Phase Diagrams of Binary Systems

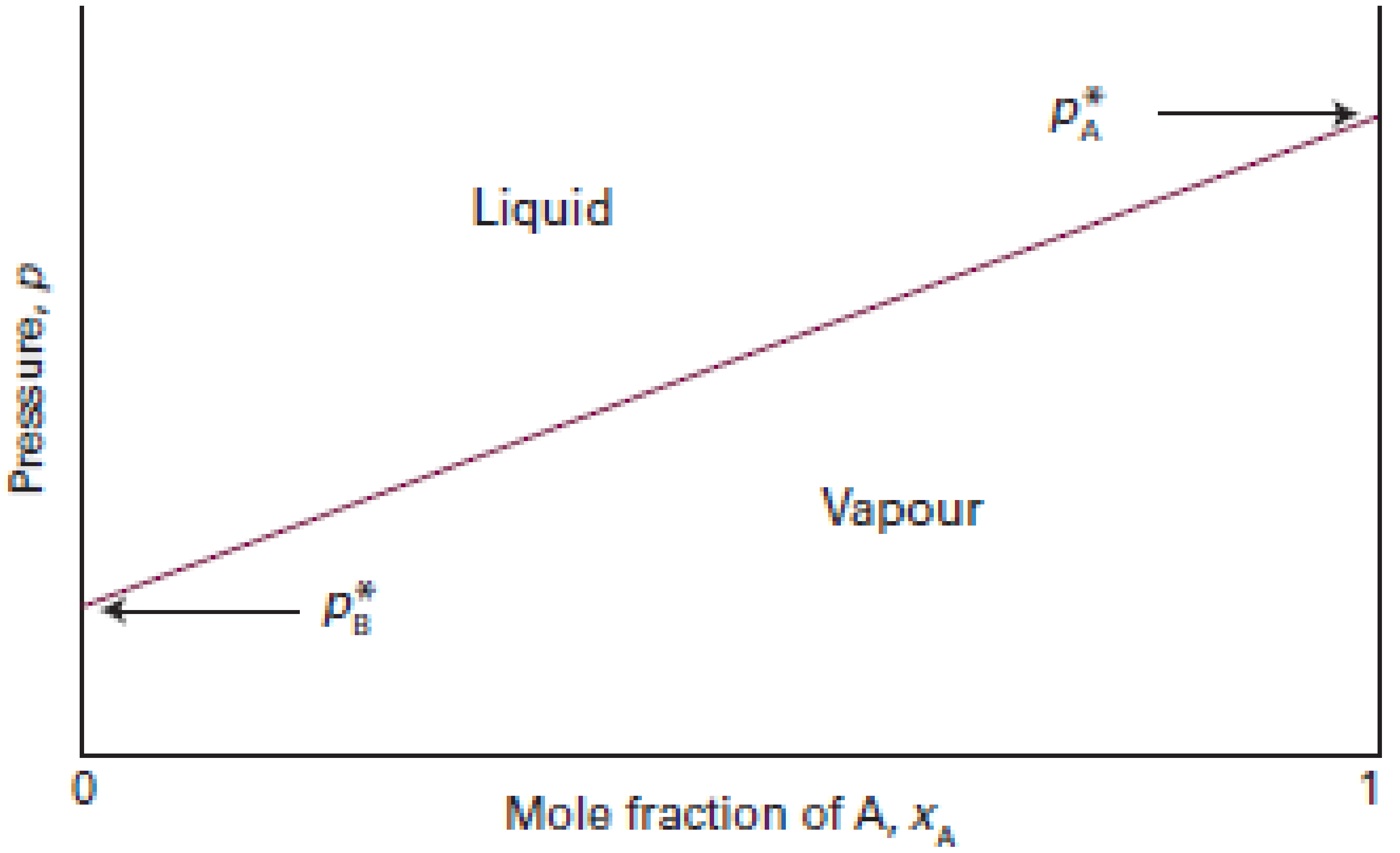
The partial vapour pressures of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixture by Raoult's law

$$p_A = x_A p_A^*$$
$$p_B = x_B p_B^*$$

p_A = the vapour pressure of pure A

p_B = the vapour pressure of pure B

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*) x_A$$ Total Vapour Pressure



