4.2.1 Alcohols

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The smaller alcohols (up to 3 carbons) are soluble in water because they can form hydrogen bonds with water. The longer the hydrocarbon chain the less soluble the alcohol.

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Uses of alcohols
Ethanol is ‘alcohol’ in alcoholic drinks. Ethanol is commonly used as a solvent in the form of methylated spirits. Methanol is used as a petrol additive to improve combustion and is increasing important as a feedstock in the production of organic chemicals;

Classifying Alcohols

Primary alcohols are alcohols where 1 carbon is attached to the carbon adjoining the oxygen

Secondary alcohols are alcohols where 2 carbon are attached to the carbon adjoining the oxygen

Tertiary alcohols are alcohols where 3 carbon are attached to the carbon adjoining the oxygen

Reactions of alcohols

Complete Combustion
In excess oxygen alcohols will burn with complete combustion

The products of complete combustion are CO\textsubscript{2} and H\textsubscript{2}O.

\[
\text{CH}_3\text{CH}_2\text{OH} \text{ (l)} + 3 \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 3 \text{H}_2\text{O(l)}
\]
Oxidation reactions of the alcohols

Potassium dichromate $K_2Cr_2O_7$ is an oxidising agent that causes alcohols to oxidise.

The exact reaction, however, depends on the type of alcohol, i.e. whether it is primary, secondary, or tertiary, and on the conditions.

Partial Oxidation of Primary Alcohols

**Reaction:** primary alcohol $\rightarrow$ aldehyde

**Reagent:** potassium dichromate (VI) solution and dilute sulphuric acid.

**Conditions:** (use a limited amount of dichromate) warm gently and distil out the aldehyde as it forms:

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It always has the C=O bond on the first carbon of the chain so it does not need an extra number.

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**Observation:** the orange dichromate ion ($Cr_2O_7^{2-}$) reduces to the green $Cr^{3+}$ ion.

Distillation

In general used as separation technique to separate an organic product from its reacting mixture. Need to collect the distillate of the approximate boiling point range of the desired liquid.

Note the bulb of the thermometer should be at the T junction connecting to the condenser to measure the correct boiling point.

Note the water goes in the bottom of the condenser to go against gravity. This allows more efficient cooling and prevents back flow of water.

Electric heaters are often used to heat organic chemicals. This is because organic chemicals are normally highly flammable and could set on fire with a naked flame.

When writing the formulae of aldehydes in a condensed way write $CHO$ and not $COH$ e.g. $CH_3CH_2CHO$.

Write the oxidation equations in a simplified form using [O] which represents O from the oxidising agent.

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Full Oxidation of Primary Alcohols

**Reaction:** primary alcohol → carboxylic acid  
**Reagent:** potassium dichromate(VI) solution and dilute sulphuric acid  
**Conditions:** use an excess of dichromate, and **heat under reflux:** (distill off product after the reaction has finished)

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 2\left[\text{O}\right] \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{H}_2\text{O}
\]

**Observation:** the orange dichromate ion \(\text{Cr}_2\text{O}_7^{2-}\) reduces to the green \(\text{Cr}^{3+}\) ion

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**Reflux**

Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

**Never seal the end of the condenser** as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated including the distillation set up.

Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling by **making small bubbles** form instead of large bubbles.

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Propanoic acid
Oxidation of Secondary Alcohols

**Reaction**: secondary alcohol → ketone

**Reagent**: potassium dichromate(VI) solution and dilute sulphuric acid.

**Conditions**: heat under reflux

Ketones end in -one

When ketones have 5C’s or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one

There is no further oxidation of the ketone under these conditions.

**Tertiary alcohols** cannot be oxidised at all by potassium dichromate: This is because there is no hydrogen atom bonded to the carbon with the OH group

**Observation**: the orange dichromate ion (Cr$_2$O$_7^{2-}$) reduces to the green Cr$^{3+}$ ion

**Reaction of alcohols with Dehydrating agents**

**Reaction**: Alcohol → Alkene

**Reagents**: Concentrated Sulphuric or Phosphoric acids

**Conditions**: warm (under reflux)

**Role of reagent**: dehydrating agent/catalyst

**Type of reaction**: acid catalysed elimination

Some 2$^o$ and 3$^o$ alcohols can give more than one product, when the double bond forms between different carbon atoms

Butan-2-ol can form both alkenes although more but-2-ene would be formed

But-2-ene could also exist as E and Z isomers

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Substitution reactions of Alcohols to form Haloalkanes

A mixture of a halide ions with concentrated acid NaCl + H₂SO₄ can be used for substituting a halogen on to an alcohol

Various other halogenating compounds can be used to substitute the –OH group for a halogen

**Reaction:** Alcohol → Haloalkane

**Reagents:** Concentrated Sulphuric and sodium halide

\[ \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl} \]

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{H}_2\text{O} \]