HEATING UNDER REFLUX (SYNTHESIS OF AN ORGANIC PRODUCT):

If a reaction that involves heating requires an organic volatile liquid, heating under reflux is used. The method boils a liquid and has a vertically mounted condenser with a pear-shaped flask so any volatile/evaporating liquids will condense and return to the reaction mixture. This prevents escape of substances and promotes further reaction if possible.

1. Reactants are added to a pear-shaped flask with a few anti-bumping granules.
2. The flask is not stoppered as this would build up pressure and could cause the glassware to crack.
3. Attach the condenser vertically to the flask so that the water flows in through the condenser bottom and out the top. This ensures all internal surfaces of the condenser are cooled; all parts are filled with cold water.
4. Heat the reaction mixture gently with a Bunsen burner or a heating mantle. Indirect heating (heating a beaker of water below the pear-shaped flask) is a safe method.

If the organic product needs distilling to prevent further reaction then non-reflux heating is used. In his case, quick fit distillation apparatus may be used during synthesis. Non-reflux is shown on the right.
**Simple distillation (separating miscible liquids)**

A mixture of substances will separate off into fractions when heated as each substance will have a different boiling point. By heating the mixture, each pure component is vaporised, condensed and collected. A thermometer is used to keep track of the range at which a substance can be distilled off at.

The substance with the lowest boiling point will evaporate off first. Quick fit glassware is commonly used. Grease/Vaseline is used to seal joints to prevent loss of reagents.

1. Put the mixture into a pear-shaped flask and add a few anti-bumping granules. Set up the distillation apparatus as shown below.

2. Gently heat the mixture with a heating mantle or a Bunsen flame (maybe indirectly by heating a beaker of water below which the pear-shaped flask is submerged in).
   Heating mantles are safer than Bunsen burners for organic liquids; they do not have a naked flame.

3. When the thermometer reads 2°C below the boiling point of the liquid you are about to collect, put the beaker in place. Collecting the distilled liquid until the temperature rises above (+0.5°C) of the liquid you are collecting. Stop heating.

4. The process can be repeated for another compound of a higher boiling point following on from step 3. A clean beaker must be used.
Purifying an organic liquid (separating immiscible liquids):

Synthesised organic liquids are usually crude and contain a mixture of reactants, solvents or impurities of side reactions.

1. The organic product is mixed with another immiscible liquid (usually aqueous liquid i.e. water). This mixture is placed in a separating funnel. The liquids separate into two layers with the denser forming at the bottom. Run off and dispose of the aqueous layer. Run the organic product layer into a clean conical flask.

2. 
   a. If acidic purities are present then some sodium hydrogen carbonate solution is added to remove them. A stopper is added to the funnel and the mixture must be well shaken. Gas will be produced so pressure inside the separating funnel must periodically be released. Repeat this step until no effervescing is observed.

   b. If the crude product is alkaline and needs neutralising then add dilute acid until the mixture is neutral. Testing regularly with damp universal litmus paper.

3. Dry the crude product by adding anhydrous sodium sulfate (a common drying agent) and swirling the mixture. Other anhydrous (group 1 / 2) salts like calcium chloride (or magnesium sulfate) could be used instead.

4. The product is then separated by distillation.

   The aqueous layer in the separating funnel can be detected by simply adding more water. The larger layer will then clearly be the aqueous one. Most organic solvents float on top of an aqueous phase, though important exceptions are most halogenated solvents.
**Vacuum filtration:**

Vacuum filtration is used to separate a solid from a filtrate/solution rapidly.

1. Connect a conical flask to a pump via the side arm.
2. Dampen a piece of filter paper with distilled water and place in the Buchner funnel.
3. Switch the vacuum pump on and carefully pour in the mixture to be filtered. Cover the top of the Buchner funnel with the palm of your hand and press down gently.
4. The pump will create a partial vacuum so that the filtrate gets pulled through quicker.
5. Disconnect the flask from the vacuum pump before turning the pump off to prevent ‘suck back’.
6. If necessary, wash the filtered solid with distilled water to remove excess soluble impurities, then allow solid to dry.

![Diagram of vacuum filtration](image-url)
Recrystallisation:

Recrystallisation is used to purify solid crude organic compounds with small amounts of impurities (both soluble/insoluble). A suitable hot solvent (e.g. ethanol) is chosen based on the desired product.

1. Select a suitable solvent which the desired substance is very soluble at high temperatures and insoluble, or nearly so, at lower temperatures.
2. Dissolve the crude mixture in a minimum amount of the hot solvent (less solvent equates to higher yields).
3. Any insoluble impurities are then filtered off and the filtrate (solution) is retained. It is best to preheat the funnel and conical flask to prevent any solids crystallising out at this stage.
4. The filtrate/flask is then cooled (sometimes in an ice bath) until crystals begin to form. These are filtered off using suction filtration (to remove soluble impurities).
5. A very small amount of hot solvent may be dropped over the crystals while the filtrate is removed to removed excess impurities.
6. The crystals are left to dry (covered by an inverted funnel).

