## CHAPTER 1

# Experimental Methods and Manipulation

## 1.1 Introduction

**Introduction: T**his book will help the students to learn the basic skills involved in the identification of unknown organic compounds and show them how practical chemistry relates to theoretical work. The experiments are designed to be straight forward, and have been well tested for reproducibility and reliability.

The following procedure will ensure a student's success in the laboratory.

Always know exactly what you are trying to do!

(i) Read all the details of the experiments before the laboratory class, then if you have any doubts you can ask the demonstrator before you make a mistake.

(ii) Carry out the identification and structure assignment of the given unknown compound.

(iii) Write up each experiment or analysis as soon as it is finished.

(iv) Ensure that you are able to answer in the laboratory note-book any questions asked at the end of the experiment. These questions are designed to test your understanding of the experimental procedures and theory behind it.

(v) Treat your samples with care. Label properly all the specimens of derivatives that you have made.

Do not rush for anything, and if you have any doubt ask demonstrator.

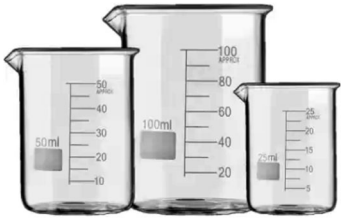
## 1.2 Apparatus used in the Laboratory

Every student should own a pair of safety glasses or goggles and should be required to wear these at all times in the laboratory. Accidents involving the eyes are extremely serious and usually arise most unexpectedly and from trivial causes.

