Lesson 9: Key Steps in Laboratory Synthesis 1

*Read through the lesson notes. You can write them out, print them or save them.

*Once you have tried to understand the lesson answer the questions that follow and self-evaluate your work by checking the answers.

Learning Intention

-Learn about the laboratory technique heating under reflux.

-Learn about methods of isolating products from a reaction mixture, these include; distillation, vacuum filtration and solvent extraction.

Background

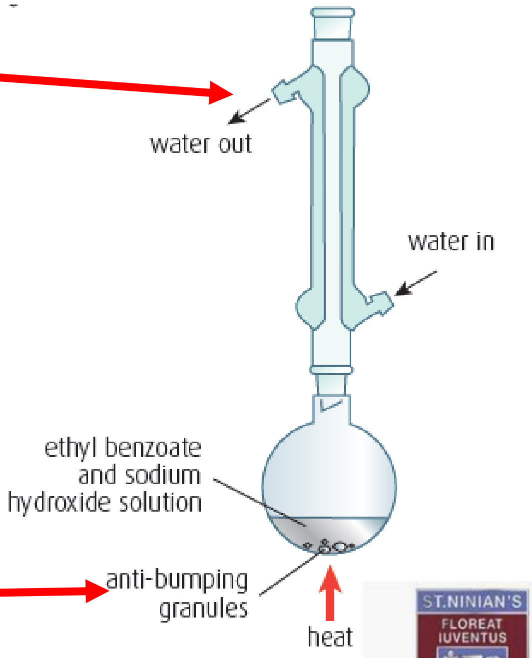
From the Organic Chemistry unit we learned about many reactions and the use of reagents that aid in the formation of new products. During the following three lessons, we consider the apparatus and techniques that are used in these reactions. Moreover, we also consider the methods to isolate organic products from reaction mixtures.

Heating Under Reflux

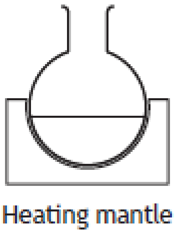
The synthesis of most compounds in the laboratory involves using the complex assembly of apparatus. However, one commonly used and straight-forward assembly is that of refluxing. This is the process of boiling a reaction mixture and condensing the vapours back into the reaction flask. It is also known as heating under reflux.

When reflux apparatus is set up, it is important to notice that the cold water is fed in via a lower inlet of the condenser and is allowed to circulate and leave via an upper outlet.

A few anti-bumping granules (also called boiling stones) are added to the reaction mixture. This prevents the reaction mixture from boiling in a violent manner.



The flask used for the reaction is normally a round-bottom flask and fits into a heating mantle which is an electrical piece of appartus used to heat the reaction mixture.

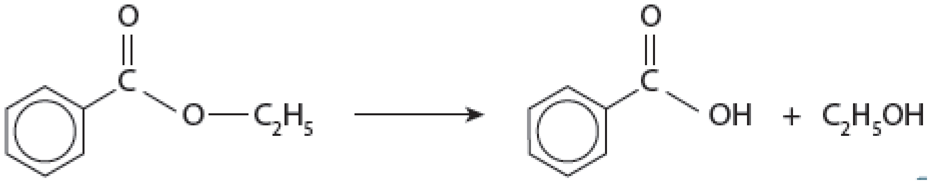


The heating mantle has settings which allows the reaction mixture to be heated to different degrees of intensity.

An advantage of heating under reflux is that reaction mixtures are heated over an extended period of time <u>without volatile substances escaping</u>. The purpose of the condenser is to prevent the escape of any volatile reactants or products from the apparatus. The water inlet and outlet connection is important because if it is set up incorrectly the condenser will only partially fill with cold water and will not effectively return any of the warm vapours to the reaction flask.

Example (hydrolysis of ethyl benzoate)

A common Advanced Higher Chemistry experiment is the alkaline hydrolysis of the ester ethyl benzoate to produce benzoic acid.