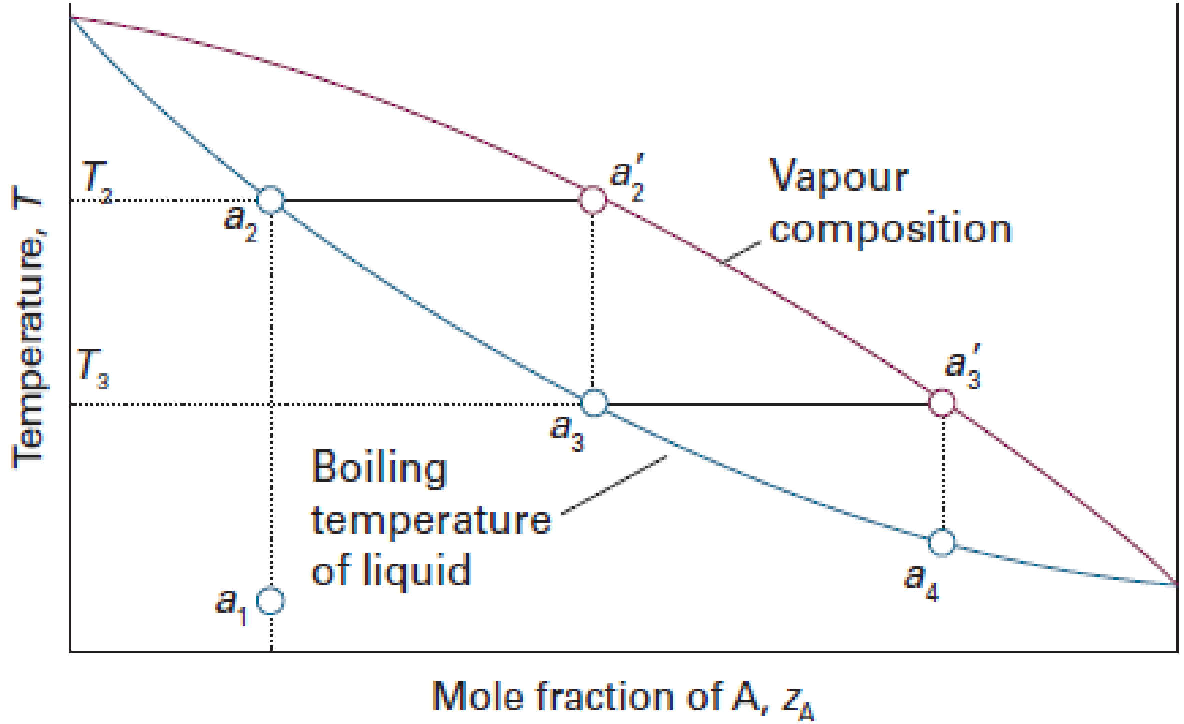
Raoult's law

$$p_A = x_A p_A^*$$

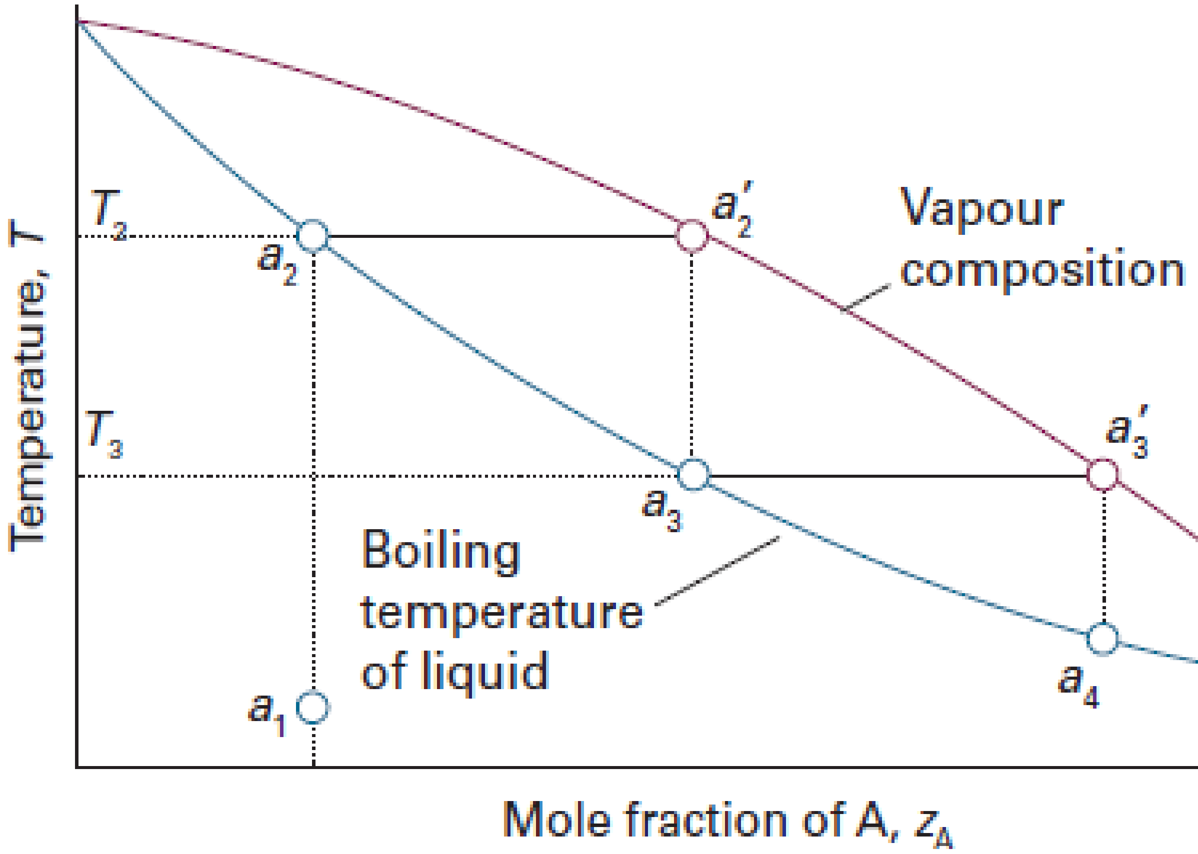
$$p_B = x_B p_B^*$$

Temperature–Composition Diagrams

Temperature–composition diagram is a phase diagram in which the boundaries show the composition of the phases that are in equilibrium at various temperatures (and a given pressure, typically 1 atm).



Successive boilings and condensations of a liquid originally of composition $a1$ lead to a condensate that is pure A.
The separation technique is called **fractional distillation.**