### APPARATUS

**Glass Apparatus:**

Tripod stand




Graduated beakers

Spirit lamp

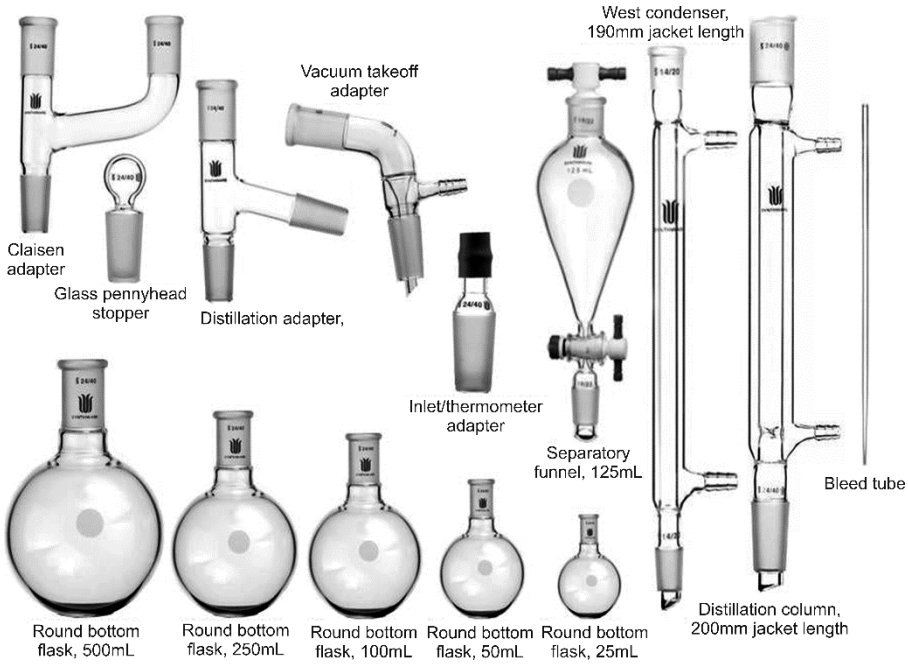
100ml 250ml 500ml 1l

Polythene Wash bottles

Test tubes stand with holder

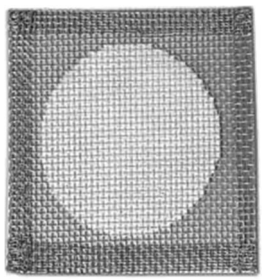
Forceps

Tongs




Watch Glass

Spatula



Wire Guaze

Droppers

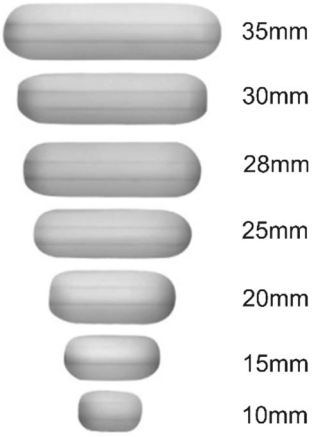
Boiling Tubes With Stand

Glass Rods

Vacuum Desiccator

Magnetic Stirrer with Hot Plate

Different Types of Stirrers

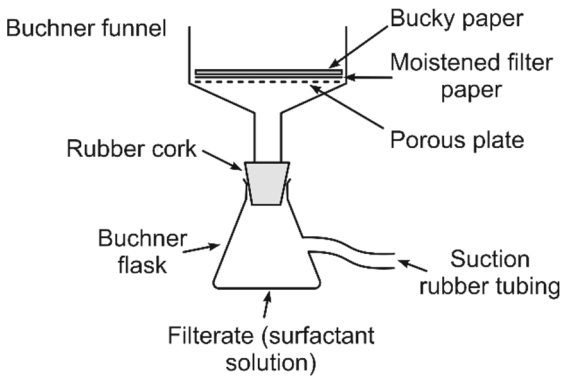


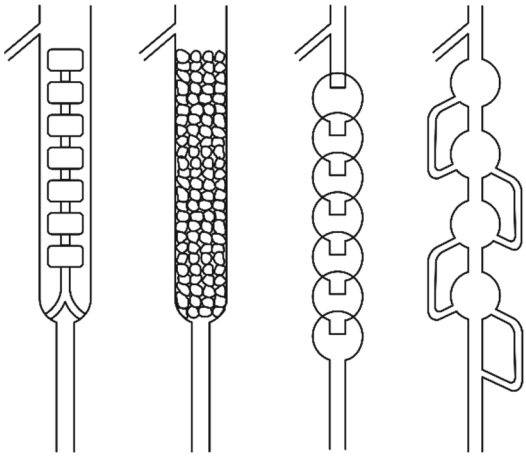

Teflon Magnetic Bars

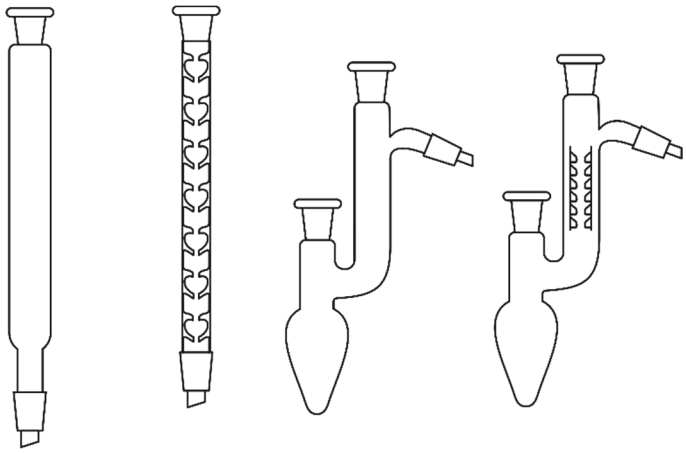
Glass Funnels

Filtration Set

Dropping Funnel



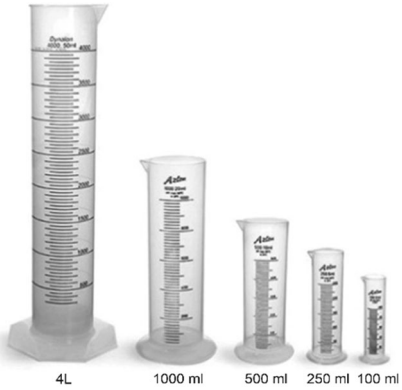





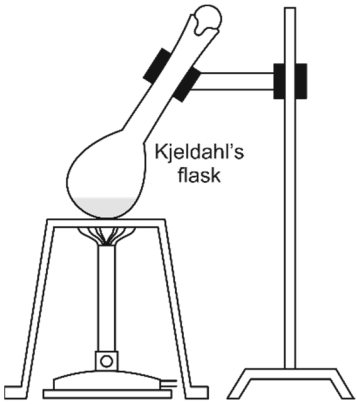
open column Vigreux column Claisen flask Claisen-Vigreux flask

Retort stand

Iron rings

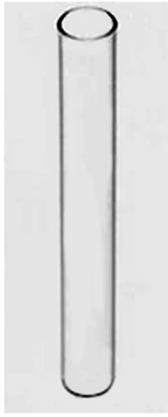



Graduated measuring jars



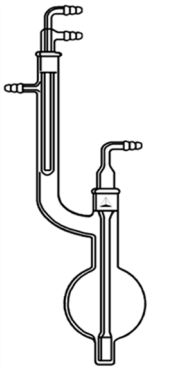

Kjeldahl flask (mp)

