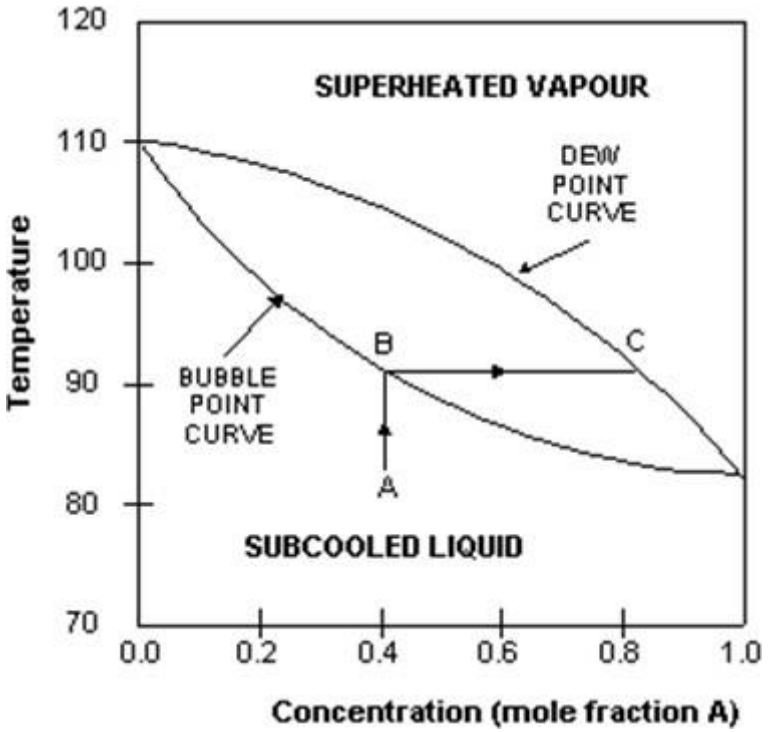
The Boiling Point Diagram

The boiling point diagram shows how the equilibrium compositions of the components in a liquid mixture vary with temperature at a fixed pressure. Consider an example of a liquid mixture containing 2 components (A and B) – a binary mixture. This has the following boiling point diagram.



The boiling point of A is that at which the mole fraction of A is 1. The boiling point of B is that at which the mole fraction of A is 0. In this example, A is the more volatile component and therefore has a lower boiling point than B. The upper curve in the diagram is called the dew-point curve while the lower one is called the bubble-point curve. The dew-point is the temperature at which the saturated vapour starts to condense. The bubble-point is the temperature at which the liquid starts to boil.

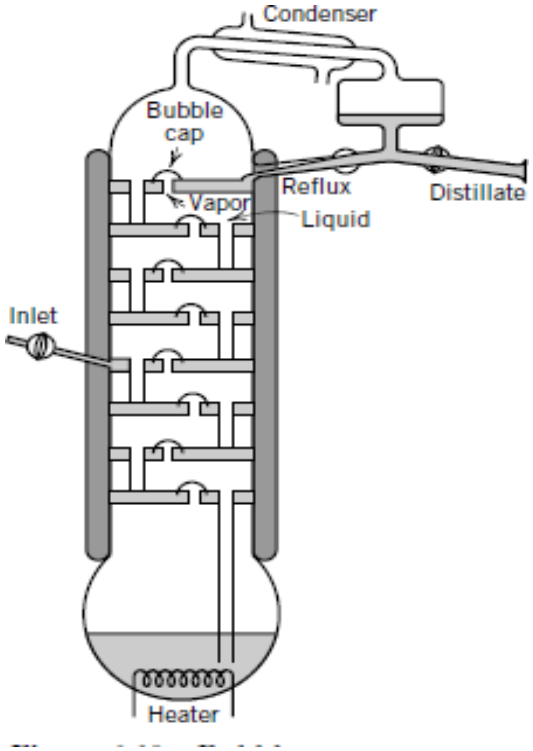
The region above the dew-point curve shows the equilibrium composition of the superheated vapour while the region below the bubble-point curve shows the equilibrium composition of the subcooled liquid.

For example, when a subcooled liquid with mole fraction of A= 0.4 (point A) is heated, its concentration remains constant until it reaches the bubble-point (point B), when it starts to boil. The vapours evolved during the boiling has the equilibrium composition given by point C, approximately 0.8 mole fraction A. This is approximately 50% richer in A than the original liquid.

This difference between liquid and vapour compositions is the basis for distillation operations.

Distillation

Distillation columns are designed based on the boiling point properties of the components in the mixtures being separated. Thus the sizes, particularly the height, of distillation columns are determined by the vapour liquid equilibrium (VLE) data for the mixtures.



