

2106NSC

Physical & Analytical Chemistry

Thermodynamics 9

Mixtures of volatile liquids

Why do or don't things mix – Gases

Free energy change when mixing two ideal gases:

$$G_{\text{initial}} = n_A \cdot [\mu_A^\ominus + R \cdot T \cdot \ln (p/p^\ominus)] + n_B \cdot [\mu_B^\ominus + R \cdot T \cdot \ln (p/p^\ominus)]$$

$$G_{\text{final}} = n_A \cdot [\mu_A^\ominus + R \cdot T \cdot \ln (p_A/p^\ominus)] + n_B \cdot [\mu_B^\ominus + R \cdot T \cdot \ln (p_B/p^\ominus)]$$

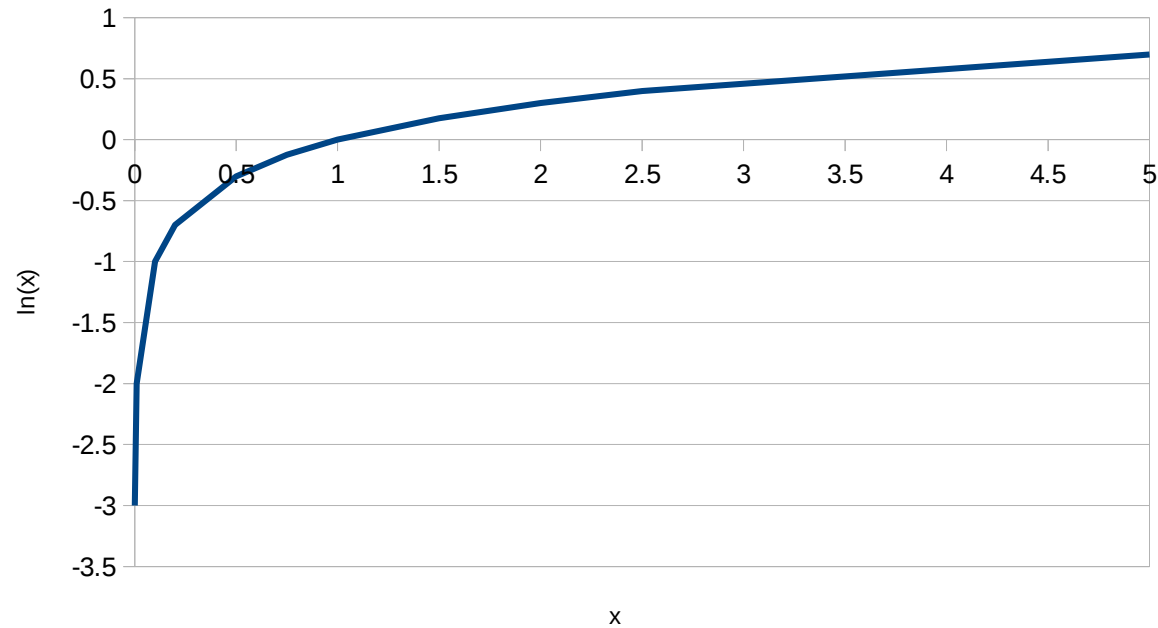
$$\Delta_{\text{mix}}G = G_{\text{final}} - G_{\text{initial}} = n_A \cdot R \cdot T \cdot \ln (p_A/p) + n_B \cdot R \cdot T \cdot \ln (p_B/p)$$

$$= n_A \cdot R \cdot T \cdot \ln (x_A) + n_B \cdot R \cdot T \cdot \ln (x_B)$$

$$= n \cdot R \cdot T \cdot [x_A \cdot \ln (x_A) + x_B \cdot \ln (x_B)]$$

Why do or don't things mix – Gases

$$\Delta_{\text{mix}}G = n \cdot R \cdot T \cdot [x_A \cdot \ln(x_A) + x_B \cdot \ln(x_B)]$$



$$0 \leq x_A \leq 1 \quad \Rightarrow \quad \ln(x_A) < 0 \quad \Rightarrow \quad \Delta G_{\text{mix}} < 0 \quad \Rightarrow \quad \text{gases mix!}$$

Why do or don't things mix – Gases

In ideal gases at constant temperature, $\Delta_{\text{mix}}H = 0$.