Graduated
pipette

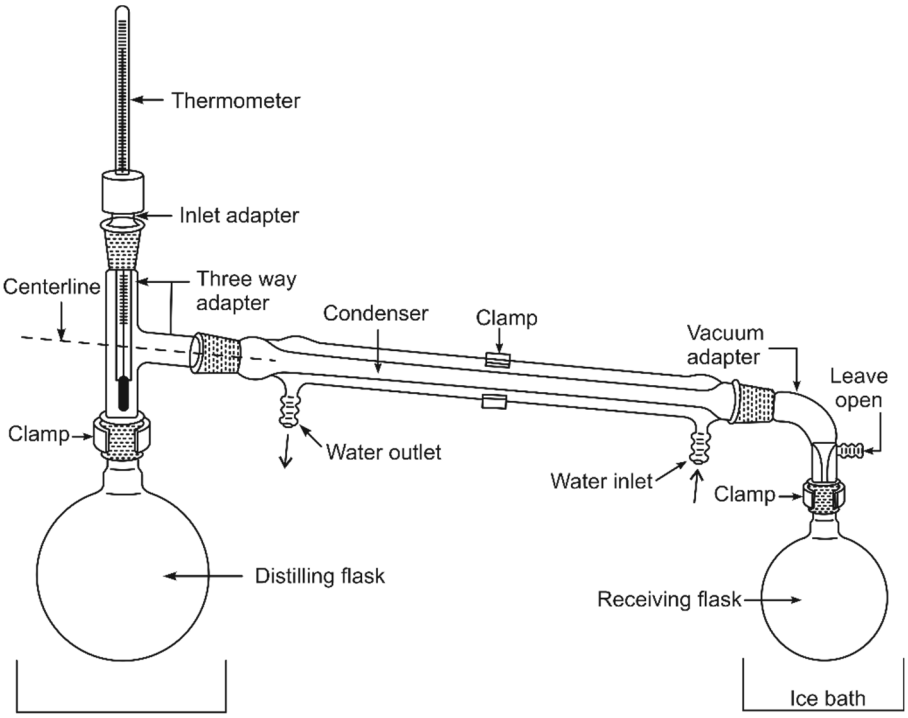


Boiling Tube

Sample tubes



Hydrogenation Apparatus (Micro scale)




**Distillation apparatus**

Guard Tube (to be filled with dry $CaCl_2$)

Melting point apparatus

## 1.3 Cleaning Glass Apparatus

**Use of Pipette**

(a) Use clean glassware at all times

(b) Before pipetting a solution, rinse the pipette using 2-5 ml of the solution to be measured. Discard the solution.

(c) Using a pipette bulb fill the pipette with the solution so that it is just above the calibration mark.

(d) Press the valve on the pipette with the solution to run down so that the shadow of the bottom of the meniscus is level with the calibration mark.

(e) Discharge the contents of the pipette into the appropriate flask. Touch the tip of the pipette against the surface of the liquid in the flask. Do not blow out the last drop of liquid from the pipette, the pipette is calibrated to account for this drop!

**Use of a Burette**

(a) Rinse the burette using 2-5 ml of the solution to be measured. Discard the solution.

(b) Have a wash bottle with distilled water ready for washings.

(c) Place a small funnel in the top of the burette and fill with the solution.

(d) Remove the funnel

(e) Open the burette tap so that the portion below the tap is full of solution to be used with no air bubbles.

(f) Make a "sail" with a filter paper to give a white back ground against which the meniscus can be viewed. Place a filter paper under the flask containing the solution to be analyzed to give a white back ground to view color changes.

(g) It should be able to record the level of the burette to two decimal places.

(h) Add the solution to the reaction flask. Regularly swirl the flask to ensure good mixing.

(i) Rinse down the sides of the flask with distilled water during the titration to ensure all of the reactants are utilized.

(j) As the end point is approached decrease the rate of addition. You should be able to add half a drop by touching the tip of the burette with the reaction flask and rinse down the sides of the flasks. Swirl the flask after each addition. Ensure there are no bubbles in the tip.

(k) Carry out all titrations in duplicate to check for consistency. The titre values should be consistent ± 0.1.

(l) All glassware should be thoroughly cleaned and dried before the experiment. It is advisable to develop the habit of cleaning all glass apparatus immediately after their use. Otherwise, it becomes difficult if the dirty apparatus is allowed to stand for a longer period, particularly if volatile solvents have evaporated in the mean time.