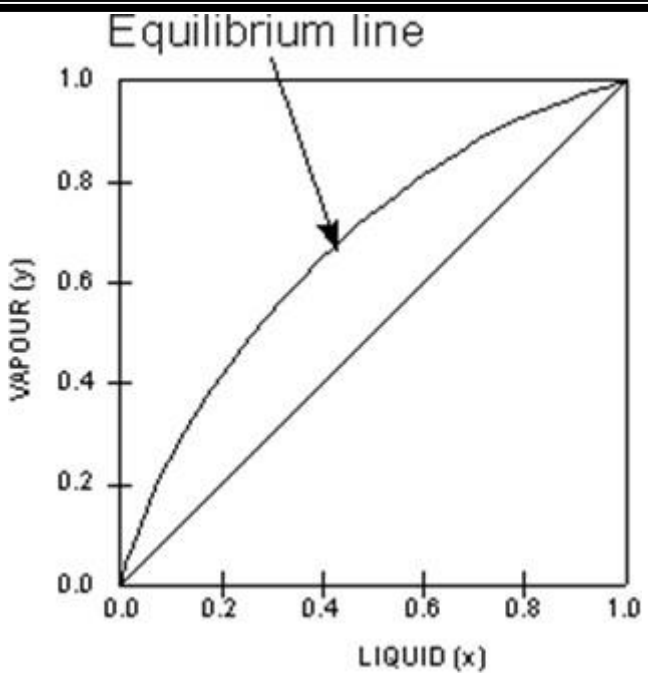
Each vaporization and condensation represented by the line *abcde* corresponds to an idealized process in that only a small fraction of the vapor is condensed and only a small fraction of the condensate is re-vaporized. It is more practical to effect the separation by means of a distillation column, such as a bubble-cap column illustrated in Figure below.

Each layer of liquid on the plates of the column is equivalent to the boiling liquid in a distilling flask, and the liquid on the plate above it is equivalent to the condenser. The vapor passes upward through the bubble caps, where it is partially condensed in the liquid and mixed with it. Part of the resulting solution is vaporized in this process and is condensed in the next higher layer, while part of the liquid overflows and runs down the tube to the next lower plate. In this way there is a continuous flow of redistilled vapor coming out the top and a continuous flow of re-condensed liquid returning to the boiler at the bottom. To make up for this loss of material from the distilling column, fresh solution is fed into the column, usually at the middle. The column is either well insulated or surrounded by a controlled heating jacket so that there will not be too much condensation on the walls. The whole system reaches a steady state in which the composition of the solution on each plate remains unchanged as long as the composition of the liquid in the distilling pot remains unchanged.

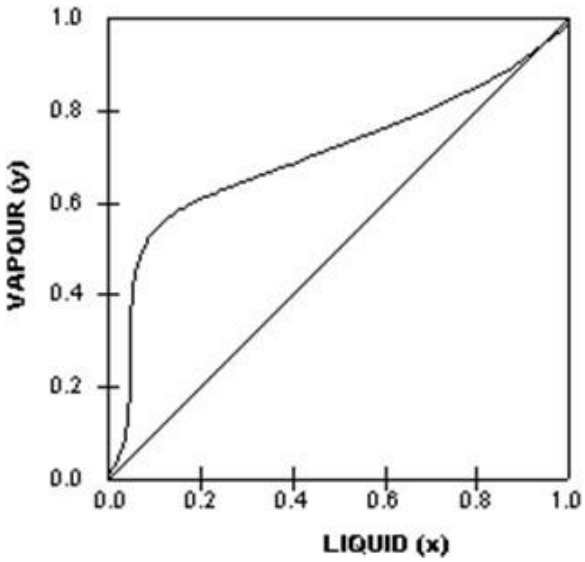
A distillation column may alternatively be packed with material that provides efficient contact between liquid and vapor and occupies only a small volume, so that there is free space to permit a large throughput of vapor. Helices of glass, spirals of screen, and different types of packing are used with varying degrees of efficiency.