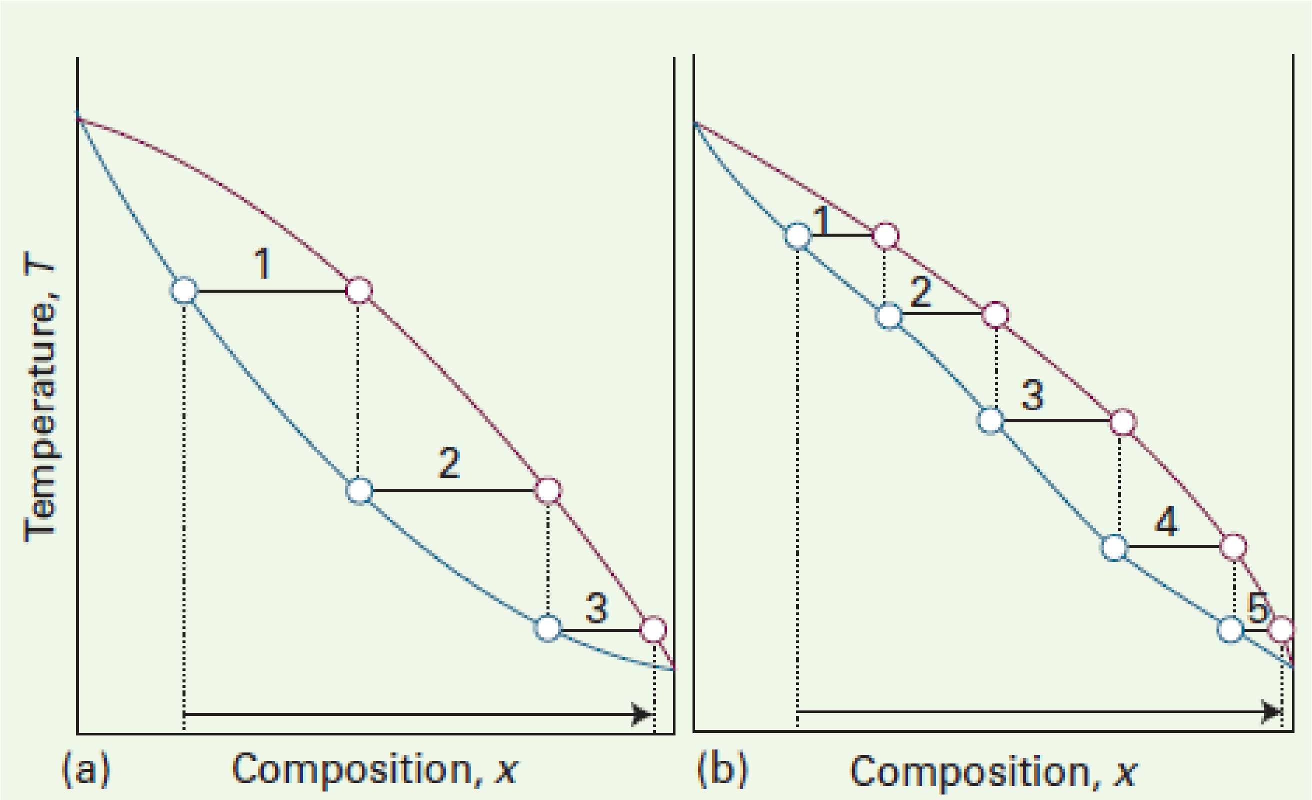


In a simple distillation, the vapour is withdrawn and condensed.
This technique is used to **separate a volatile liquid from a non-volatile solute or solid**.

In fractional distillation, the boiling and condensation cycle is repeated successively.
This technique is used to **separate volatile liquids**.

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

