Chap. 6. Phase diagrams

Phase - a state of matter that is uniform throughout, not only in chemical composition but also in physical state

Constituent - chemical species that is present

Component - chemically independent constituent of a system

Number of phases

Phase Rule:

$$F = C - P + 2$$

Number of components

Variance - number of intensive variables that can be changed independently without disturbing the number of phases - Pressure, Temperature, Relative Compositions

Phase Rule: F= # of intensive variables - # of constraints

Consider systems with C components and P phases.

# of intensive variables: 2 + $\underline{(C\text{-}1)P}$

↑ Pressure
and
Temperature

↑ For a phase α, C mole fractions $x_1^\alpha, \cdots, x_C^\alpha$ which satisfy the condition

$$x_1^\alpha + x_2^\alpha + \cdots + x_C^\alpha = 1$$

⟶ C-1 independent variables for each phase

# of constraints: C(P-1)

For a component J, $\Big|\ \mu_J(\alpha) \mathrel{|}\!\!= \mu_J(\beta) \mathrel{|}\!\!= \cdots \mathrel{|}\!\!= \mu_J(P)\ \Big|$

P-1 constraints for each component

$$F = 2 + (C-1)P - C(P-1) = 2 + CP - P - CP + C = C - P + 2$$

One-component system: $F = 3 - P$ ➡ More than three phases cannot coexist

Two-component system: $F = 4 - P$ ➡ More than four phases cannot coexist

Two-component system $F = 4 - P$

1. Vapor pressure diagrams of two volatile liquids A and B

Rault's law: $p_A = x_A p_A^*$ **and** $p_B = x_B p_B^*$

Mole fraction of A in liquid ↰ **Mole fraction of B in liquid** ↰

$$p = p_A + p_B = p_B^* + (p_A^* - p_B^*)x_A$$

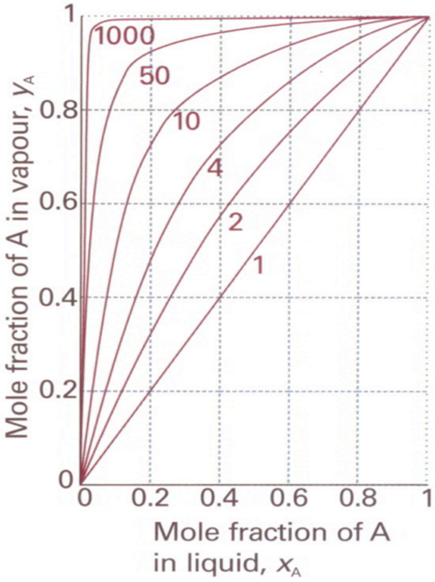
Dalton's law: $y_A = \frac{p_A}{p} = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A}$ **and** $y_B = \frac{p_B}{p} = \frac{x_B p_B^*}{p_A^* + (p_B^* - p_A^*)x_B}$

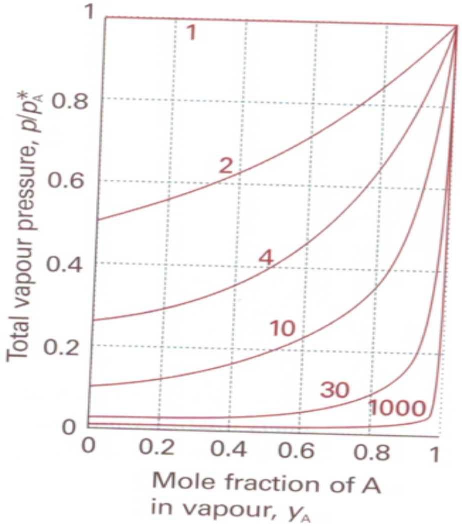
↰ **Mole fraction of A in gas** ↰ **Mole fraction of B in gas**