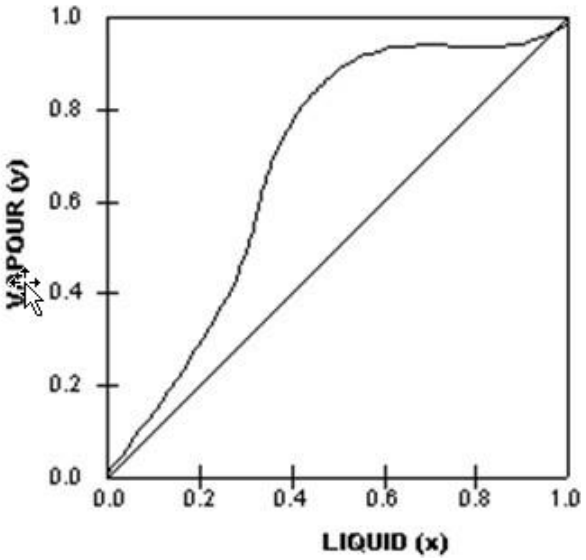
Vapour-Liquid-Equilibrium (VLE) Curves

Constant pressure VLE data is obtained from boiling point diagrams. VLE data of binary mixtures is often presented as a plot, as shown in the figure below. The VLE plot expresses the bubble-point and the dew-point of a binary mixture at constant pressure. The curved line is called the equilibrium line and describes the compositions of the liquid and vapour in equilibrium at some fixed pressure.



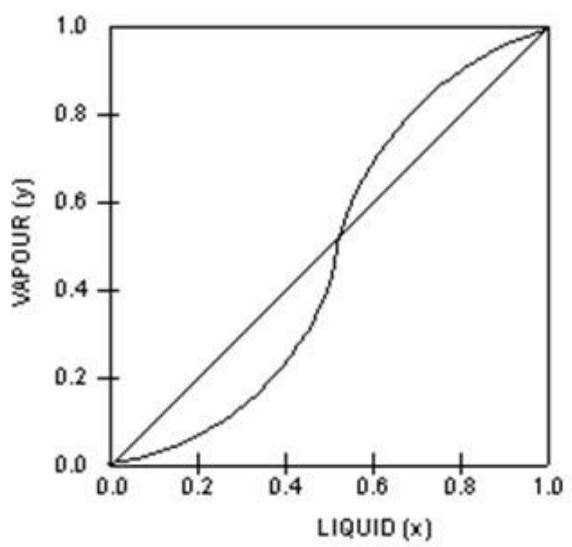
This particular VLE plot shows a binary mixture that has a uniform vapour-liquid equilibrium that is relatively easy to separate. The next two VLE plots below on the other hand, shows non-ideal systems which will present more difficult separations.



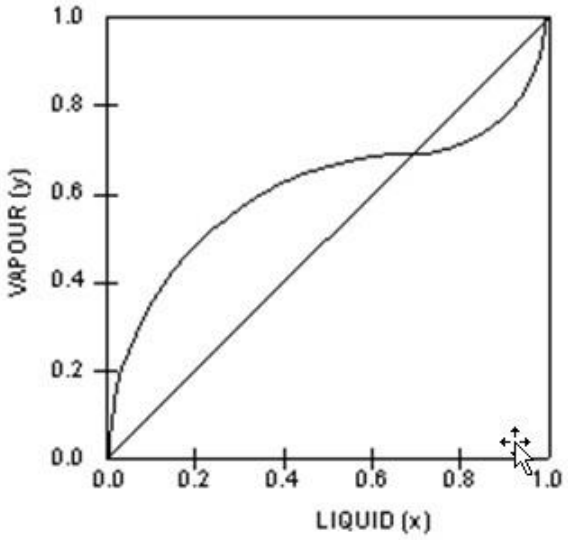


The most intriguing VLE curves are generated by azeotropic systems. An azeotrope is a liquid mixture which when vaporized, produces the same composition as the liquid. The two VLE plots below, show two different azeotropic systems, one with a minimum boiling point and one with a maximum

boiling point. In both plots, the equilibrium curves cross the diagonal lines, and this are azeotropic points where the azeotropes occur. In other words azeotropic systems give rise to VLE plots where the equilibrium curves crosses the diagonals.



Maximum Boiling Point



Minimum Boiling Point

Note the shapes of the respective equilibrium lines in relation to the diagonal lines that bisect the VLE plots. Both plots are however, obtained from homogenous azeotropic systems. An azeotrope that contains one liquid phase in contact with vapour is called a homogenous azeotrope. A homogenous azeotrope cannot be separated by conventional distillation. However, vacuum distillation may be used as the lower pressures can shift the azeotropic point. Alternatively, an additional substance may added to shift the azeotropic point to a more ‘favorable’ position.

- When this additional component appears in appreciable amounts at the top of the column, the operation is called azeotropic distillation.
- When the additional component appears mostly at the bottom of the column, the operation is called extractive distillation.

The VLE curve in figure below is also generated by an azeotropic system, in this case a heterogeneous azeotrope. Heterogeneous azeotropes can be identified by the ‘flat’ portion on the equilibrium diagram.

They may be separated in 2 distillation columns since these substances usually form two liquid phases with widely differing compositions. The phases may be separated using settling tanks under appropriate conditions.