So mixing is a purely entropic effect.

In real gases, there are changes in ΔH upon mixing, due to intermolecular forces between molecules.

$\Delta_{\text{mix}}H$ and $\Delta_{\text{mix}}S$ depend on p and T , however $\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T \cdot \Delta_{\text{mix}}S$ is still generally negative.

Why do or don't things mix – Liquids

Free energy change when mixing two ideal liquids:

$$G_{\text{initial}} = n_A \cdot \mu_{A(l)}^* + n_B \cdot \mu_{B(l)}^*$$

$$G_{\text{final}} = n_A \cdot [\mu_{A(l)}^* + R \cdot T \cdot \ln(x_A)] + n_B \cdot [\mu_{B(l)}^* + R \cdot T \cdot \ln(x_B)]$$

$$\Delta_{\text{mix}}G = G_{\text{final}} - G_{\text{initial}} = n \cdot R \cdot T \cdot [x_A \cdot \ln(x_A) + x_B \cdot \ln(x_B)]$$

In ideal solutions at constant temperature, $\Delta_{\text{mix}}H = 0$. So mixing is a purely entropic effect .

In real liquids, there are changes in $\Delta_{\text{mix}}H$ due to intermolecular forces between molecules and they differ between A-A, B-B and A-B. Thus: $\Delta_{\text{mix}}H > 0$ is possible.

An enthalpy change may occur and dominate the entropic effect .

$\Delta_{\text{mix}}G$ can thus be positive or negative; this will determine whether or not the liquids mix.

Phase diagram of mixtures of volatile liquids

Let's assume a mixture of two volatile liquids, A and B.

When the liquid and vapour phases are in equilibrium, the compositions are not necessarily the same.

The vapour will have more of the more volatile component.

Phase diagram of mixtures of volatile liquids

The total vapour pressure p in an ideal system is given by:

$$p = z_A \cdot p_A^* + z_B \cdot p_B^* = p_B^* + (p_A^* - p_B^*) \cdot z_A \quad \Rightarrow \quad p \text{ vs. } z_A \text{ is linear}$$

z_A and z_B are the mole fractions of A and B in the liquid.

Dalton's Law:

$$y_A = p_A / p \quad ; \quad y_B = p_B / p$$

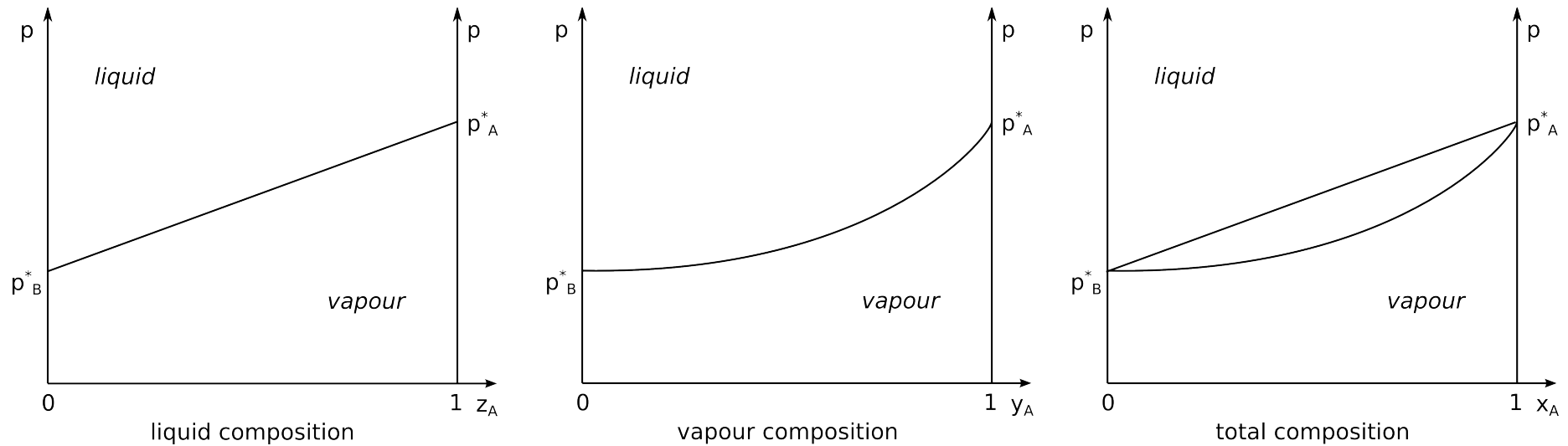
y_A and y_B are the mole fractions of A and B in the vapour.

