## DISTILLATION

**NEVER distill the distillation flask to dryness as there is a risk of explosion and fire.**

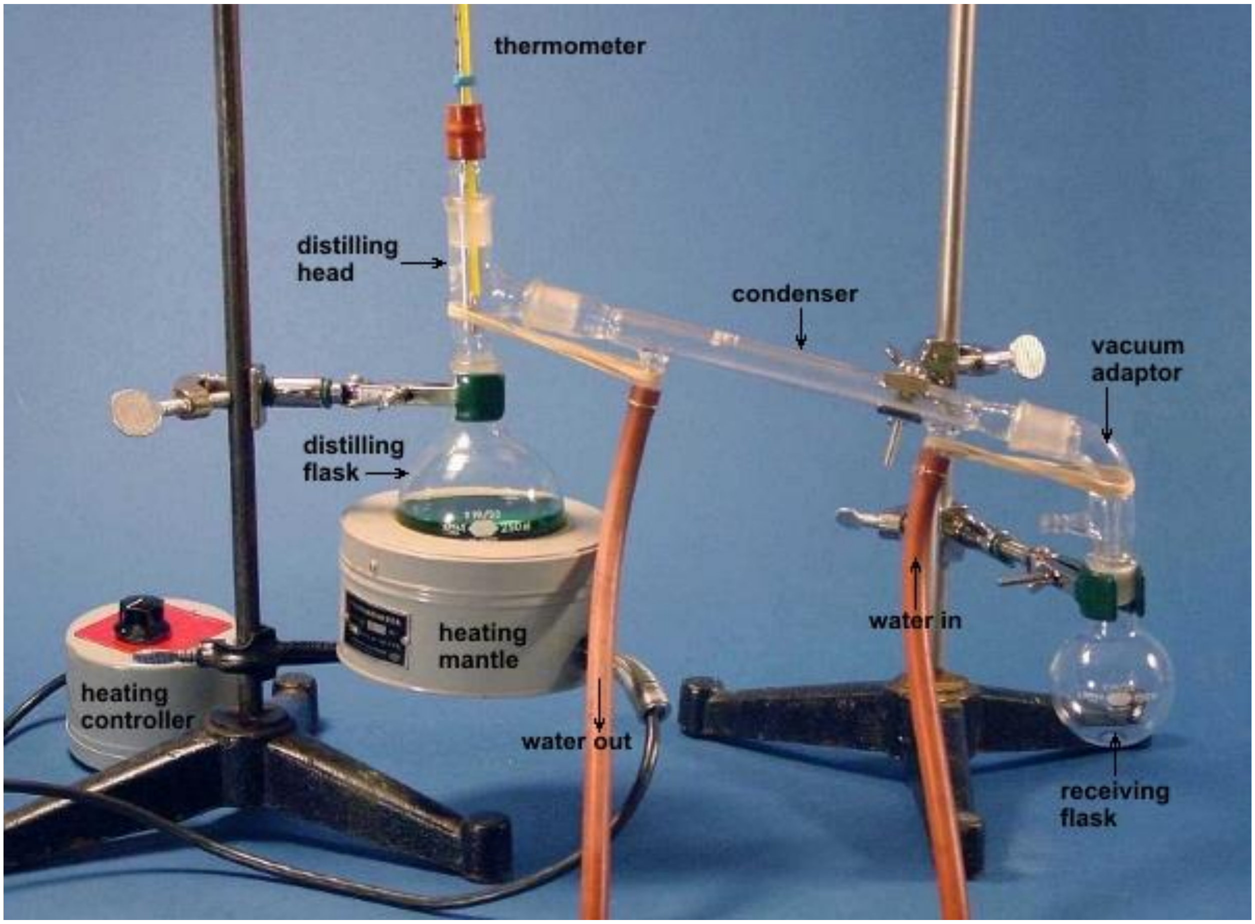
The most common methods of distillation are **simple distillation** and **fractional distillation**. Simple distillation can be used when the liquids to be separated have boiling points that are quite different. Fractional distillation should be used when the boiling points are similar. A short movie (download to watch) on setting up for fractional distillation is available.

Distillation is a separation process that involves heating a liquid to its boiling point, transferring the vapour to a different portion of the apparatus, then condensing the vapour and collecting the condensate in another container. This technique is one of the most useful for separating a mixture of liquids when the components have different boiling points. Industrially, distillation is the basis for the separation of crude oil into the various, more useful hydrocarbon fractions and of air to obtain industrial gases like nitrogen, oxygen and argon. Chemically, distillation is the principal method for purifying liquids (*e.g.* samples, or solvents for performing reactions). Successful distillation depends on several factors, including the difference in boiling points of the materials in the mixture, and therefore the difference in their vapour pressures, the type of apparatus used, and the care exercised by the experimentalist.