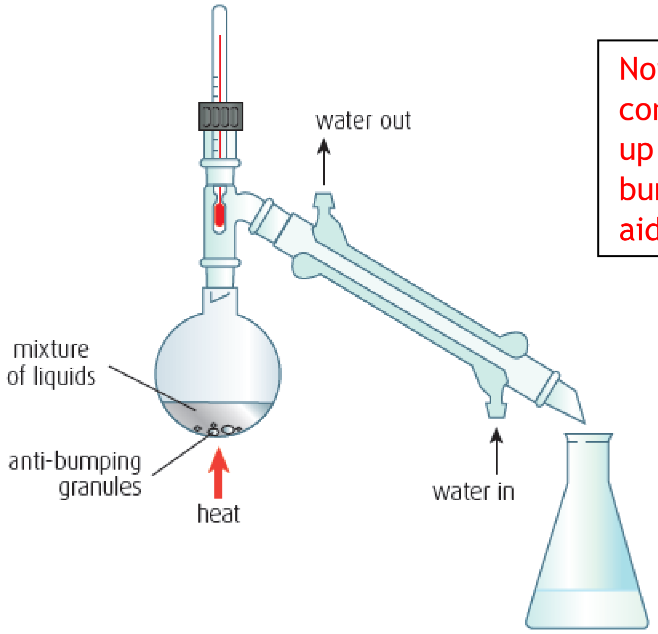
The heating process for this reaction is typically between 1-2 hours. It is important that it is carried out under reflux as this prevents the loss of any volatile substances.

Isolation

Once a reaction has been completed, the desired product is often part of a mixture. Therefore, it is important to isolate the product and separate it. This can be achieved by a number of means.

(i) Distillation

We know about distillation from fractional distillation of crude oil as taught in National 5 Chemistry. Distillation depends on the fact that different substances have different boiling points.
Distillation can be used to purify a compound by separating it from less volatile substances in a reaction mixture.
It can also be used to identify a certain substance as the boiling point can be checked against a list of substances and their known boiling points.

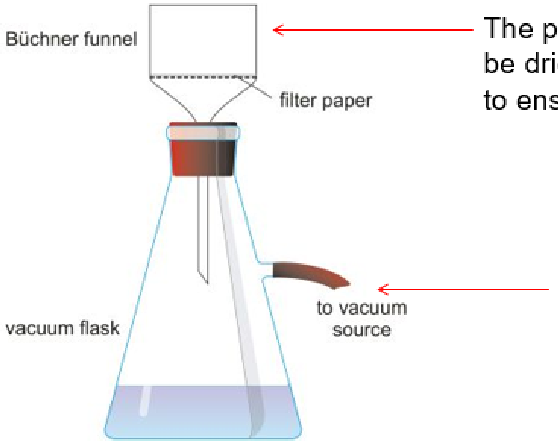


Note that for distillation, a condenser is also used but it is set up in a horizontal manner. Anti-bumping granules are also used to aid in the heating process.

A small conical flask is normally placed at the end of the condenser to collect the isolated product that drips out in the form of cooled liquid, i.e. it has condensed.

(ii) Vacuum Filtration

On many occasions, the desired product will be a solid suspended in a solution. In this instance it can be separated by vacuum filtration.
Vacuum filtration involves carrying out filtration under pressure, normally applied by connecting the equipment to a water pump. The method provides a fast system for separating out the desired solid product.
There are diiferent types of funnels that can be used (Büchner, Hirsch or sintered glass). In each case, filter paper is gently moistened with water and placed inside the funnel to collect the desired solid product.



The product is collected here. It can then be dried in an oven and later analysed to ensure it is pure.

The flask is connected to a vacuum source (normally water taps) which helps speed up the process of filtration.