Using Raoult's Law:

$$p_A = z_A \cdot p_A^* \Rightarrow y_A = z_A \cdot p_A^* / p \quad ; \quad y_B = 1 - y_A$$

$$\Rightarrow [\dots] \Rightarrow p = \frac{p_A^* \cdot p_B^*}{p_A^* + (p_B^* - p_A^*) \cdot y_A} \quad \Rightarrow \quad p \text{ vs. } y_A \text{ is curved}$$

Phase diagram of mixtures of volatile liquids



Example:

If there are 2 mol of A and 3 mol of B in the liquid: $z_A = 2/5$; $z_B = 3/5$

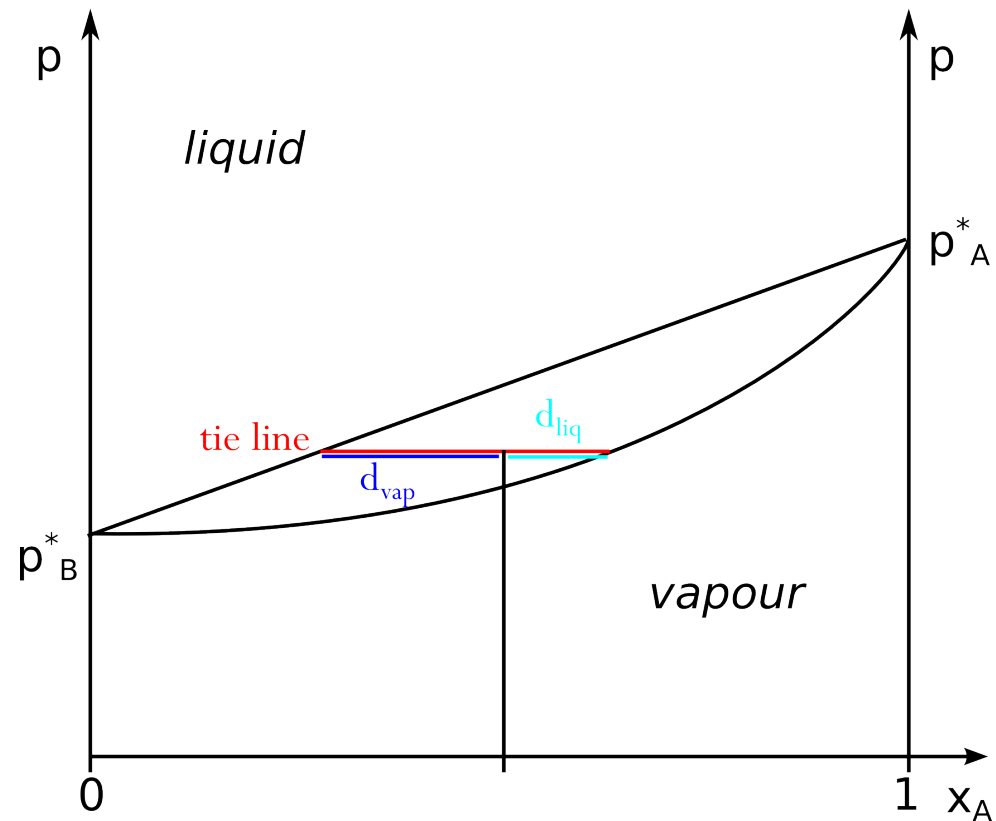
If there are 1 mol of A and 2 mol of B in the vapour: $y_A = 1/3$; $y_B = 2/3$