**NOTE**: In the equipment set up shown in the images below, a heating mantle with a heating controller is being used to heat the round bottom flask. In your equipment set up (or any of the other set ups such as reflux), the heating mantle and heating controller will be replaced by an engineered (shaped) aluminium block sitting on the top of a stirrer hot plate. This is a more modern version of a heating mantle with some distinct benefits.

### Distillation of a Pure Liquid

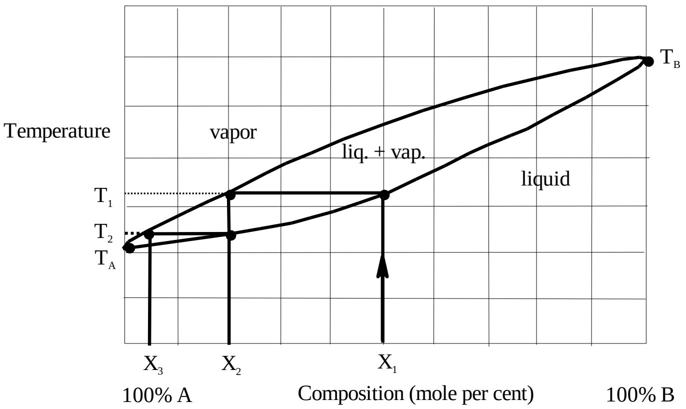
A pure liquid has a constant boiling point at a specific pressure as long as liquid and vapour are in equilibrium. In a **simple distillation** of a pure substance, as the temperature rises, the vapour pressure increases. As the vapour expands, it passes out of the heated portion of the apparatus until it comes into contact with the cold surface of the water-cooled condenser. When the vapour is cooled, it condenses and passes down the condenser into the receiver.



Simple Distillation Apparatus

**Distillation of a Mixture**

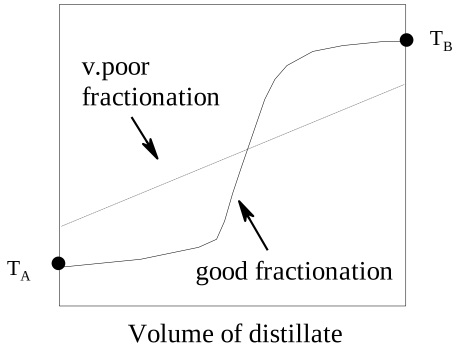
When a liquid mixture is distilled the temperature of the distillation flask will not remain constant but will gradually increase throughout the distillation as the composition of the solution in the distillation flask changes. With a mixture of two liquids A and B, each having boiling points $T_A$ and $T_B$, and different vapour pressures, the vapour will contain a higher proportion of the more volatile component. The composition of the vapour in equilibrium with a liquid mixture is shown in the vapour-liquid phase diagram.



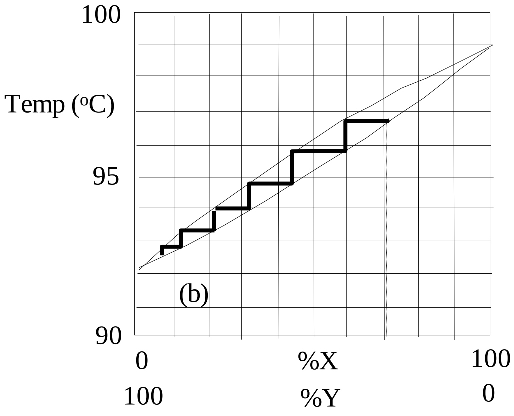
Vapour-Liquid Phase Diagram

In this diagram a liquid of composition defined by $X_1$ (in this case 50% A; 50% B) has a boiling point $T_1$. This can be seen by reading up from the x axis at $X_1$ until we meet the lower phase curve for the liquid. If we follow the $T_1$ line horizontally we can determine the composition of the vapour in equilibrium with liquid of composition $X_1$ at temperature $T_1$. This corresponds to composition $X_2$ in the diagram (read down from the vapour curve: 80% A; 20% B). Note that the vapour is considerably enriched in the more volatile component A. (since $T_A < T_B$ then A is more volatile than B). If this vapour is condensed, then a liquid of composition $X_2$ is obtained (to condense the vapour the temperature is lowered from $T_1$ to $T_2$). If the liquid of composition $X_2$ is allowed to reach $T_2$ it will exist in equilibrium with a vapour of composition $X_3$. This vapour (90% A; 10% B) can be condensed and revapourised, and so on until eventually vapour, and subsequently liquid, of pure A is obtained.

