chemicals, bringing about a large reduction in CFCs in order to preserve the ozone layer and allow for its recovery expected in 2050. This was achieved by:
  - ✓Restriction and banning of manufacturing and trade of (according to a timetable, with different phasing out periods for developed and developing countries):
    - CFCs and certain haloalkanes by 1996
    - Halons by 1994
    - HCFCs by 2013
  - ✓Providing incentives and trade sanctions to ensure its targets were achieved.
  - ✓Providing financial assistance to developing nations in order to help them reach the goals of the Protocol.
  - ✓Research initiatives for alternatives to CFCs that have little to no ODPs.
- Australia is well ahead in phasing out the use of ozone-depleting chemicals. CFCs, HCFCs, halons and tetrachloromethane are all phased out.

Advantages:

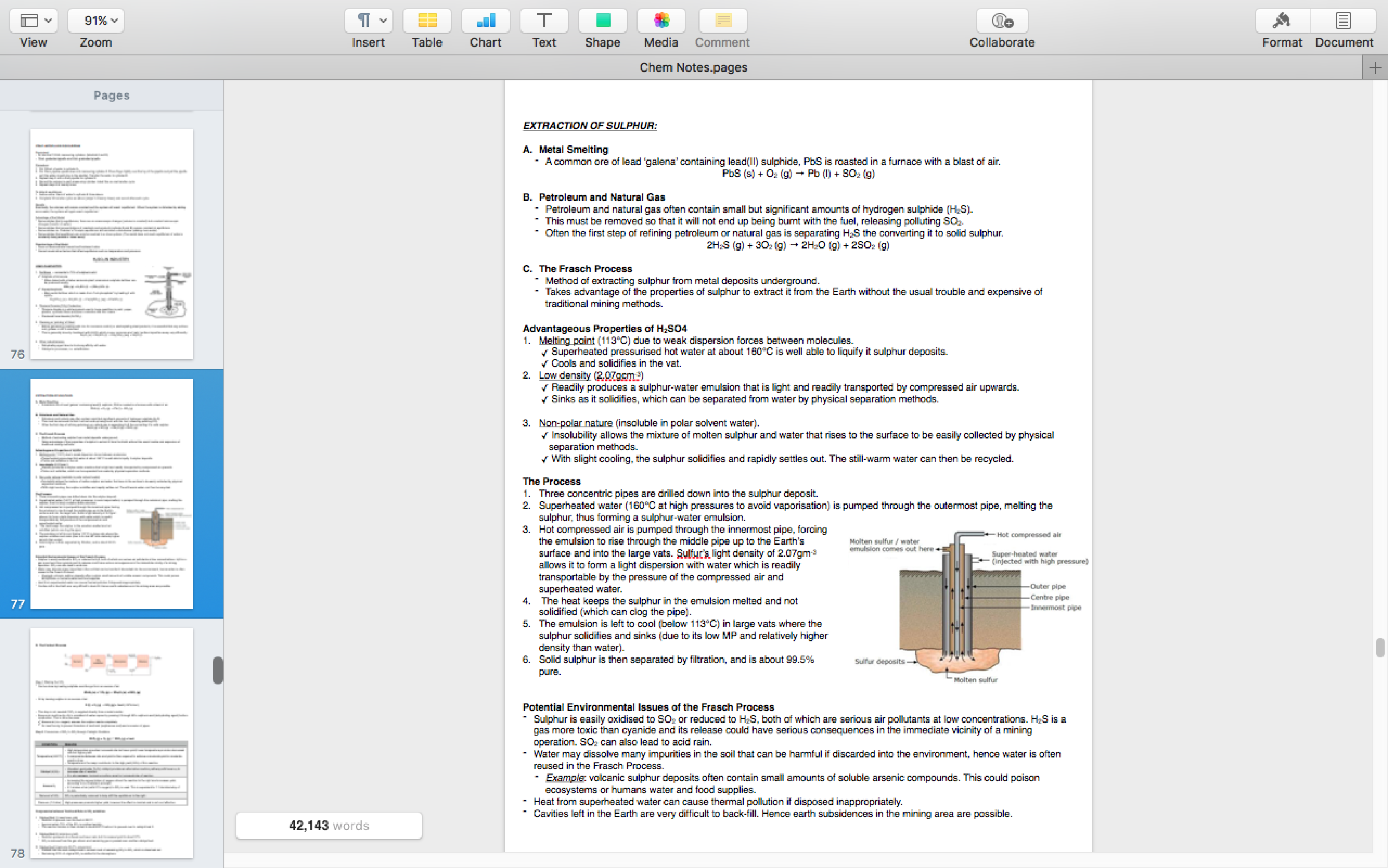
- TMP has been successful as progress in reducing emissions of CFCs worldwide appears to be quite significant (banned in most nations by 2013), and most countries are meeting the required targets. This has been largely due to the availability of acceptable alternative compounds such as HFCs to replace CFCs. Hence, with time, the ozone layer will recover.
- CFCs are replaced by an alternative: HCFs (hydrofluorocarbons). They have no trace of chlorine or bromine, and do not have the potential to deplete the ozone (0 ODP).