The simplest method for gross deposits, when access to a test-tube brush is possible, is to employ a commercial household washing powder containing an abrasive which does not scratch glass (e.g. Vim, Dish-wash, etc.). Finally, the apparatus is thoroughly rinsed with water and dried in an air oven.

Alternatively the apparatus can be cleaned by using the 'chromic acid' cleaning mixture. This is essentially a mixture of chromium trioxide and concentrated sulfuric acid, and possesses powerful oxidizing and cleaning properties.

**Preparation of chromic acid solution:** Five grams of sodium dichromate are wetted with 5 ml of water in a 250 ml beaker, 100 ml of concentrated sulfuric acid are then added slowly with constant stirring. The temperature will raise to 70-80 $^0$C. The mixture is allowed to cool to room temperature and then transferred to a dry, glass-stoppered, clean labeled bottle. Before using this mixture for cleaning purpose, the flask to be cleaned should be rinsed with water to remove water soluble organic matter. After draining away as much of the water as possible, a small quantity of the cleaning mixture is introduced into the flask, the soiled surface thoroughly wetted with the mixture. After standing for a short period with occasional rotation of the flask to spread the liquid over the surface, the flask is thoroughly washed with tap water and finally rinsed with distilled water.

## 1.4 Drying of Organic Solutions (Extracts)

The combined solvent phases resulting from extraction of an aqueous solution

will contain small amounts of water. This is usually removed before the solution is evaporated, a process usually accomplished by shaking the solution with anhydrous drying agent, which will absorb the water but do not react with the solvent or the desired solute.

***Five suitable drying agents are listed below*:**

(i) Anhydrous magnesium sulphate ($MgSO_4$)

(ii) Anhydrous sodium sulphate ($Na_2SO_4$)

(iii) Anhydrite calcium sulphate ($CaSO_4$)

(iv) Anhydrous potassium carbonate ($K_2CO_3$)

(v) Anhydrous calcium chloride ($CaCl_2$)

It is often convenient to remove final traces of water with the aid of molecular sieve and store the dried solvent in the presence of the sieve.

The term molecular sieve, applies to a group of dehydrated synthetic sodium and calcium aluminosilicate adsorbents; three types of Zeolites namely 3A, 4A, 5A and 13A are available commercially.

To dehydrate the solvent phase, add to it one-twentieth of its bulk of the selected desiccant and shake the mixture frequently during 10-20 minutes ($MgSO_4$) or allow it to stand with occasional shaking for 30 minutes or more ($Na_2SO_4$). Separate the dried solution from the spent desiccant either by filtration with suction or by means of a filter paper funnel or by careful decantation.

## 1.5 Solid Substances-Criteria for Purity

**(A) Melting points:** Calibration of a thermometer - Generally while determining the melting points, boiling points and reaction temperatures a thermometer is invariably used in the laboratory. In some situation, if the temperature is approximately determined, it does not matter. But sometimes we may have to determine the temperatures accurately. By using ordinary laboratory thermometer, we can determine the temperatures from -38 $^0$C to 360 $^0$C. Nearly all the boiling points and melting points of organic compounds fall in this range. Thermometers employed in the laboratory differ from one to other while indicating temperatures. If a given thermometer shows an error of 0.5 $^0$C in the range of $0^0$ to 100 $^0$C, and an error of $1^0$C in the range of 100 to 250 $^0$C, we can accept it. But in some thermometers the value of temperatures determined, may fall exactly in the expected region, while the temperature values in higher temperatures regions may show 3-4 $^0$C error. Because of these reasons, the student must calibrate, the thermometer given to him/her. The b.ps and m.ps of

some pure compounds are taken as standard reference for temperatures. By determining the m.ps/ b.ps of such pure compounds with a given thermometer, we can find out the error in that particular thermometer.

The following compounds are taken as standard reference compounds and their mps & bps are given in the following table.

| S.No. | Compound | Mp ( $^0$C) | Bp ( $^0$C) |
|---|---|---|---|
| 1 | Ice | $0^0$ C | ---- |
| 2 | Water | ---- | $100^0$C |
| 3 | Diphenylamine | 53.5 | ---- |
| 4 | Benzene | ---- | 80.2 |
| 5 | Vanillin | 82 | ---- |
| 6 | Resorcinol | 112 | ---- |
| 7 | Benzoic acid | 122.4 | ---- |
| 8 | Chlorobenzene | ---- | 132 |
| 9 | Salicylic acid | 158.3 | ---- |
| 10 | Hydroquinone | 170 | ---- |
| 11 | Succinic acid | 189 | ---- |
| 12 | 3,5-Dinitro benzoic acid | 205 | --- |
| 13 | Nitrobenzene | --- | 210.9 |
| 14 | P-Nitrobenzoic acid | 239 | ---- |