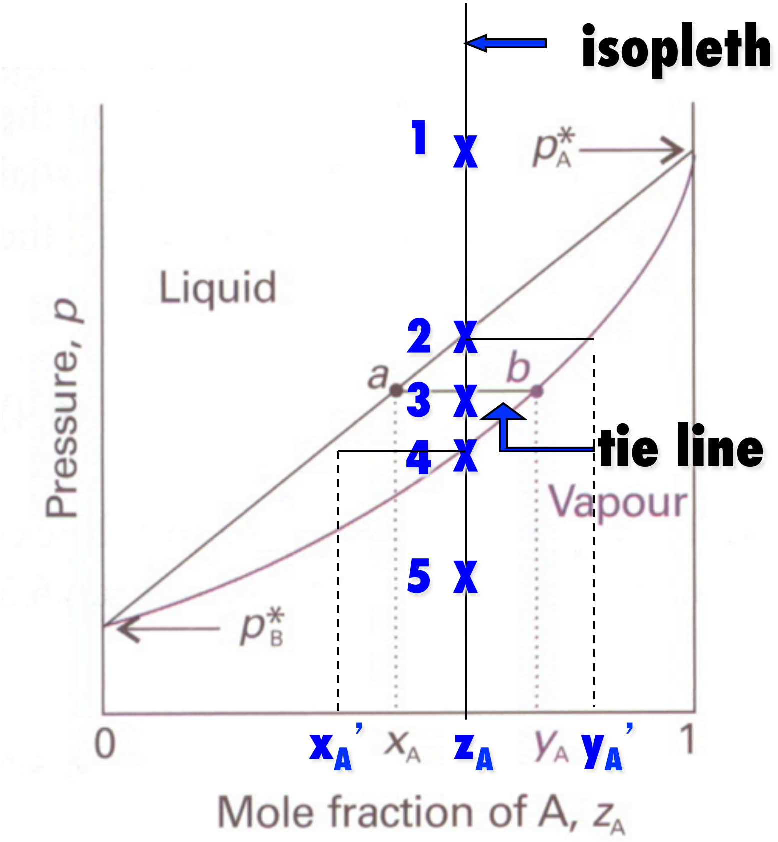
If $p_A^* > p_B^*, y_A > x_A$ $p = p_B^* + (p_A^* - p_B^*)x_A = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*)y_A}$

Curves of y_A for different values of

$$\frac{p_A^*}{p_B^*}$$







1 - only liquid of component z_A

2 - liquid of composition z_A, gas of composition y_A' forming

3 - liquid of composition x_A in equilibrium with gas of composition y_A

4 - gas of composition z_A, liquid trace of composition x_A'

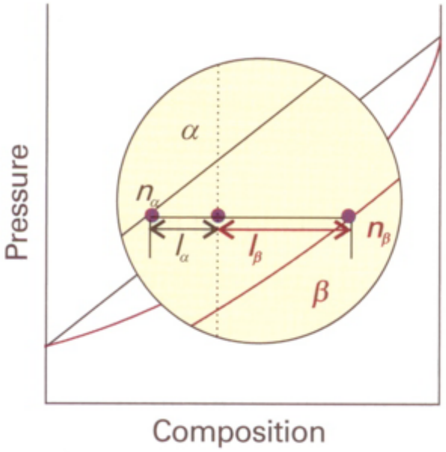
5 - gas of composition z_A

Lever rule $n_\alpha l_\alpha = n_\beta l_\beta$

$$n = n_\alpha + n_\beta$$

$$n z_A = n_\alpha x_A + n_\beta y_A = n_\alpha z_A + n_\beta z_A$$

$$n_\alpha l_\alpha = n_\alpha (z_A - x_A) = n_\beta (y_A - z_A) = n_\beta l_\beta$$