Disadvantages:

- Although the Montreal Protocol resulted in most first world nations banning CFC use, they are still used in developing nations. Hence, the protocol has not been completely effective in stopping CFC, HCFC and halon emissions as some countries did not ratify the protocol.
- Current emissions of CFCs, HCFCs and halons reduced, however there are still large amounts of these particles in the stratosphere due to past emissions. These can continue to deplete the ozone layer and hence there is no beneficial short-term effect to the protocol. Measures are needed to reduce the effects of problems caused by CFCs. These include:
  - Using sunscreens with his sun protection ratings (at least SPF 30+)
  - Use of UV stabilisers in polymers to reduce breakdown by UV radiation (titanium dioxide)
- Many of these alternatives (HFCs) are either less efficient, expensive or contribute greatly to global warming. Thus the permanence of HFCs are questionable.

	HCFC	**HFC**
DESCRIPTION	As well as chlorine and fluorine groups, HCFCs have typical hydrogen atoms linked to the carbon atoms. **Moderately effective in minimising ozone depletion.**	HFCs replace all chlorine atoms with hydrogen atoms. Widely used as replacements for CFCs and HCFCs. **Very effective in minimising ozone depletion.**
ADVANTAGES	- More likely to breakdown in troposphere due to the high reactivity of their bonds, which are susceptible to attack by reactive radicals and atoms. - Lower ODP than CFCs (only a small % reach the stratosphere where ozone destruction rapidly occurs) - Shorter overall lifespan than CFCs - Replaced CFCs in refrigeration and used as a foam blowing agent	- Breaks down easily in the troposphere - Contains reactive C-H bonds (so they degrade in the troposphere) and have no chlorine (does not form radicals) - Most widely used HFC is HFC-134a (non-flammable), which is used in refrigeration and air conditioning - ODP of zero
DISADVANTAGES	- More expensive than CFCs - Contains chlorine atoms which (when tried into a free radical), destroy ozone - Long-term toxicity to living organisms is yet to be determined - Absorbs long wavelength radiation - Phased out by 2030	- More expensive than CFCs - Not as effective propellant or refrigerant - Less efficient than CFCs - Absorbs long wave radiation - Corrosive

Judgement: Although the solution has not been *completely* effective in the short-term, it can effectively alleviate the problem of



__EXTRACTION OF SULPHUR:__

A. Metal Smelting

- A common ore of lead 'galena' containing lead(II) sulphide, PbS is roasted in a furnace with a blast of air.

$$PbS\ (s) + O_2\ (g) \rightarrow Pb\ (l) + SO_2\ (g)$$

B. Petroleum and Natural Gas

- Petroleum and natural gas often contain small but significant amounts of hydrogen sulphide (H_2S).
- This must be removed so that it will not end up being burnt with the fuel, releasing polluting SO_2.
- Often the first step of refining petroleum or natural gas is separating H_2S the converting it to solid sulphur.

$$2H_2S\ (g) + 3O_2\ (g) \rightarrow 2H_2O\ (g) + 2SO_2\ (g)$$

C. The Frasch Process

- Method of extracting sulphur from metal deposits underground.
- Takes advantage of the properties of sulphur to extract it from the Earth without the usual trouble and expensive of traditional mining methods.