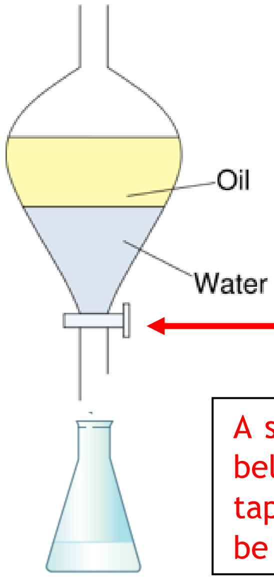
(iii) Solvent Extraction

On occasions, it may not be practicable to isolate the product directly from the mixture by filtration or simple distillation. In such cases a technique known as solvent extraction can be used.

If the desired product is present in an aqueous mixture, i.e. water is the solvent, it can be removed or extracted from the mixture by the addition of a second solvent. The choice of the second solvent is critical:

-It must be immiscible with water.
-The product must not react with the solvent.
-The product must be more soluble in the solvent than in water. (Hence, on adding the solvent to the aqueous mixture the product will move out of the aqueous layer and into the solvent layer, from which it can be more readily separated).

The process of solvent extraction uses a separating funnel to isolate the desired product. The aqueous mixture and non-polar solvent are all placed in a separating funnel and shaken vigorously for several minutes. The desired product moves to the non-polar solvent. It is then “ran off” from the separating funnel and collected in a flask. Finally, the desired product in the non-polar solvent is evaporated to produce a pure sample.



When carried out in practice, due to the immiscibility of the two solvents, distinct layers form. This makes it easy to separate out the layers.

Tap to run off each layer.

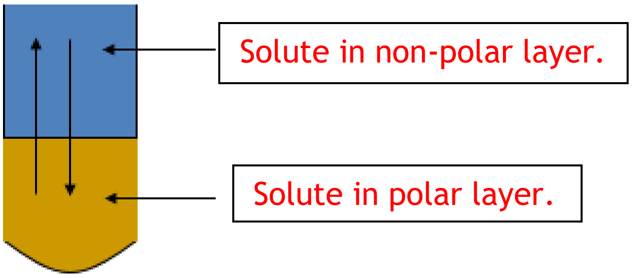
A small conical flask is normally placed below the separating funnel. When the tap is open, one layer will “run off” and be collected before the tap is closed.

*Key point

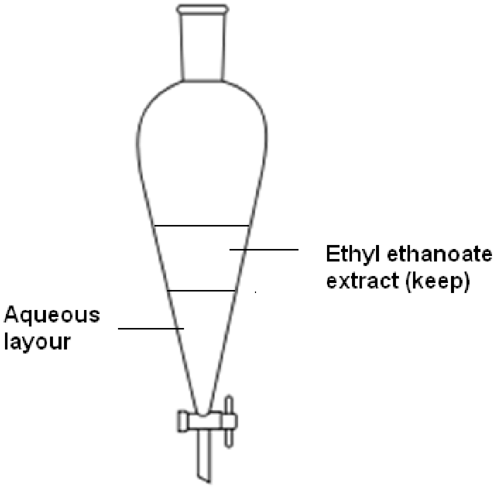
In practice, it is better to carry out solvent extraction using smaller volumes of the chosen solvent. For example, if there are 50cm^3 of solvent available, it would be more efficient to carry out two extractions using 25cm^3 portions of solvent rather than carrying out one extraction using the full 50cm^3 of solvent.

*Key point

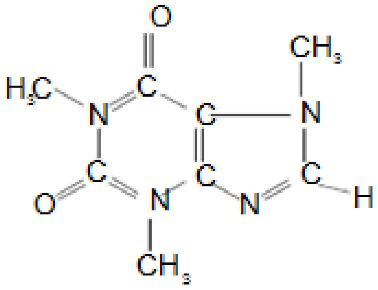
The desired product (solute) distributes itself between the two layers. This in actual fact sets up an equilibrium. The concentration of the solute can be determined in both layers and the equilibrium constant, K, calculated. In this context, the equilibrium constant is referred to as a partition coefficient.



A common Advanced Higher Chemistry project is the extraction of caffeine from tea or coffee. In this investigation the non-polar solvent, ethyl ethanoate, is used to extract the caffeine from the aqueous tea or coffee solution.



