

COMMON DISTILLATION METHODS

Simple Distillation

Nonvolatile solid dissolved in a liquid

Only one component is volatile, so distillation of the volatile component is easy. The nonvolatile solid will precipitate in the still pot as the liquid distills and is isolated afterwards by filtration. The BP of the solution is raised by the presence of the soluble nonvolatile solute. The still head temperature corresponds to the BP of the volatile component. The still pot temperature is higher than the still head temperature due to the nonvolatile solute dissolved in the solvent.

BP elevation is the basis for a MWt measurement technique for the nonvolatile solute component.

MWt determination requires very accurate temperature measurement to ± 0.01 - 0.001 °C

$$\Delta BP = i K_B m,$$

where

K_B = BP elevation constant,

m = molality = (wt solute/MWt solute)/kg solvent,

i = Van'tHoff factor (for electrolytes = total # of ions formed per mole on dissociation)

Miscible liquids:

The vapor above the liquid is enriched in the more volatile component. The composition of the distillate and the still head temperature change continuously throughout the distillation until all of the most volatile component has distilled. Good separation does not occur unless BP's of liquids are very far apart. (ΔBP of 50-100 °C.)

$$\text{eqns. } P_{\text{total}} = P^{\circ}X_A + P^{\circ}X_B \quad \text{where } X_A = (\text{mole fraction of A}) = n_A / (n_A + n_B)$$

Immiscible liquids

Normally, immiscible liquids would be separated using a separatory funnel, since they form two layers and this would be much more rapid than distillation. However, steam distillation, described below, is an example of a simple distillation of immiscible liquids.

The vapor composition in this case is not dependent on the relative amounts of A and B in the liquids, since they are in separate layers. The vapor consists of a mixture proportional to the vapor pressures of the individual pure components. The BP of the mixture is below either pure liquid BP, and remains constant until all of one component has distilled.

$$\text{eqns. } P_{\text{total}} = P^{\circ}_A + P^{\circ}_B$$

Steam Distillation

A water immiscible liquid is distilled below its normal BP using steam. This avoids thermal decomposition at the normal BP of the immiscible liquid. If the liquid is miscible with water, normal fractional distillation, described below, occurs.

$$\text{eqns. } P_{\text{total}} = P^{\circ}_A + P^{\circ}_B$$

Using $PV = nRT$ for each component, a ratio can be set up, and since V, R & T are the same for both components in the same flask, we get:

$$wt_A / wt_B = (MWt)_A \cdot P_A / (MWt)_B \cdot P_B$$

This allows the relative masses of water and immiscible component which codistill to be calculated if the MWt and vapor pressure of the immiscible component at 100 °C are known. Because the MWt of water is so low (18), substantial amounts of immiscible component will codistill even if it has a vapor pressure of only 1-10 mm at 100 °C.

Fractional Distillation (same equations as for miscible liquids on pg. 1)

Miscible liquids

As BP's become closer, separation becomes more difficult, requiring the use of a fractionating column. Multiple evaporations/condensations take place in the fractionating column. If the column is efficient, the still head temperature remains fairly constant near the BP of the most volatile component until it has all distilled, then rapidly rises to the BP of the least volatile component.

Theoretical plates are a measure of the separating capability (efficiency) of the column. A theoretical plate corresponds to a single evaporation/condensation step occurring in the column.

Types of Fractionating columns: Packed column, Vigreux, Spinning band

Column parameters: Holdup, Throughput, Backpressure, Efficiency (theoretical plate count)

Azeotropic Distillation

This is a case of fractional distillation with a severe deviation from ideal v/l behavior, in which there is a certain liquid composition, called an azeotrope, which distills at a constant temperature, without a change in composition. The BP of the azeotrope is generally lower than either pure component. This constant boiling mixture cannot be separated by distillation and may be mistaken for a pure liquid due to its constant BP.

Azeotropes may be useful, however, as in the case of the toluene/water azeotrope, which can be used to remove water from a reaction mixture. Azeotropes which boil at a temperature higher than either pure components also occur, but are less common.

Vacuum Distillation

The external pressure is lowered to reduce the BP to avoid thermal decomposition at the normal, ($P=760$ mm) BP. A Pressure vs Temperature nomograph may be used to estimate the BP vs pressure. Vacuum distillation is not commonly done on microscale due to product losses into the vacuum pump.

Water aspirator, $P = 10-30$ torr, depending on water temperature (vs 1 atm. = 760 torr).