The mole fractions of the total system are thus: $x_A = 3/8$; $x_B = 5/8$

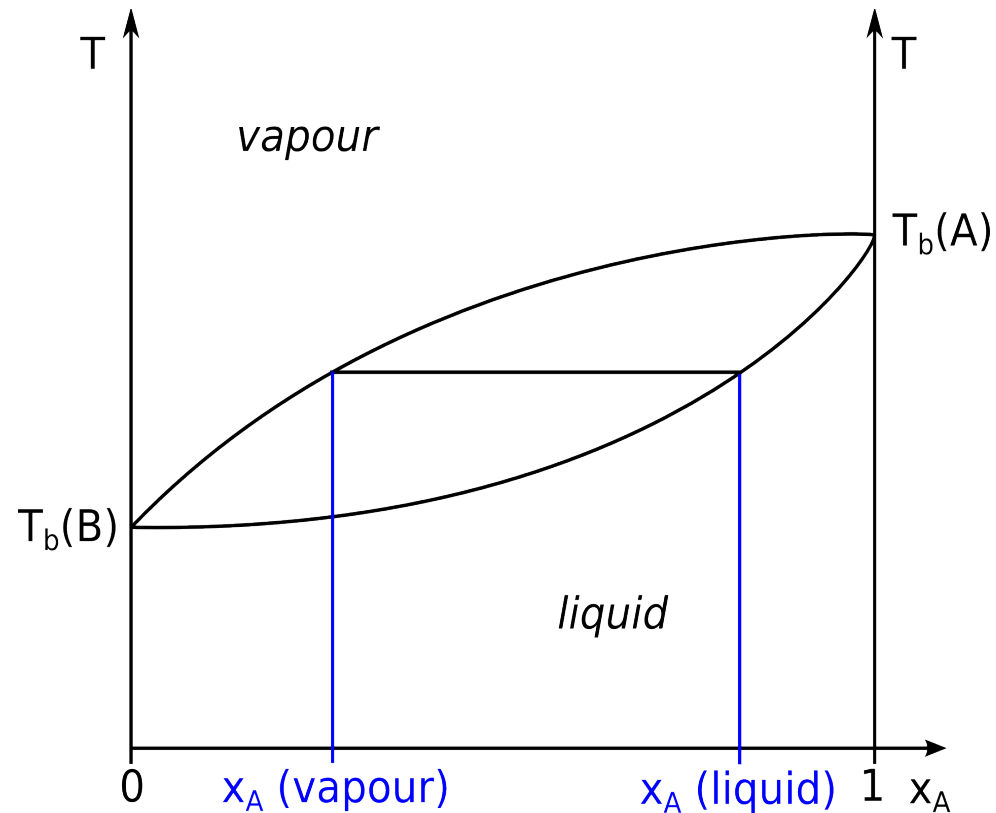
Phase diagram of mixtures of volatile liquids

Lever rule:

$$\frac{n_{\text{liquid}}}{n_{\text{vapour}}} = \frac{d_{\text{liq}}}{d_{\text{vap}}}$$