Advantageous Properties of H_2SO4

1. Melting point (113°C) due to weak dispersion forces between molecules.
   - ✓ Superheated pressurised hot water at about 160°C is well able to liquify it sulphur deposits.
   - ✓ Cools and solidifies in the vat.
2. Low density (2.07gcm^{-3})
   - ✓ Readily produces a sulphur-water emulsion that is light and readily transported by compressed air upwards.
   - ✓ Sinks as it solidifies, which can be separated from water by physical separation methods.

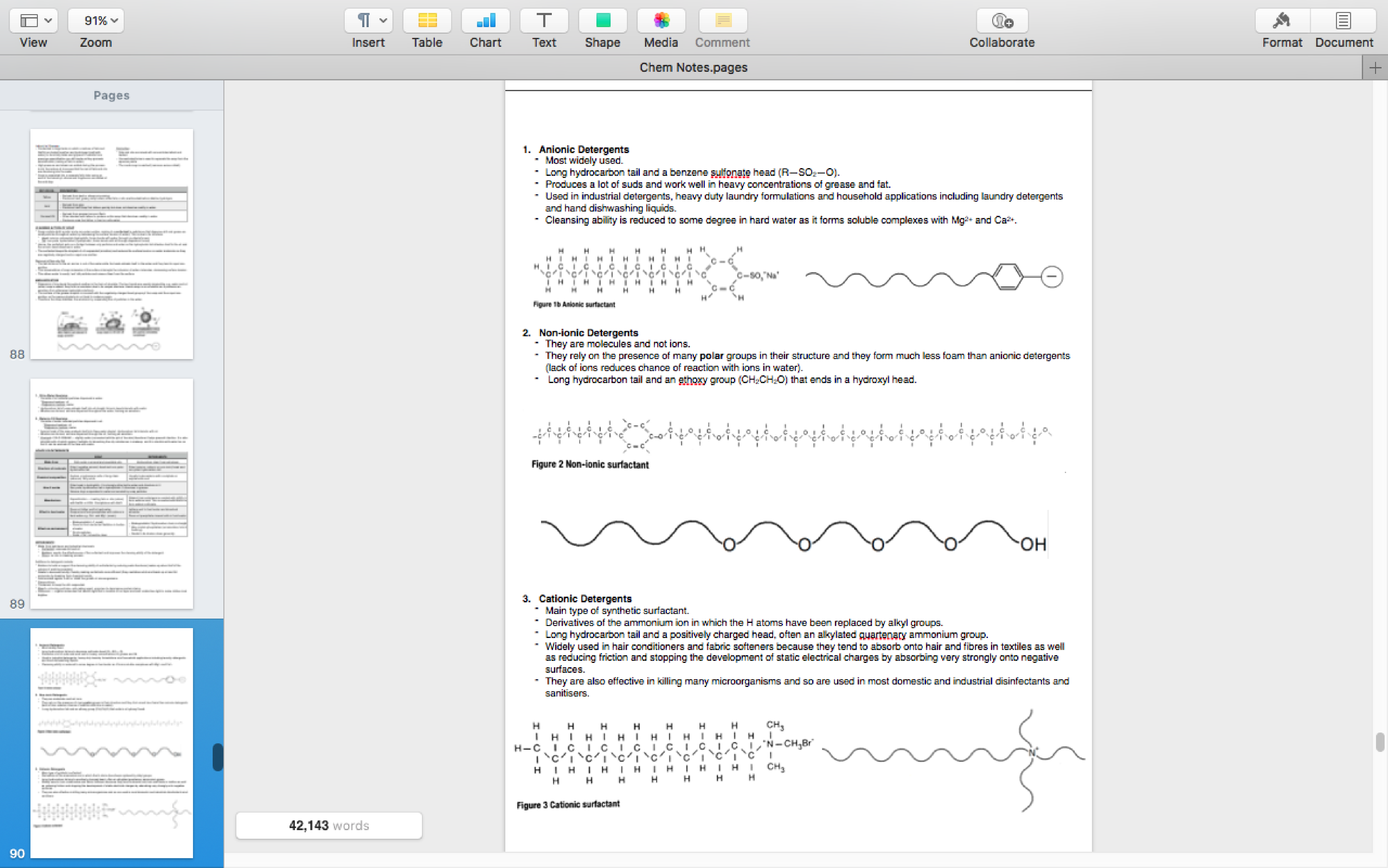
3. Non-polar nature (insoluble in polar solvent water).
   - ✓ Insolubility allows the mixture of molten sulphur and water that rises to the surface to be easily collected by physical separation methods.
   - ✓ With slight cooling, the sulphur solidifies and rapidly settles out. The still-warm water can then be recycled.