Theoretical Plates



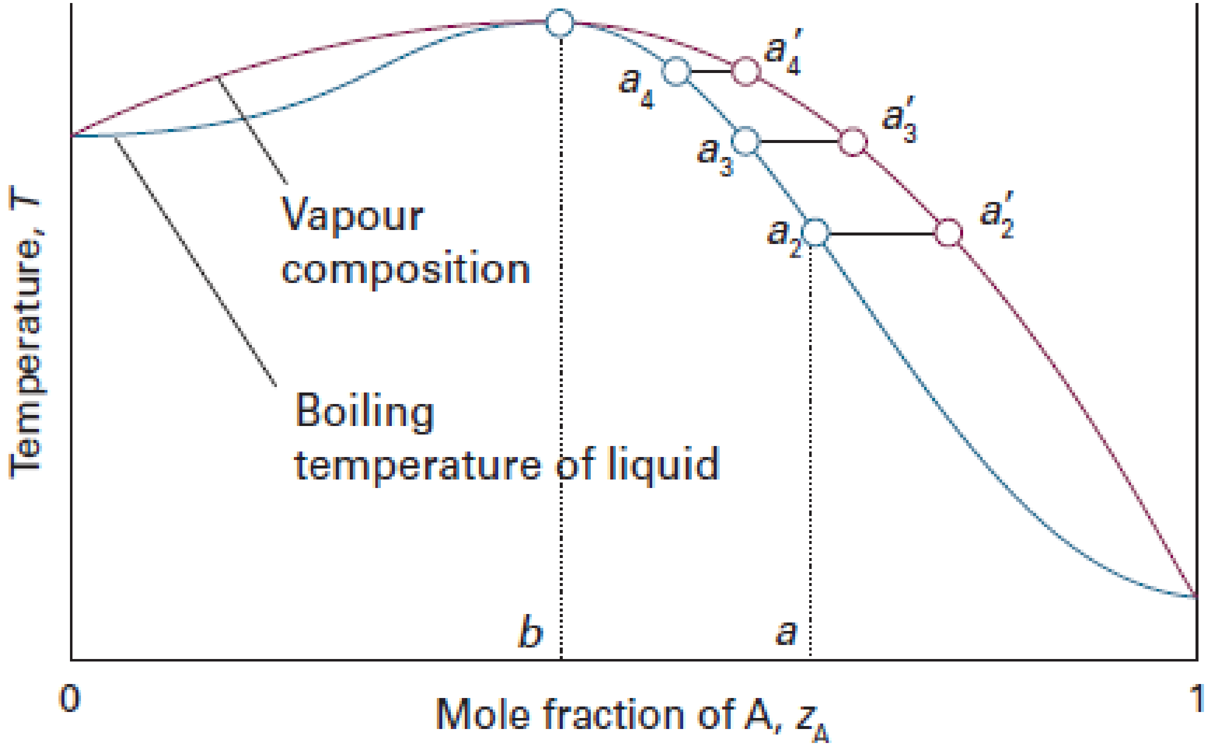
In figure a, the fractionating column must correspond to **three theoretical plates**.

In figure b, the fractionating column must be designed to correspond to **five theoretical plates**.

The number of theoretical plates is the number of steps needed to bring about a specified degree of separation of two components in a mixture.