Rotary vacuum pump, $P = 0.001-10$ torr

Diffusion pump, $10^{-8}-10^{-3}$ torr

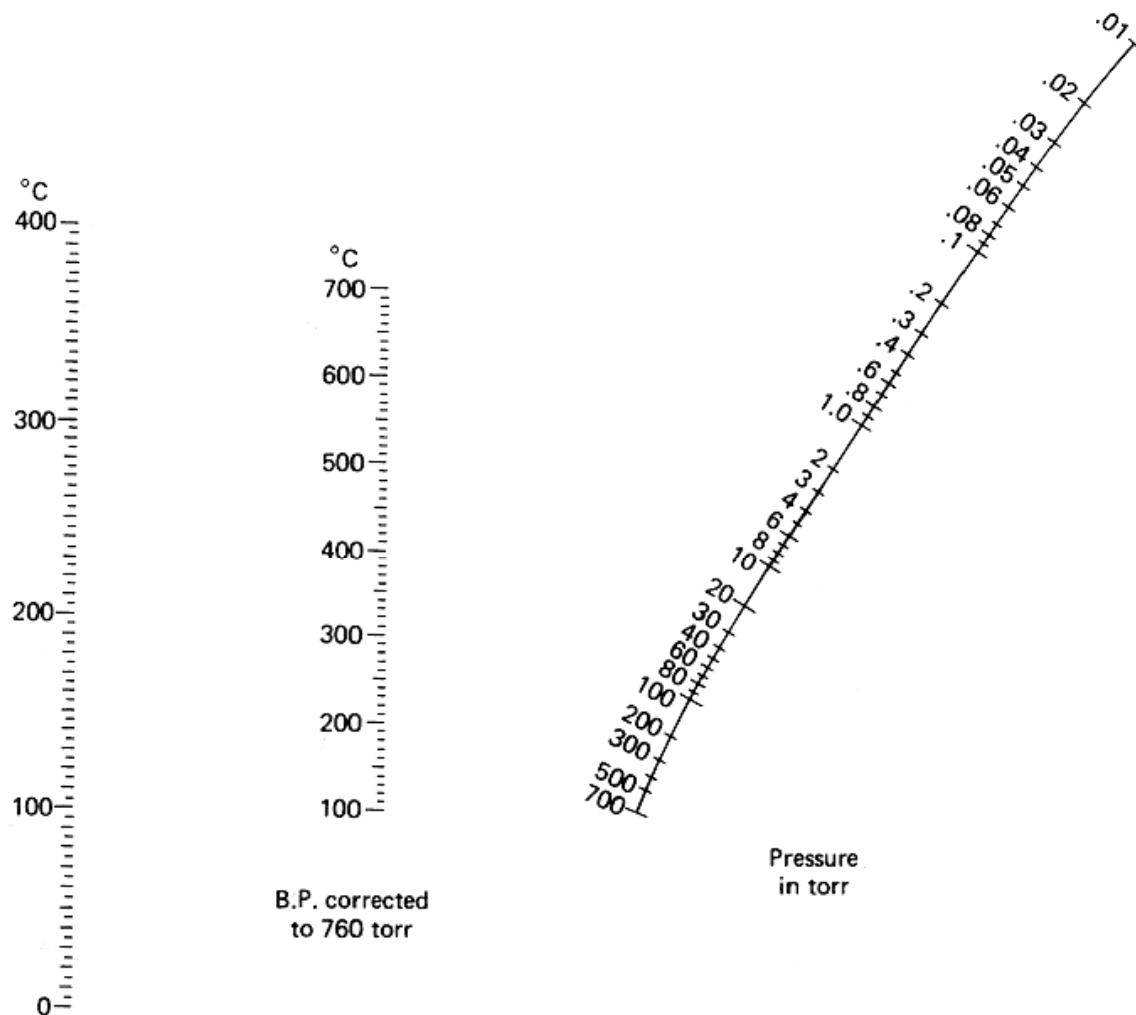
CAUTION: There is some danger of apparatus implosion; check all glassware for flaws, use a face shield and wrap large glassware with tape.

Reflux

Not actually a distillation. The solution is heated to its boiling point and a condenser is used to return the vapors to the still pot so that no loss of volatiles occur. This is commonly used to

maintain a reaction at a fixed elevated temperature to speed up a reaction. Reaction temperature may be easily changed by substituting another solvent with a higher or lower BP.

Nomograph for Calculating Boiling Points Under Vacuum



Observed B.P.

Determining the boiling point of a liquid under a certain vacuum

As an example, assume that a vacuum source pulls 20 mmHg (20 torr), and that you want to determine the boiling point of water at that vacuum. The boiling point of water at 1 atm is 100°C. With the aid of a ruler, draw a line from 20 mmHg in the pressure graph (to the right), through 100°C in the middle graph ("boiling point corrected to 760 torr", this is 1 atm), and where this line intersects the line to the left ("Observed boiling point"), take your reading which should be about 15°C. This means that at a vacuum of 20 mmHg, water will boil at 15°C..

Determining the strength of an unknown vacuum

Water is our example again. When distilling, you observe that the water comes over at a temperature of 40°C after you have waited for the temperature to stabilize. You know that the normal boiling point of water is 100°C. Draw a line through 40°C in the leftmost graph, through 100°C in the middle one, and notice where the line intersects the pressure graph. This should be about 100 mmHg. This is the pressure that the vacuum pump is producing

Note: Aspirators produce 20-30 mm Hg typically. Vacuum pumps easily pump down to <1 mm Hg.