The Process

1. Three concentric pipes are drilled down into the sulphur deposit.
2. Superheated water (160°C at high pressures to avoid vaporisation) is pumped through the outermost pipe, melting the sulphur, thus forming a sulphur-water emulsion.
3. Hot compressed air is pumped through the innermost pipe, forcing the emulsion to rise through the middle pipe up to the Earth's surface and into the large vats. Sulfur's light density of 2.07gm^{-3} allows it to form a light dispersion with water which is readily transportable by the pressure of the compressed air and superheated water.
4. The heat keeps the sulphur in the emulsion melted and not solidified (which can clog the pipe).
5. The emulsion is left to cool (below 113°C) in large vats where the sulphur solidifies and sinks (due to its low MP and relatively higher density than water).
6. Solid sulphur is then separated by filtration, and is about 99.5% pure.

Potential Environmental Issues of the Frasch Process

- Sulphur is easily oxidised to SO_2 or reduced to H_2S, both of which are serious air pollutants at low concentrations. H_2S is a gas more toxic than cyanide and its release could have serious consequences in the immediate vicinity of a mining operation. SO_2 can also lead to acid rain.
- Water may dissolve many impurities in the soil that can be harmful if discarded into the environment, hence water is often reused in the Frasch Process.
  - *__Example__*: volcanic sulphur deposits often contain small amounts of soluble arsenic compounds. This could poison ecosystems or humans water and food supplies.
- Heat from superheated water can cause thermal pollution if disposed inappropriately.
- Cavities left in the Earth are very difficult to back-fill. Hence earth subsidences in the mining area are possible.



1. **Anionic Detergents**
   - Most widely used.
   - Long hydrocarbon tail and a benzene sulfonate head ($R—SO_2—O$).
   - Produces a lot of suds and work well in heavy concentrations of grease and fat.
   - Used in industrial detergents, heavy duty laundry formulations and household applications including laundry detergents and hand dishwashing liquids.
   - Cleansing ability is reduced to some degree in hard water as it forms soluble complexes with Mg^{2+} and Ca^{2+}.

Figure 1b Anionic surfactant

2. **Non-ionic Detergents**
   - They are molecules and not ions.
   - They rely on the presence of many **polar** groups in their structure and they form much less foam than anionic detergents (lack of ions reduces chance of reaction with ions in water).
   - Long hydrocarbon tail and an ethoxy group (CH_2CH_2O) that ends in a hydroxyl head.

Figure 2 Non-ionic surfactant

3. **Cationic Detergents**
   - Main type of synthetic surfactant.
   - Derivatives of the ammonium ion in which the H atoms have been replaced by alkyl groups.
   - Long hydrocarbon tail and a positively charged head, often an alkylated quartenary ammonium group.
   - Widely used in hair conditioners and fabric softeners because they tend to absorb onto hair and fibres in textiles as well as reducing friction and stopping the development of static electrical charges by absorbing very strongly onto negative surfaces.
   - They are also effective in killing many microorganisms and so are used in most domestic and industrial disinfectants and sanitisers.

Figure 3 Cationic surfactant