Ideally, this is the sequence of events taking place in a distillation apparatus and is called <u>fractionation</u> (and hence fractional distillation). The processes of condensation and revapourisation take place in the cooler parts of the distillation apparatus as the ring of condensate gradually makes its way up the apparatus until it reaches the condenser. No further fractionation takes place after this point; the apparatus is too cold to allow any significant vapourisation. Thus, if the distillation is carried out sufficiently slowly that equilibrium conditions are approached, and if the height from the distillation flask to the take-off arm on the still-head is sufficient to allow for the necessary number of processes to take place, pure liquid can be obtained. The simple distillation apparatus shown on page 2 would only separate liquids of widely different boiling points. This is represented by the solid line in the diagram of the distillation curves. If a separation were attempted of two liquids with similar boiling points, or if a distillation were carried out too quickly and not allowing time for equilibration, then the dotted line would result. Pure A and B would not be obtained in this case, but the condensate would contain more A initially with gradually increasing amount of B.



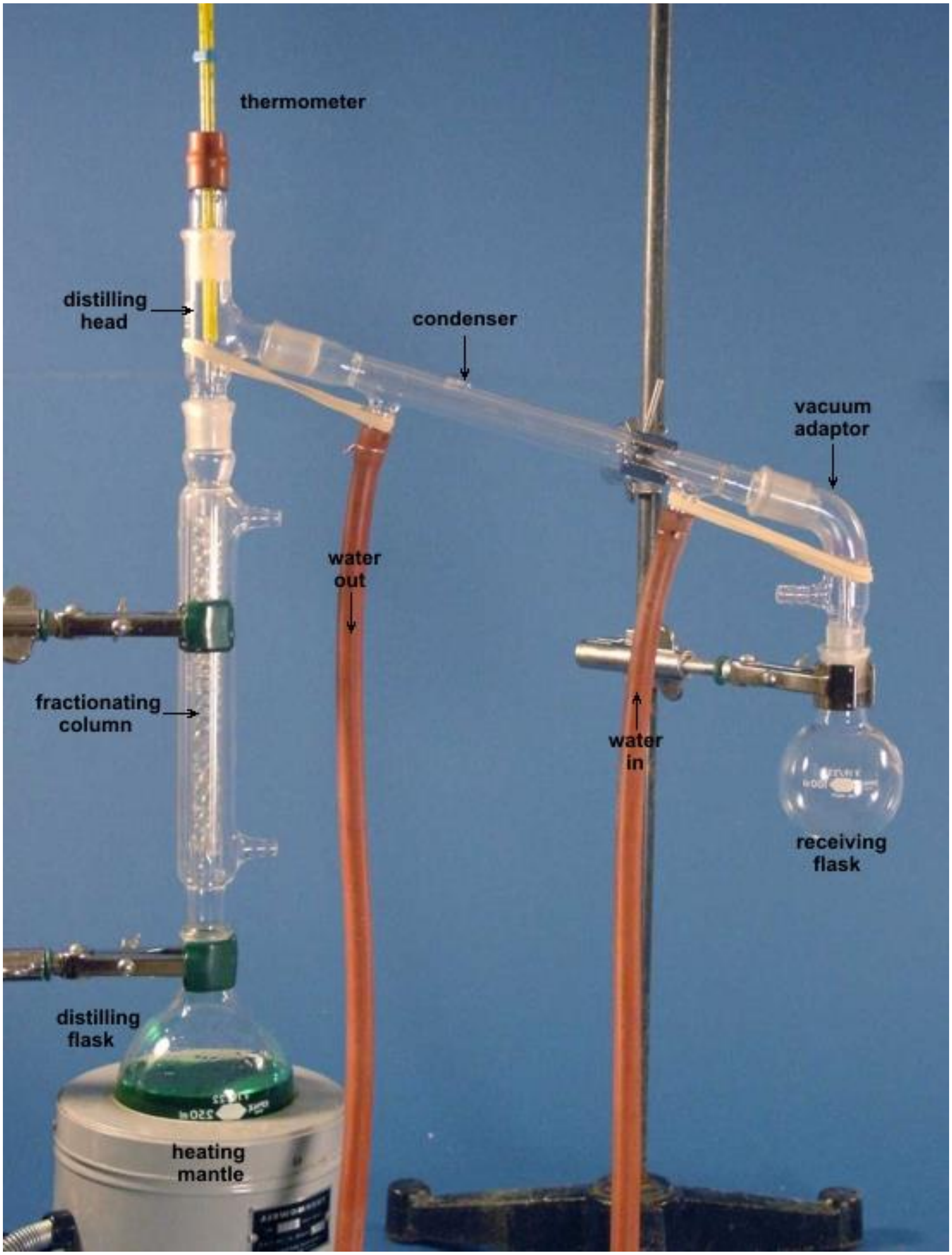
<u>Distillation curves</u>



<u>Vapour-Liquid Phase Diagram</u>

The vapour-liquid phase diagram for two liquids, X and Y, differing in boiling point by 7°C is shown above (right). To obtain pure Y a large number of fractionations are required (as shown schematically by the steps in the diagram) and this cannot be accomplished using a simple distillation apparatus.