Temperature-composition diagrams

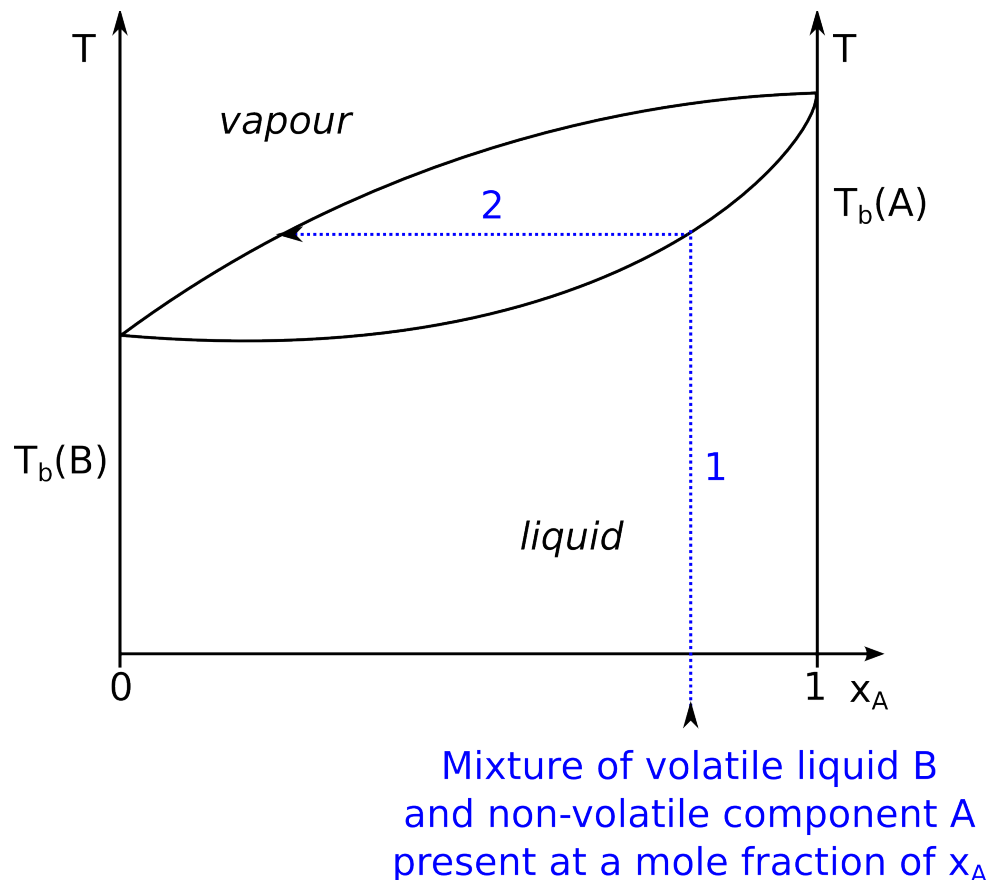


Temperature-composition diagrams show states at a single pressure.

Typical diagram for many real mixtures.

Distillation: temperature-composition diagrams

Distillation is based on vapour and liquid having different compositions.



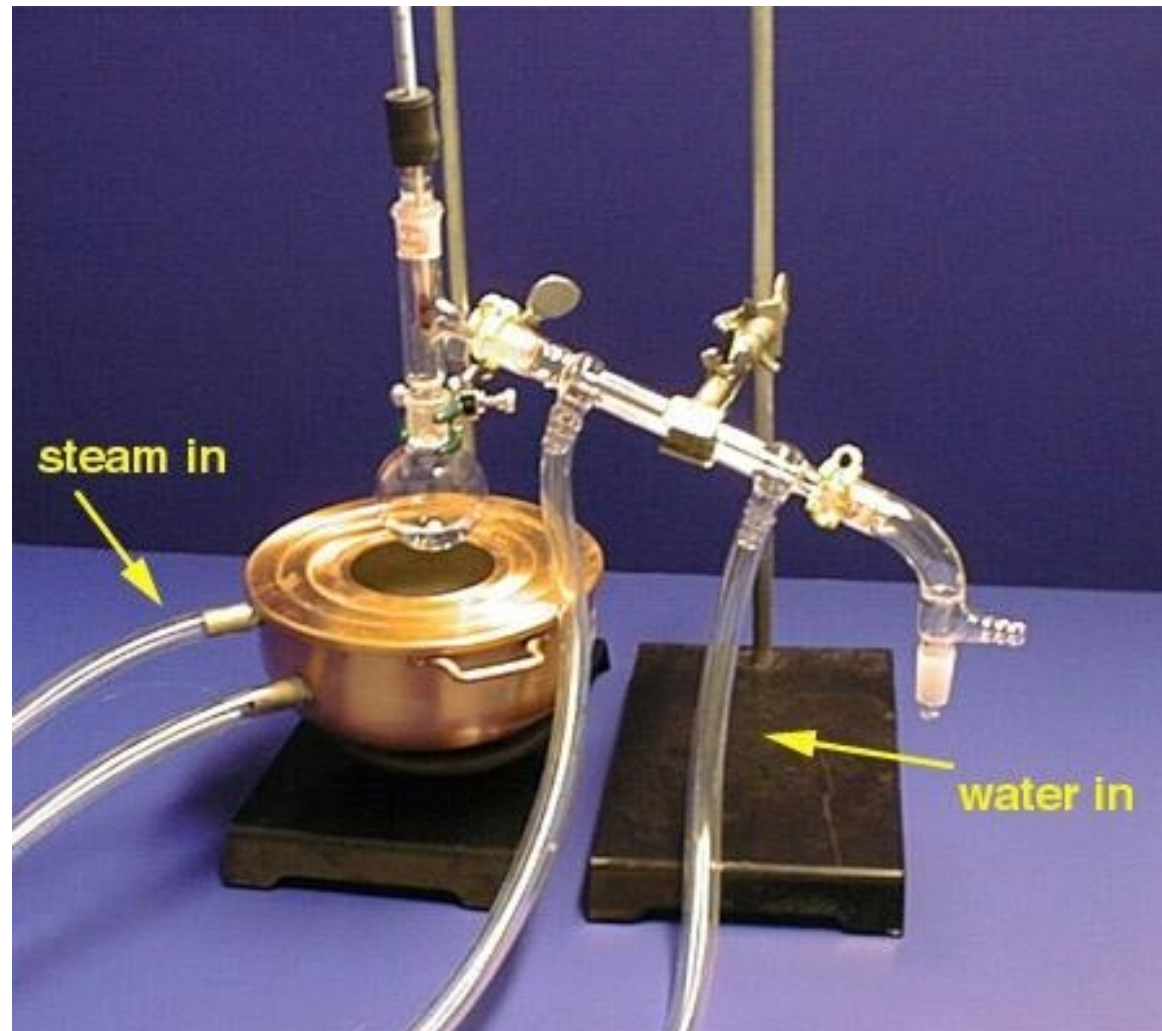
1 – A mixture of volatile liquid B and non-volatile component A is heated.