Caffeine molecule



Once the caffeine is successfully extracted, it can be analysed and its purity determined by comparison with a known sample of caffeine.

This lesson gives an insight into the setting up of laboratory equipment. To help visualise these concepts better, the video clips below will facilitate your understanding of the main points to the lesson.

https://www.youtube.com/watch?v=bTukJeHFF8o

https://www.youtube.com/watch?v=R64pHuh_49o

https://www.youtube.com/watch?v=e1KKfVYjv4U

https://www.youtube.com/watch?v=1tmqUVSVPo4

https://www.youtube.com/watch?v=RIbff5iD0GQ&pbjreload=101

→ Some recommended reading (not mandatory) is given below.

→Read Scholar Heriot-Watt/ Researching Chemistry Section 6.2, 6.3, 6.4 and 6.6.

→ Read Bright Red text book pages 90, 91, 92 and 93.

→ Answer the questions from Sheet 4.9 and check the answers when you have completed them.

4.9 Key Steps in Laboratory Synthesis 1

1. The apparatus used to carry out a reflux and distillation is essentially the same. However, the outcome of both techniques is different.

   a) Outline, the ways in which the apparatus is set up differently for both techniques.

   b) Why are reaction mixtures heated under reflux?

   c) If you had a sample of a liquid organic compound, how could you use distillation to prove the identity of the compound?

   d) Explain how the water connections (inlet and outlet) are set up for both reflux and distillation.

   e) Why are anti-bumping granules added to the reaction mixture before it is heated under reflux?

2. Give one advantage of carrying out vacuum filtration over simple filtration.

3. A pupil wanted to investigate which solvent was best for the extraction of caffeine, (sample X) from aqueous samples.

   In one investigation, the student used dichloromethane, CH_2Cl_2, which is more dense than water. When the student analysed both layers, they calculated the equilibrium constant, K to be 5.

   $$X(H_2O) \rightleftharpoons X(CH_2Cl_2) \qquad K = 5$$

   a) When choosing an appropriate solvent, which factors should the student take into consideration?

   b) Draw a separating funnel to show how the two layers would be positioned. Moreover, use the value of equilibrium constant to show how much solute is in each layer. (You may wish to illustrate the solute particles by drawing dots).

4. When a solute dissolves in each of two immiscible liquids the ratio of the concentrations of the solute, at equilibrium, in the two liquids is called the partition coefficient. The partition coefficient for an organic compound (X) between ether and water is 12.

Density of water = 1.0 g cm^{-3} Density of ether = 0.714 g cm^{-3}

a) State which layer forms the upper layer in the separating funnel. Give a reason for you answer.

b) If 1.1g of x is dissolved in 100cm^3 of water, how much of this compound will be extracted (after shaking the funnel for several minutes) with 100cm^3 of ether?

c) Explain why many organic compounds are more soluble in ether than in water.

5. Succinic acid $(CH_2COOH)_2$, is a dicarboxylic acid, can be partitioned between water and diethyl ether. To find the partition coefficient, 2.36g of succinic acid was dissolved in 100cm^3 of water in a separating funnel and 100cm^3 of diethyl ether was added. After shaking the mixture, the aqueous layer was removed and titrated with 1 mol l^{-1} sodium hydroxide. It required 34.8cm^3 to neutralise the aqueous acid solution.

$2NaOH + (CH_2COOH)_2 \rightarrow Na_2(CH_2COO)_2 + 2H_2O$

a) Calculate the number of moles of acid in the aqueous layer before the addition of ether.

b) How many moles of the acid will be dissolved in the <u>ether layer</u> after shaking?

c) Calculate the partition coefficient of succinic acid between the ether layer and aqueous layer.
(The partition coefficient can be calculated in this investigation by dividing the number of moles of acid in ether layer by the number of moles of acid in the aqueous layer).

d) How could the experiment be modified to reduce the concentration of acid in the aqueous layer while still using the same total volume of ether and the same mass of succinic acid?