Using a given thermometer, determine the Mps/Bps of the above compounds & find out the error and record data in the following table:

**Example:**

| S.No. | Standard compound used for calibration | Mp/Bp of pure compound | Temperature shown by thermometer | Error (in degrees) |
|---|---|---|---|---|
| 1. | Hydroquinone | $170^0$ | $174^0$ say | $+4^0$ |

**(B) Determination of melting points:** *The melting point is the prop*erty of an organic solid which is most frequently used as a criterion of purity. A pure compound has a sharp melting point (i.e. melts over + or – $1^0$C temperature range).

**Procedure:** Crush a small amount of the sample on a watch glass with a small spatula. Cut double-sealed melting point capillary in to half or use commercially available melting point capillaries. Introduce a little of the powder into the open end of a capillary tube and tap it down to the closed end by gently stroking with a file. The column of solid

should be no more than 3 mm in length and should be tightly packed. Select a thermometer with a short bulb (0-360$^0$C). Do not rely on digital displays. Record the temperature at which melting begins, and the temperature at which the last traces of solid disappear. This is the melting point range of the sample. You will not obtain accurate melting points if the sample is heated too rapidly.

Here one can use Kjeldahl flask for determining the melting points in addition to commercial melting point apparatus.

**(C) Mixed melting points:** Pure organic compounds exhibit sharp melting points. If they are contaminated with impurities, their melting points will be lower when compared to the melting point of pure compounds.

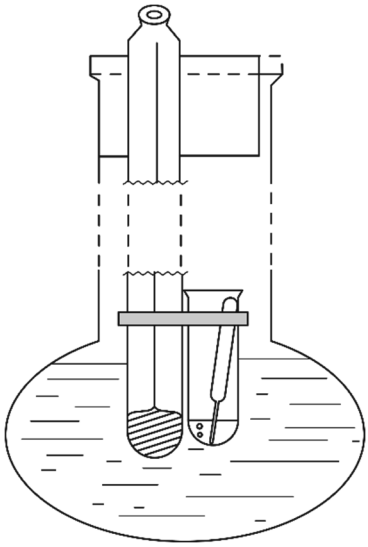
## 1.6 Liquid Substances - Determination of Boiling Point on a Semi-micro Scale

### Boiling points of pure liquids

**Procedure Part 1**

Using a small Bunsen flame, draw out a centre part of a melting point capillary tube so that its diameter is reduced to about one-third of the original. To do this, hold the capillary tube horizontal between your hands gripping the tube at either end with a thumb or forefinger. While rotating the tube backwards and forwards, heat the centre section in the side of a blue flame, about 2 cm up from the flame outlet. The tube will glow orange and suddenly soften. Immediately pull out of the flame and move your hands apart in one continuous movement. Say to your- self at normal speed “Out and Pull”. You should then have a drawn out centre section of around 6 inches in length. With tweezers, snap off 1 inch (2 cm) lengths of the thinned section (safety glasses!) and seal one end of each length with the Bunsen flame. Store in a sample bottle until needed.

**Procedure Part 2**



Obtain a *melting point* apparatus and a seal capillary tube at one end as you would for *melting point* determination. With tweezers, carefully place one of your specially drawn out tube *inside* the capillary tube so that the open end of the inner tube points towards the sealed end of the larger outer tube. Using a syringe, inject around 15 microlitres of the liquid whose boiling point you wish to determine into the capillary tube, ensuring that the syringe needle reaches down to the sealed end of the capillary. The assembly should appear as in the diagram. Do not add too much of the liquid.

Place the capillary tube in the melting point apparatus and heat it up as if you were finding a melting point. As the boiling point of the liquid is reached, a *continuous* stream of bubbles will appear from the open end of the inner tube. Immediately note the temperature ($T_1$) and stop heating. As the apparatus cools, note the temperature ($T_2$) at which the bubbles just *cease* to emerge from the tip of the inner tube. Both temperatures should be similar and denote the boiling point (if the difference is significant, the measurement obtained on cooling ($T_2$) is usually the most accurate).

N.B. One of the older style melting point apparatus can be used.