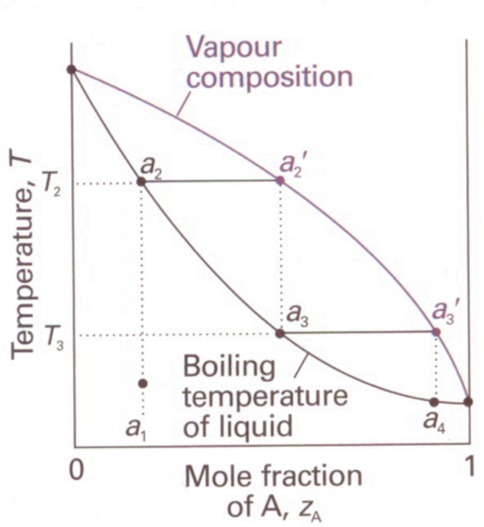


Temperature-composition diagram

Simple distillation - the vapor is withdrawn and condensed

Fractional distillation - repeated boiling and condensation

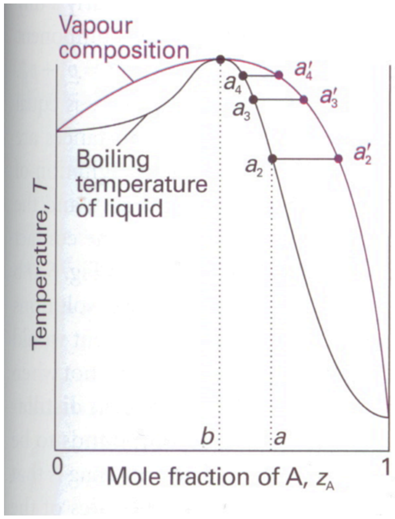
# of theoretical plates: # of effective vaporization/condensation steps

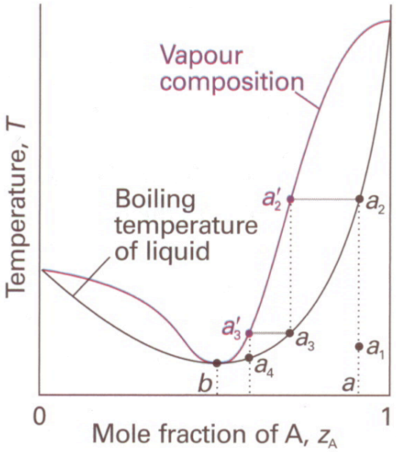


Azeotrope - the point where the liquid and the vapor has the same (non-pure) composition at the same temperature

High boiling azeotrope - the most stable

Low boiling azeotrope - the least stable





Liquid-liquid mixture

Immiscible liquids : $p = p_A^* + p_B^*$ **- always 2 phases, F=2**

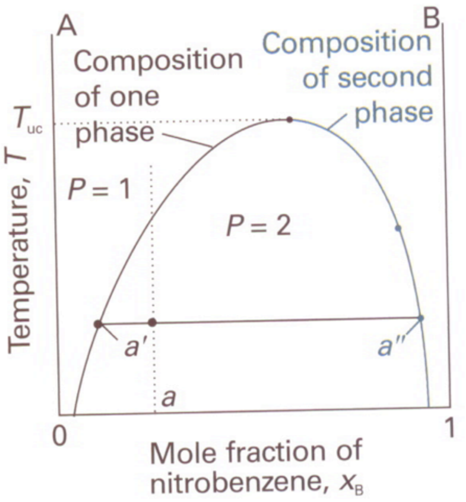
Partially miscible: mixes partially depending on temperature

F=3 or 2

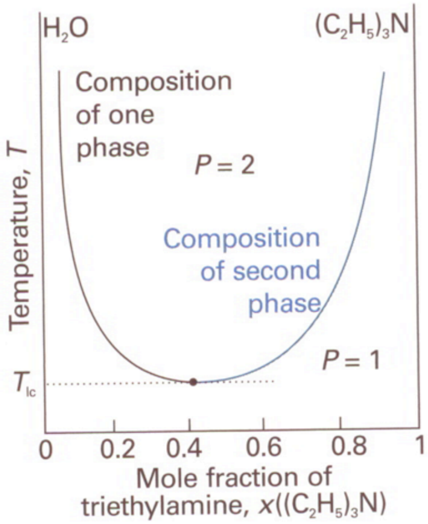
T_{uc}**: upper critical solution temperature**

