The Proportion by Mass of Organic Compound in a Steam Distillate

The dervation below applies to *steam distillation*. In this procedure a liquid compound with a fairly high boiling point (*e.g.* ~200°C) and which is insoluble in water, is distilled in the presence of water or steam. It shows how one may calculate the percentage by mass of the compound in the distillate under steam distillation, or alternatively the molar mass of the non-aqueous component.

If the liquid compound and water are truly immiscible[1], the vapour pressure of the mixture (P_{tot}) is equal to the sum of the vapour pressures of the individual components – here water and the organic compound – at the boiling point of the mixture. This will usually be close to, but a little below, the boiling point of water, and well below the boiling point of the compound alone. This means that compounds may be distilled at a much lower temperature than would normally be the case, and protected from atmospheric oxygen by the presence of steam. This is particularly useful for temperature-sensitive compounds and those susceptible to oxidation.

The calculation is only approximate for two main reasons:

- No compound is completely immiscible with water.
- Ideal behaviour is assumed, since the ideal gas law is invoked. Gases depart from ideal behaviour to the greatest extent when they are close to the temperature at which they condense (clearly the case here.)
- The compound is assumed to be pure. Clearly this is not the case with a crude extract from cloves, for example.

Since

$PV = nRT$ and since $n = \dfrac{m}{M}$, where m is the mass of vapour or gas, and M is its molar mass.

$P \propto \dfrac{n}{M}$ at a given temperature and pressure (e.g. the boiling point of the mixture at atmospheric pressure).

Let m_w, M_w and P_w refer to the number of mass and partial pressure of water in a certain volume of the vapour before it condenses., and m_c, M_c, and P_c refer to the number of moles and partical pressure of the compound, in the same volume of the vapour. The temperature is the boiling point of the mixture, as recorded by a thermometer adjacent to the entrance to the condenser.

Dividing P_c by P_w gives:

$$\frac{P_c}{P_w} = \frac{m_c M_w}{m_w M_c}$$

$$\therefore \frac{P_c M_c}{P_w M_w} = \frac{m_c}{m_w}$$

$\therefore$ But proportion by mass of the compound in the distillate is given by $\dfrac{m_{lc}}{m_{lw} + m_{lc}}$, where m_{lc} and m_{lw} refer to the masses of compound and water in the liquid distillate. Since the liquid has the same composition as the vapour it condenses from

$$\text{Proportion by mass of compound in distillate} = \frac{m_{lc}}{m_{lw} + m_{lc}} = \frac{m_c}{m_w + m_c} = \frac{M_c P_c}{M_w P_w + M_c P_c}$$

At the boiling point of the mixture, atmospheric pressure, $P_{at}, = P_w + P_c$, and so:

$$\text{Proportion of compound in mixture} = \frac{(P_{at} - P_w)M_c}{P_w M_w + (P_{at} - P_w)M_c}$$

Given the values of $P_w, P_{at}, M_w,$ and M_c, the proportion by mass of the organic compound in the distillate may be calculated.

Alternatively, given P_w, P_{at}, and M_w, the molar mass of the compound may be estimated.

The proportion by mass is usually expressed as a percentage.

Note that the percentage by mass of the compound in the distillate will be lower for higher-boiling compounds, and greater for ones of greater molar mass.

[1] Note that the *vapours* will always be completely miscible.