## 1.7 Vacuum Distillation (Distillation at Reduced Pressure)

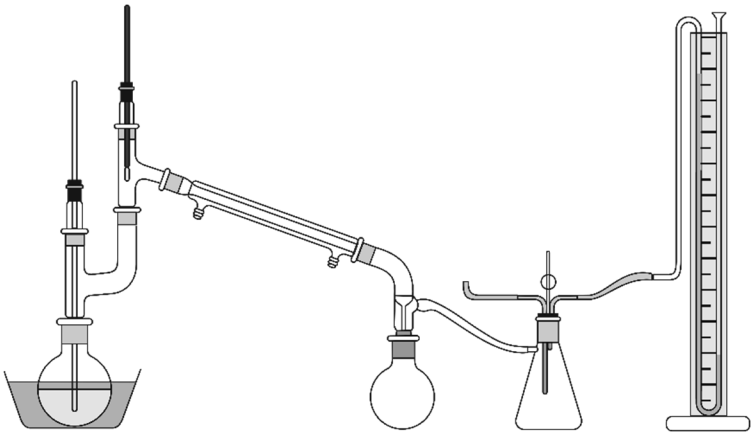
High boiling liquids, or those which decompose at normal boiling point, are generally distilled at lower temperature under reduced pressure.

Use a round bottom flask as the distillation pot. The size of the flask depends on the volume to be distilled, but ideally it should be between one quarter and one half full – and no more. In order to prevent the *extremely bad bumping* that occurs with *every* vacuum distillation, the liquid should be stirred with a magnetic stirrer bar. The distillation pot is then fitted with a still head, quickfit thermometer (see demonstrator), condenser and a pig (2-way receiver adapter) with 2 round bottom flasks (see diagram below).

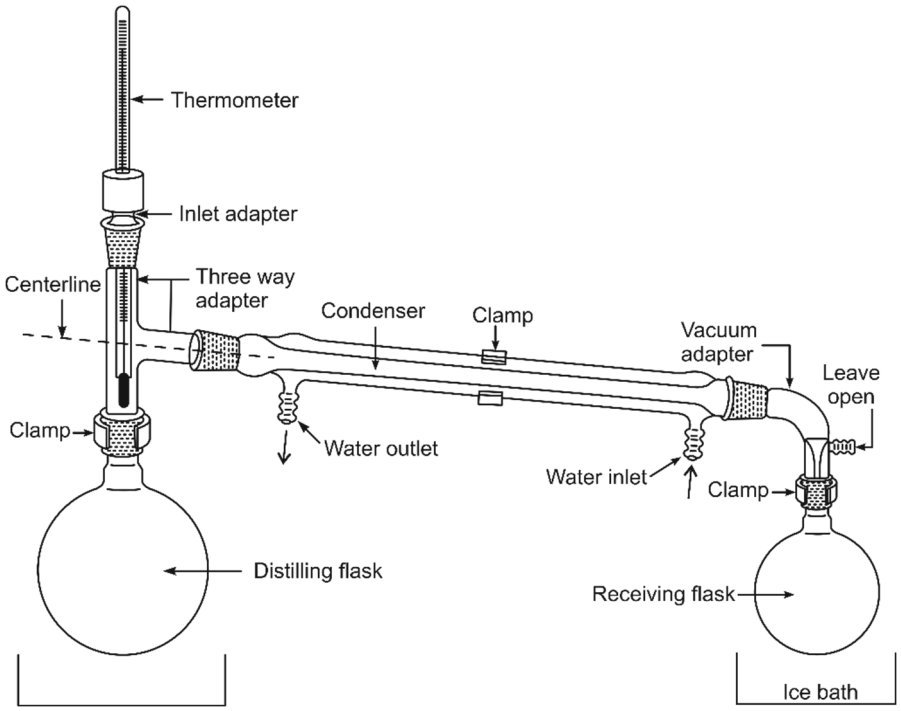
Place the liquid in the distillation pot and assemble the apparatus, all the ground glass joints should be lightly greased, with vacuum grease not Vaseline. Remember to support the collection flasks, until the system is under vacuum, gravity rules! Start stirring vigorously but do not heat. Turn the tap for the water pump on full before connecting the tubing to the system. Once connected, use the stopcock on the trap to carefully apply the vacuum. Ensure that the contents of the pot do not froth over and contaminate the collection flasks. If this happens, dismantle the apparatus and start again. Only when the apparatus is fully evacuated can the heater be switched on.

Therefore, if you purify a sample by distillation at reduced pressure, it is acceptable to quote the boiling range at which you collected the sample as long as you quote the pressure. With a water pump a pressure of 10-20 mmHg can be obtained, under these conditions, boiling points are reduced to approximately 100 $^{O}$C.