In a case like this, in order to separate a mixture of X and Y it is necessary to use a fractionating column. A typical fractional distillation apparatus is shown on the following page.



Fractional Distillation Apparatus

As the distillation proceeds, the fractionation steps (vapourisation – condensation cycle) occur in the fractionating column. As the vapours climb up the fractionating column, the mixture gradually becomes richer in the lower boiling component and the boiling point of the condensate mixture decreases.

**Raoult's Law**

The observation that the vapour in equilibrium with a mixture is richer in the more volatile component is expressed quantitatively as Raoult's Law.

When two liquids that are completely soluble in one another are mixed together, the total vapour pressure is the sum of the two partial vapour pressures. The contribution of each component to the total vapour pressure is a function of the composition of the mixture.

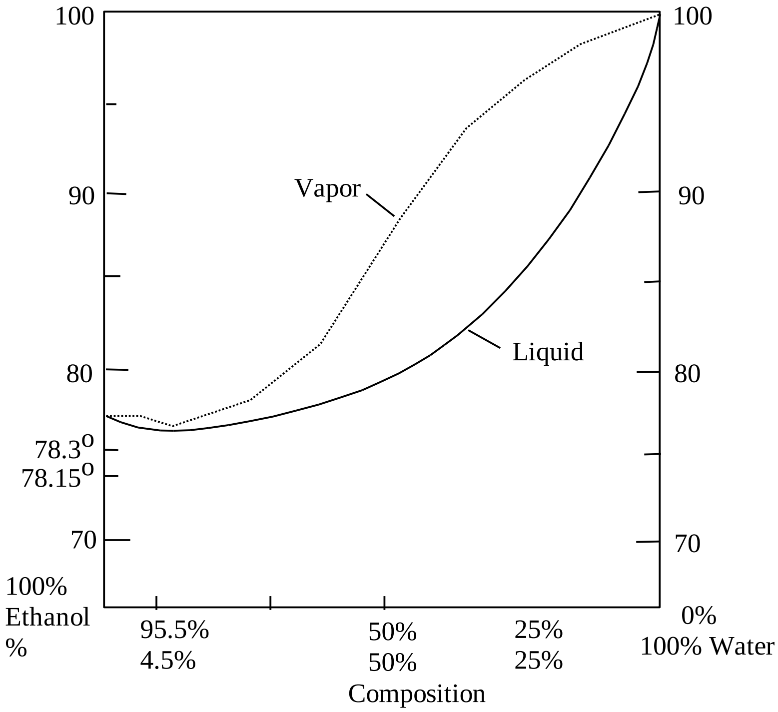
Miscible pairs of liquids are said to behave ideally if the contribution of each component to the total vapour pressure is directly proportional to its mole fraction, i.e.

$$P_A = x_A P_A^o; \quad P_B = x_B P_B^o$$

and

$$P_{TOTAL} = P_A + P_B = x_A P_A^o + x_B P_B^o$$

where $P_A$ and $P_B$ are the vapour pressures of A and B above a solution of mole fraction $x_A$ and $x_B$, and $P_A^o$ and $P_B^o$ are the vapour pressures of pure A and pure B at that particular temperature. This type of behaviour is often referred to as "ideal behaviour" or "behaviour according to Raoult's Law".