Azeotropes

- Although many liquids have temperature–composition phase diagrams resembling the ideal version, in a number of important cases there are



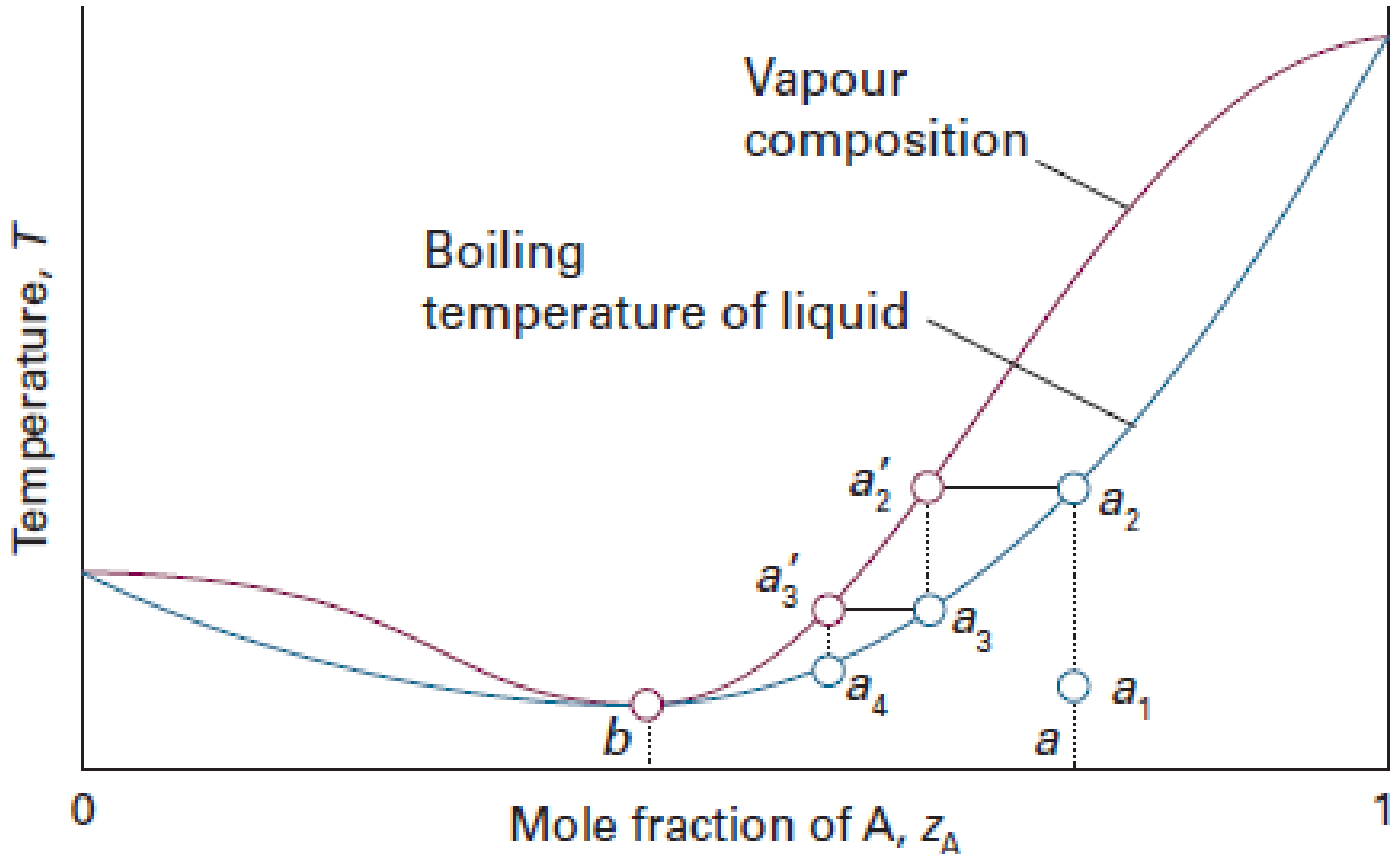
High-boiling azeotrope

A maximum in the phase diagram may occur when the favourable interactions between A and B molecules reduce the vapour pressure of the mixture below the ideal value and so raise its boiling temperature:

in effect, the A–B interactions stabilize the liquid.

Trichloromethane/propanone

Nitric acid/water



Low-boiling azeotrope

Phase diagrams showing a minimum indicate that the mixture is destabilized relative to the ideal solution,

the A–B interactions then being unfavourable;

in this case, the boiling temperature is lowered.

Dioxane/water

Ethanol/water