Vigorous stirring is maintained throughout the distillation and fractions are collected by rotation of the pig at the appropriate point. When distillation is complete, turn of the heating and allow the apparatus to cool. Then, holding the collecting flasks, release the vacuum by opening the stopcock on the trap. Do not swish the water pump off before releasing the vacuum.



**Vacuum distillation apparatus**



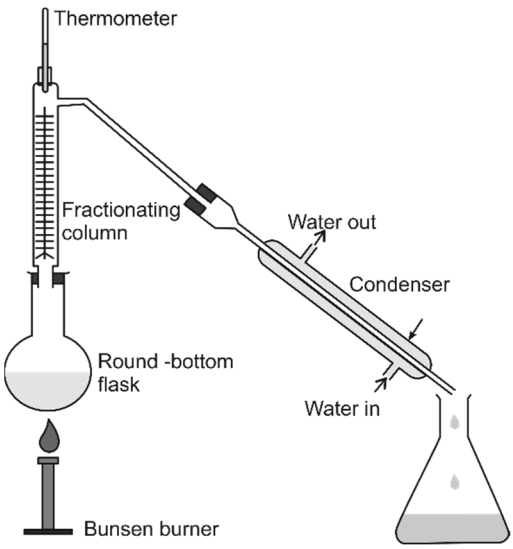

**Simple distillation apparatus**

## 1.8 Purification of a Liquid by Fractional Distillation

### Fractional Distillation

Distillation and recrystallisation are the two chief methods of purifying organic compounds. Several kinds of distillations are possible, including simple distillation, fractional distillation, and steam distillation. This experiment is concerned with the separation, by fractional distillation, of two miscible liquids, methylene chloride and carbon tetrachloride.

Place 50 ml of the given mixture in the distilling flask and add a small boiling stone (to prevent bumping and to facilitate even boiling). Connect the flask to the apparatus and heat it gently with a small non-luminous Bunsen flame. The slower the distillation, the better will be the separation. Collect the 5 ml fraction of the distillate in a small measuring cylinder and note the temperature at which each fraction distils. Transfer each fraction to a clean, dry, numbered test-tubes; stopper the test-tubes and set them aside for subsequent g. l. c. examination.




**Fractional Distillation**

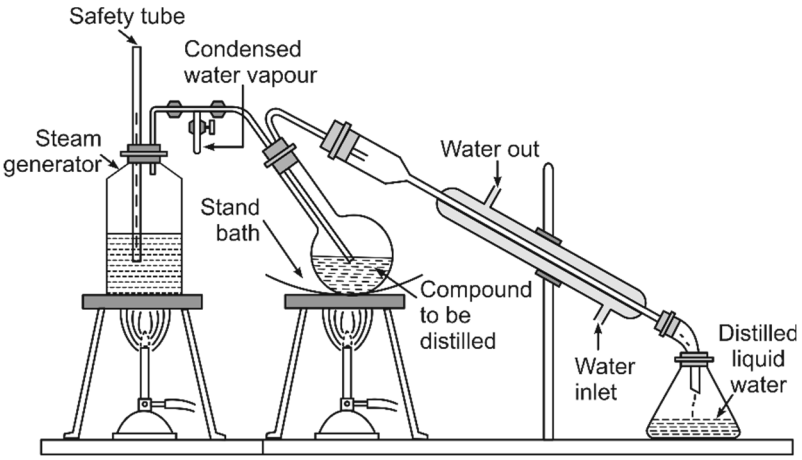
## 1.9 Steam Distillation

The diagram for steam distillation is given below:

(i) It is a chemical process where a mixture which is made up of two or more components with different boiling points is separated.

(ii) The **mixture is heated until one of** the components boils (turns to vapor).

Steam is introduced into the distillation apparatus, **lowering the boiling points of the compounds**. The goal is to heat and separate the components at temperatures below their decomposition point.




**Steam Distillation**

## 1.10 Recrystallisation

Purification of Organic Compounds: Solids by Recrystallisation

Crystallisation is an efficient method for the purification of solid organic substances. It is first necessary to find a suitable organic solvent, i.e. one which will readily dissolve the material when hot but only to a small extent when cold.

You will be required to recrystallise many of the compounds you prepared in order to purify them. Follow the simple procedure to ensure a good recrystallisation.

(a) Dissolve the given sample in the **minimum** amount of boiling solvent. Some insoluble impurities may be present. Ensure you do not add too much solvent trying to dissolve this portion. It is better to lose a little sample at this stage in order to get a very clean product.