Boiling Point - Compositions Curves for Ethanol - Water Mixtures

Not all liquids form ideal solutions and conform to Raoult's Law. Ethanol and water are such liquids. Due to the molecular interactions, a mixture of 95.5% (by weight) of ethanol and 4.5% of water boils below (78.15°C) the boiling point of pure ethanol (78.3°C). Thus, no matter how efficient the distillation apparatus, 100% ethanol cannot be obtained by distilling a mixture containing less than 95.5% ethanol. A mixture of liquids with a definite composition that distills at a constant temperature without change in composition is called an azeotrope; 95% ethanol is such an azeotrope. The boiling point - composition curve for the ethanol - water mixture is shown on the next page. To prepare 100% ethanol the water is removed as an azeotrope with still another liquid. An azeotropic mixture of 32.4% ethanol and 67.6% benzene (bp 80.1°) boils at 68.2°. A ternary azeotrope (bp 64.9°) contains 74.l% benzene, l8.5% ethanol, and 7.4% water. Absolute alcohol (l00% ethanol) is made by addition of benzene to 95% alcohol and removal of the water in the volatile benzene-water-alcohol azeotrope.

A pure liquid has a constant boiling point (at constant pressure). A change in boiling point during distillation is an indication of impurity. The opposite proposition, however, is not always true, and a constant boiling point does not necessarily mean that the liquid is pure. For instance, if two miscible liquids, that have similar chemical structures, and which boil at the same temperature individually, are mixed, then the mixture will have nearly the same boiling point as the components. Also, as noted previously, azeotropes have constant boiling points that can be either above or below the boiling points of the individual components.

### **Assembling the Fractional Distillation Apparatus** movie (download to watch)

The apparatus should be assembled starting with the appropriate sized round bottomed flask fitting into the heating mantle and working outwards toward the receiving flask. In order to select your flask size, remember that the flask should only be about 2/3 full of the liquid to be distilled. It is useful to support the heating system on a wooden block or lab jack *etc*. so that heating may be discontinued immediately. Note that clamping of the round bottomed flask, which is advisable, becomes essential if the heating system is to be removed.

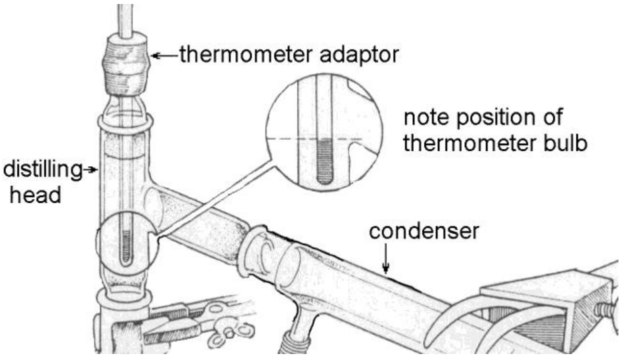
Check that the joints remain tightly sealed periodically throughout the distillation; a gap, particularly at the still-head, would lead to a serious (and potentially dangerous) loss of material. You may wish to use elastic bands or clips to prevent joints from opening. However, do not rely on these as your principal means of holding the apparatus together; the bands often break if the distillation temperature is relatively high.

Remember that the distilling flask should only be 2/3 full of the liquid to be distilled. A boiling stone or stirrer must be added to the **cold** liquid to ensure smooth distillation and prevent "bumping". Without a boiling stone or stirrer, bubbles of vapour do not escape easily from the body of the liquid, with the result that the liquid becomes superheated and the vapour is expelled periodically in a sudden uncontrollable burst that causes the apparatus to “bump”. Never add a boiling stone or stirrer to the heated liquid as you will run the risk of releasing large amounts of vapour at once. Since the pores of the boiling stone fill with liquid as soon as boiling ceases, boiling stones cannot be reused.

The fractionating column (vertical) is assembled using the wider of your two condensers. This has three indentations at the bottom of the inner glass tube, and introducing 2-3 small pieces of glass tubing into the bottom of the column to plug the end prevents the smaller beads from passing through the column. Fill the column with glass beads. The glass beads provide the large surface area necessary for the multiple condensation-revapourisation process of fractionation.

The condensing column (diagonal) needs to be secured (carefully clamped) and correctly connected to a supply of cooling water in and waste water out. As long as the condenser is cold to the touch at the lower end, then the flow of water is sufficient. Too high a flow of water is wasteful and more likely to result in leaks and floods. As a rule of thumb, turning the water on until one gets an “unbroken flow” is typically good.

It is important to position the thermometer correctly to accurately measure the distillation temperature. The bulb (or tip) of the thermometer should be just below the elbow in the distilling head. If the thermometer bulb / tip is tool low, it will read high, if the bulb / tip is too high then it will read low as the hot vapours will pass below the thermometer into the condenser.



It is very important that the distilling flask is **NEVER** distilled to dryness, as this creates a potential risk of explosion.