2 – When the boiling point of the mixture at this mole fraction is reached, a vapour phase with a much lower mole fraction of x_A is obtained.

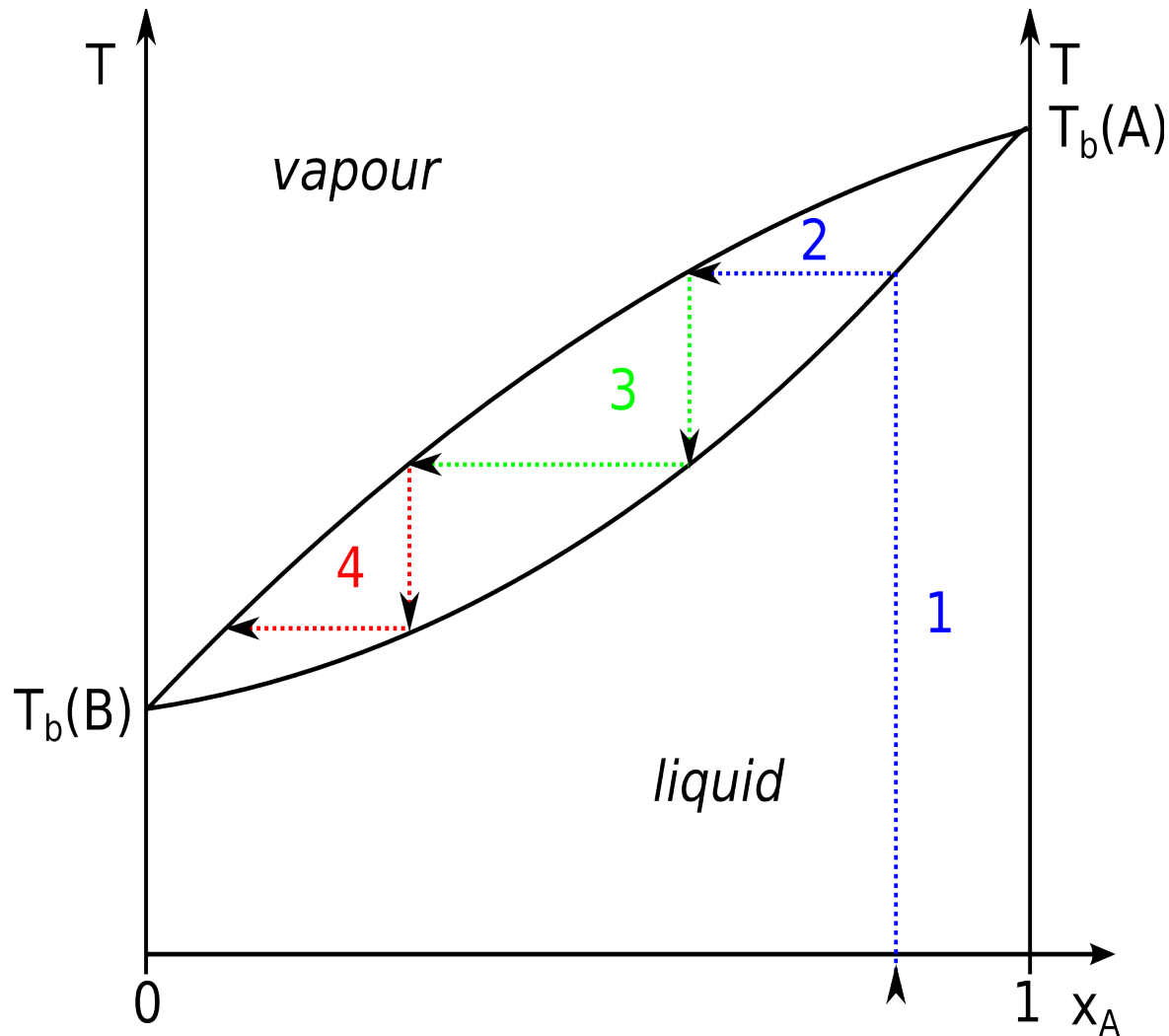
The vapour is withdrawn and condensed. The condensate consists of liquid B at higher purity.