(b) Filter the solution while hot to remove any insoluble impurities. This is usually done through a fluted filter paper. Filter the portions meanwhile keeping the remaining solution hot. If crystals form in the funnel wash them through with more hot solvent.

(c) Cool the filtrate and if necessary place in an ice-salt (NaCl) bath. The salt bath is prepared by mixing ice, a little water and some salt together. This will give a bath below 0 $^{O}$C.

(d) Filter the precipitate by suction using a Karl Georg Büchner funnel to collect the purified product. The product may be washed with a little **cold** solvent. Continue to suck air over the crystals for a few minutes to help in drying.

## 1.11 Solvent Extraction

Separation Techniques in the purification of Organic Compounds

Solvent extraction is an operation very frequently used in practical organic chemistry. In this experiment one can apply this technique to the purification of a crude organic acid.

Many organic acids are sparingly soluble in water but are readily soluble in organic solvents such as benzene or methylene chloride. In contrast the sodium salts of these acids, which are obtained by the reaction of acids with aqueous sodium hydroxide, are readily soluble in water and insoluble in organic solvents. This is because the salts are ionic while the free acids are relatively un-dissociated.

This experiment makes use of these differences in solubility. You will be supplied, by your demonstrator, with a solution of an impure organic acid dissolved in benzene or any other organic solvent.

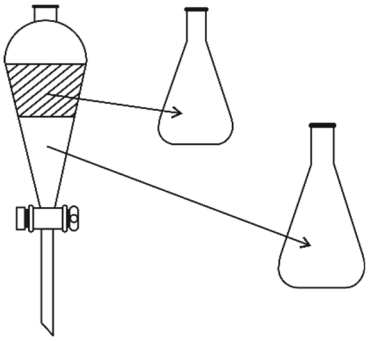
**(i) Formation of the sodium salt:** Place the given solution (20 ml) in a separating funnel and add 20 ml of dilute sodium hydroxide solution. Close the funnel with a stopper and shake the contents thoroughly. Clamp the funnel vertically and allow the two layers to separate. The upper layer is benzene, the lower layer is sodium hydroxide solution. This treatment will have converted the organic acid into its water-soluble sodium salt which will be present in the lower alkaline solution. Non-acidic impurities will remain in the upper benzene layer.

Remove the stopper from the funnel and run the lower layer into a beaker. To make sure that all the organic acid has been removed from the benzene layer, re-extract this layer with a further 20 ml of dilute sodium hydroxide solution. Combine the two alkaline solutions in the beaker and discard the benzene solution in the funnel.

**(ii) Regeneration of the Free Organic Acid:** Add dilute hydrochloric acid with stirring to the alkaline solution in the beaker until the mixture is just acid (test with Congo Red indicator paper which turns blue in acid solution). This treatment will cause most of the organic acid to be precipitated as a white solid. Pour the resulting suspension of the organic acid into a clean separating funnel.

**(iii) Re-extraction of the Organic Acid:** Add methylene chloride (15 ml.) to the suspension in the separating funnel, stopper the funnel and shake the contents thoroughly. Allow the layer to separate. The organic acid will now have dissolved in the lower methylene chloride layer. N.B. Methylene chloride, unlike benzene is denser than water and hence forms the lower layer at this stage. Run off the lower layer into a beaker. Re-extract the upper layer remaining in the funnel with a further 15 ml. of methylene chloride. This should extract the last traces of the organic acid from the aqueous layer. Combine the two methylene chloride solutions in the beaker and discard the aqueous layer in the funnel.

**(iv) Purification of the Extract:** Pour the methylene chloride solution of the organic acid into a clean separating funnel, add 20 ml. of cold water and shake the mixture thoroughly. Traces of inorganic salts will dissolve in the water. Remove the stopper, allow the layers to separate and run the lower methylene chloride solution into a small, clean dry conical flask. Add a few grams of solid anhydrous sodium sulphate to the methylene chloride extract and after swirling the flask, allow it stand for 10 minutes. This removes the traces of water from the organic solution.



**(v) Isolate of the Pure Organic Acid:** Decant the clear methylene chloride solution into a small round-bottomed flask. Rinse the remaining sodium sulphate with a small additional amount of methylene chloride and decant the washings into a round-bottomed flask. Add a small piece of carborundum (boiling stone) and remove the methylene chloride solvent by distillation on the steam bath using the simple distillation apparatus. A residue of the purified organic acid will remain in the round-bottomed flask.

Recrystallise the material from the minimum amount of boiling water. Collect, dry and weigh the crystals. Determine the melting point of the pure dry organic acid and place the crystals in a labelled sample tube.