T_{lc} **: lower critical solution temperature**

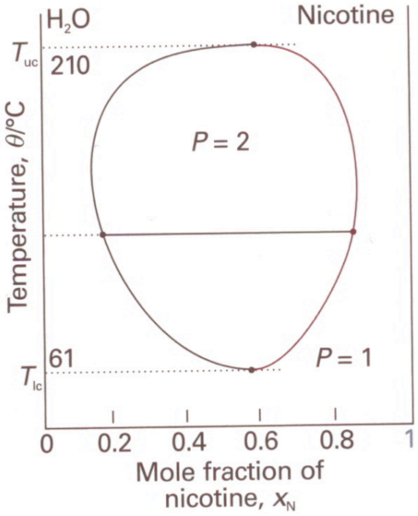
Two phases for $T < T_{uc}$



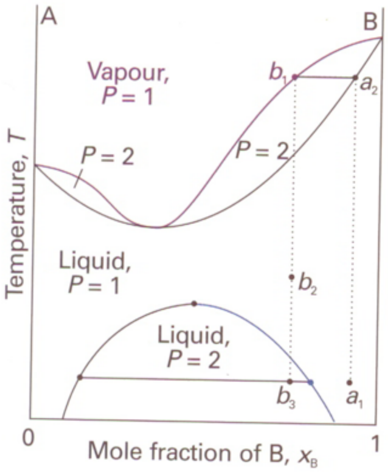
Two phases for $T > T_{lc}$



Two phases for $T_{lc} < T < T_{uc}$



Distillation of partially miscible liquids



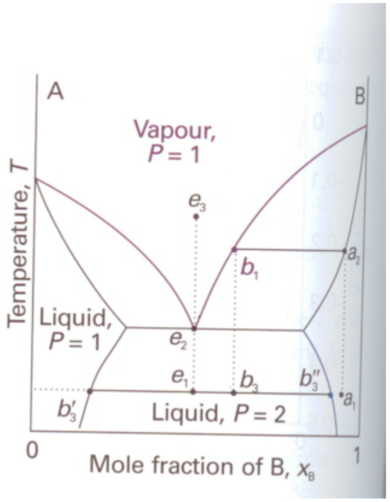
$a_1 \xrightarrow{\text{distill}} a_2$ and b_1

↓ condense

1 phase solution b_2

↓

2 phase solution b_3' and b_3''

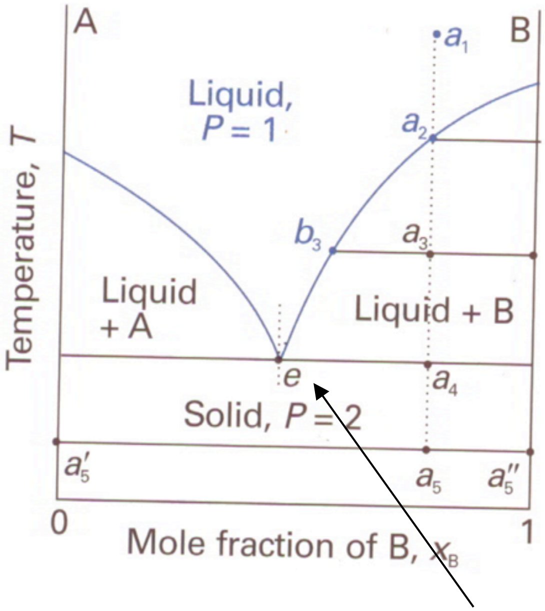


$a_1 \xrightarrow{\text{distill}} a_2$ and b_1

↓

2 phase solution b_3' and b_3''

Liquid-solid phase diagram



$a_1 \rightarrow a_2$: Pure solid of B begins to form.
Liquid of composition a_2

$a_2 \rightarrow a_3$: Pure solid of B, and liquid of composition b_3

$a_3 \rightarrow a_4$: Pure solid of B, and liquid of composition e

$a_4 \rightarrow a_5$: Pure solids A and B.

Eutectic composition: mixture with the lowest melting point. Solidifies at a single definite temperature.