=> **Simple distillation**

Simple distillation



Fractional distillation



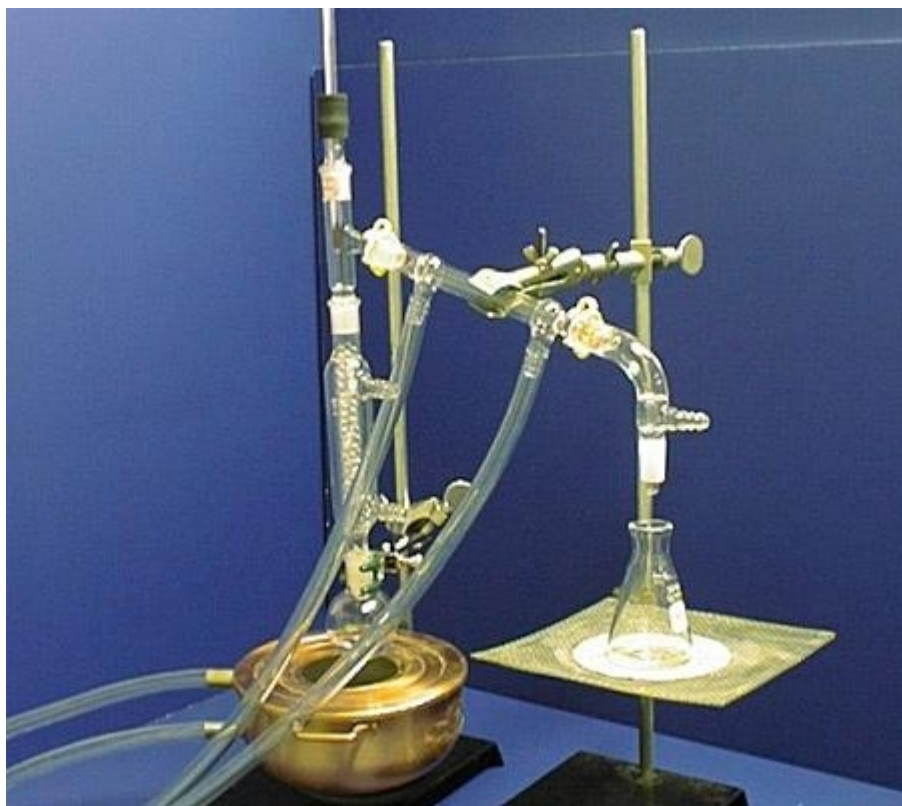
1 – A mixture of volatile liquid B and less volatile component A is heated.

2 – When the boiling point of the mixture at this mole fraction is reached, a vapour phase with a much lower mole fraction x_A is obtained.