![Figure 10 Recrystallisation of an impure solid](image)

Melting point determination:

Measuring melting points is a good method to determine if a solid organic compound is pure. Impurities will lower a substance’s melting point.

If the compound melts at or just above (+/- 0.5°C) the published melting point of the compound, it is pure. If the compound melts over a range of temperatures (typically lower) than the published melting point of the substance, it contains impurities.

1. Seal the end of a glass melting point tube by heating it to melt in a Bunsen flame and stretching it apart in the centre.
2. Tap the open end into the solid so it is picked up and then tap it again inverted so a small amount falls into the bottom of the sealed end.
3. Fix the tube in the melting point apparatus with the thermometer in line with the sample (a rubber band may be used). Heat the surrounding liquid (oil) gently, stirring to ensure even heating throughout. Temperature should rise slowly.
4. Record the temperature which the solid begins and finished melting at to obtain melting range.

![Figure 12 Melting point apparatus](image)
Thin layer chromatography (TLC) / paper chromatography:

Two techniques that can be used to separate small quantities of organic compounds, purify organic substances or follow the progress of reaction over time.

Chromatography relies on the fact that different substances have different affinities (or solubilities) with a particular solvents are carried through the chromatography medium at different rates.

- **Paper chromatography**: Uses paper as the medium/stationary phase
- **TLC**: Uses a silica plate as the medium/stationary phase.

1. Place a pencil line across the chromatography paper 1cm from its base. Spot a sample of the test mixture on the pencil line, using a capillary tube or dropper pipette. Pencil will not mix with the solvent (ink will).
2. Repeat this along different points across this line with the reference samples.
3. Place the plate in a beaker of solvent so the solvent is just below the pencil line. Cover the beaker with a lid to create a saturated environment and allow the solvent to rise up through the chromatography plate.
4. Remove the plate when the solvent front is near the top. Mark the solvent front with another pencil line. Allow the plate to then dry in a fume cupboard.
5. Place the plate in a beaker with iodine granules and shake. This will ease identification of the spots for each sample. Ultraviolet light (from UV lamp) can also be used to identify spots.
6. Match the heights reached, or $R_f$ values, with known compounds using the same chromatography solvent mix.

Enthalpy change for combustion:

1. Place the fuel in a spirit burner and weight with the lid on (using a top pan balance)
2. Fill a calorimeter can with a known volume of water (measured with a measuring cylinder) and clamp it, using a clamp stand, clamp and boss, so it is directly above the spirit burner.
3. Surround the setup with a draught excluder to help reduce energy losses.
4. Place a thermometer into the water recording the initial temperature. Add a lid with a hole for the thermometer, this will reduce heat loss by evaporation.
5. Ignite the spirit burner and so heat the water for a given time period
6. Measure the final temperature of the water and put out the spirit burner by placing the lid back on. Reweigh the burner.
7. Mass of fuel burnt, $m = $ Final mass – Initial mass (of the burner). Weigh with lid on burner in both cases so the fuel does not evaporate.
8. Temperature change $\Delta T = $ Final temperature – Initial temperature (of the water) This is measured using a thermometer.
9. Energy (KJ) = ( mass of water X C (=4.18) *$\Delta T$ ) / 1000
10. Scale up for one mole of fuel burnt using the calculation: Energy / (Mass of fuel/Mr) = (-) $\Delta H$ (KJmol$^{-1}$)
Reasons why the experimental value may be lower than the published standard enthalpy change of combustion

1. Heat loss to the surroundings/air molecules.
2. Heat loss through evaporation of the water.
3. Evaporation of the fuel from the wick of the spirit burner.
4. Incomplete combustion.
5. Energy goes into heating the calorimeter not just the water.
6. Standard conditions may not have been used in the reaction.

How to improve the accuracy of the enthalpy change result:

Use a bomb calorimeter, this has a number of features that improve accuracy:

1. Fuel is ignited electronically (combustion of another material like a wooden splint will not interfere).
2. Fuel is combusted under plentiful supply of compressed oxygen to ensure complete combustion.
3. The reaction vessel is well insulated in a thermostatted tank.
4. A platinum resistance thermometer is used to increase the accuracy of the temperature measurements.

However, the combustion occurs at a constant volume in a closed container and with a constant pressure. The results must be modified accordingly as these are not standard conditions.

Hess’ Law states that the enthalpy change of any chemical reaction is independent of the intermediate stages so long as the initial and final conditions are the same for each route.

The enthalpy change for combustion is the enthalpy change that occurs when one mole of fuel is completely combusted in oxygen under standard conditions (with elements in standard states).

NOTE: This is not experimentally possible as the exothermic reaction means H2O formed will be a vapour (steam) and not in its standard state.