3 – When the vapour from (2) is condensed and will reach the boiling point at the new mole fraction, the resulting vapour will again show a purification with respect to B.

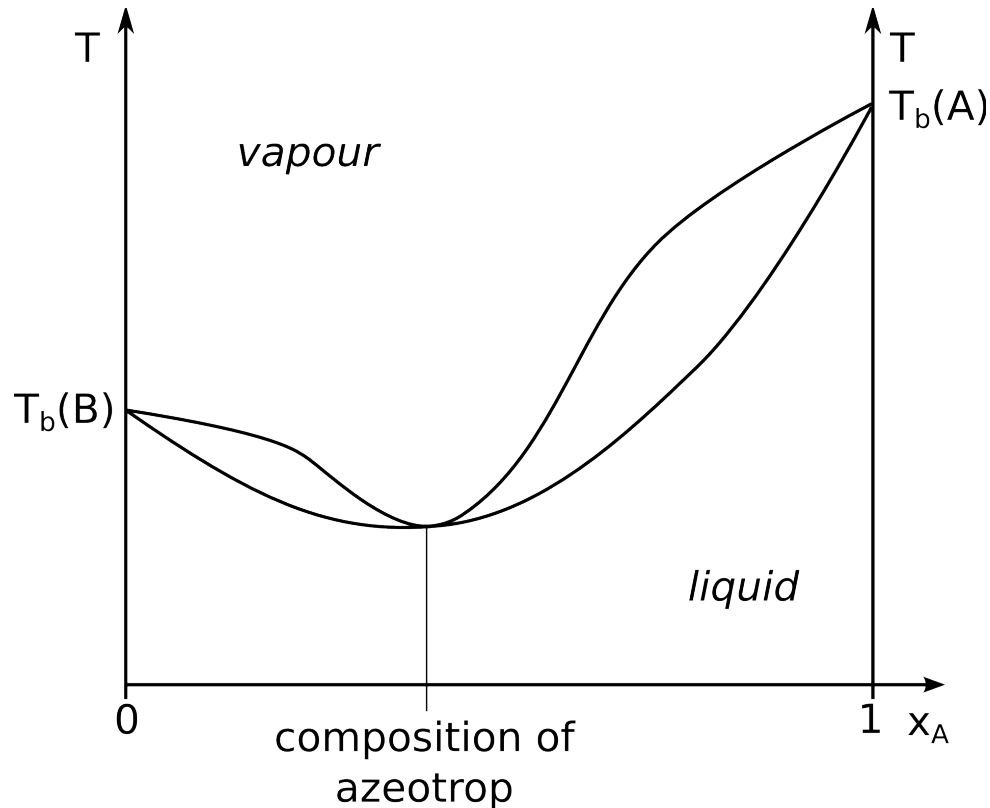
=> **Fractional distillation**

Fractional distillation



The efficiency of a fractionating column is expressed in terms of the **number of theoretical plates**. This is the number of effective vapourisation and condensation steps that are required to achieve a condensate of given composition from a given distillate.

Mixtures of volatile liquids



Azeotrope: liquid and vapour have same composition.

Evaporation will continue without changing composition.

Distillation stops being useful:
EtOH/H₂O: 4% H₂O at 78°C.

Low boiling azeotropes: less favourable to mixing than ideal; A-B interactions unfavourable; e.g. EtOH/H₂O

High boiling azeotropes: more favourable to mixing than ideal; A-B interactions stabilise solution; e.g. HCCl₃/H₃C-CO-CH₃

Distillation of immiscible liquids

If liquids are immiscible, then we can treat the solutions separately, but the vapour pressure is the sum of the two vapour pressures .

Boiling under normal conditions occurs when $p = p_A^* + p_B^* = 1 \text{ atm}$

The pair possess a lower boiling point than either pure liquid alone .

Heat-sensitive compounds can thus be distilled at lower temperature: **steam distillation**.

(These days, distillation of delicate compounds is done under reduced pressure).

Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2nd Edition, Structural Chemistry Program, Griffith University.

Sections III.1.1, III.1.2, III.5.1-III.5.5

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9th Edition, Oxford University Press.

Sections 5.2 – 5.4 (pp. 161-169)

Sections 5.6 – 5.7 (pp. 176-181)