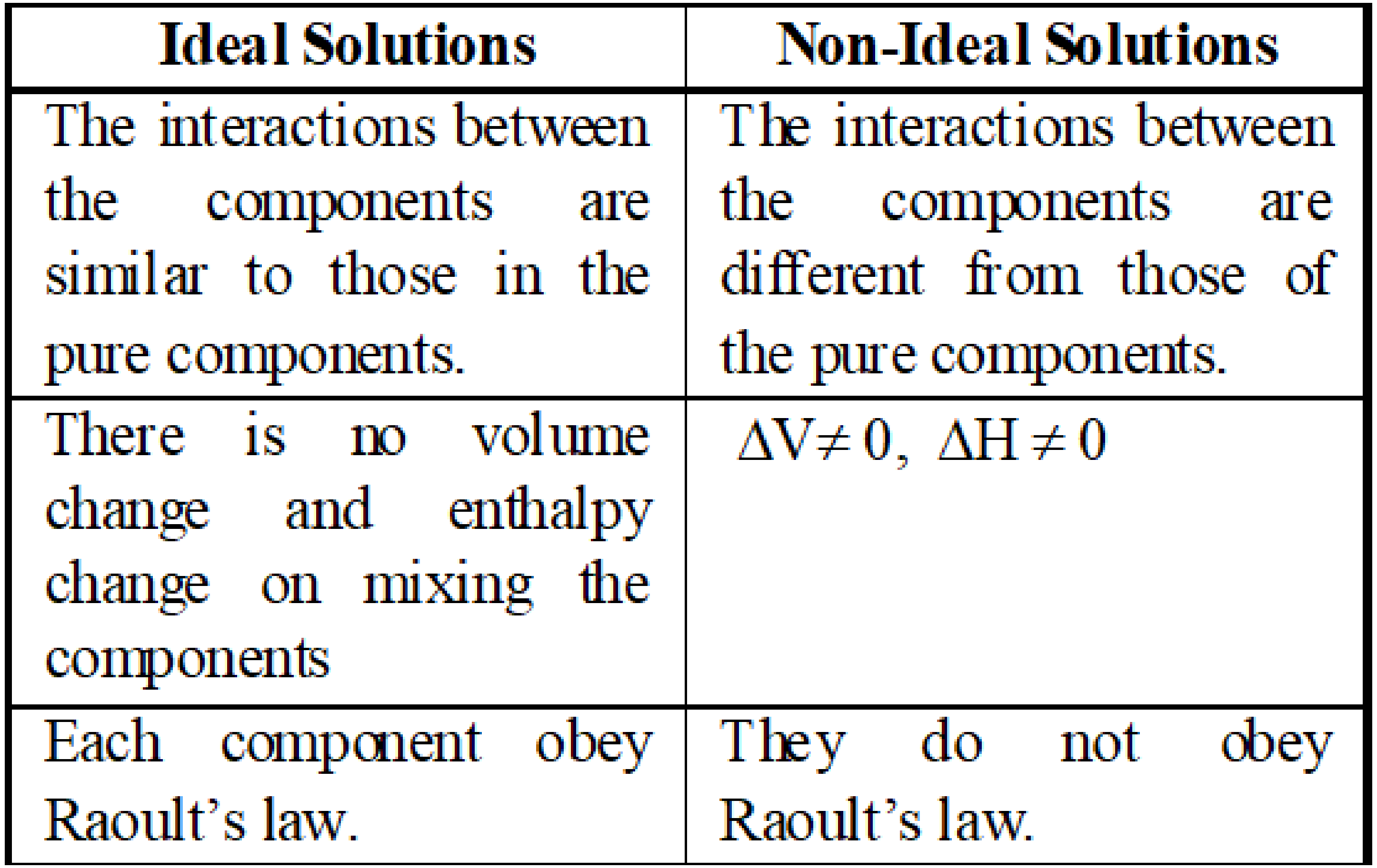
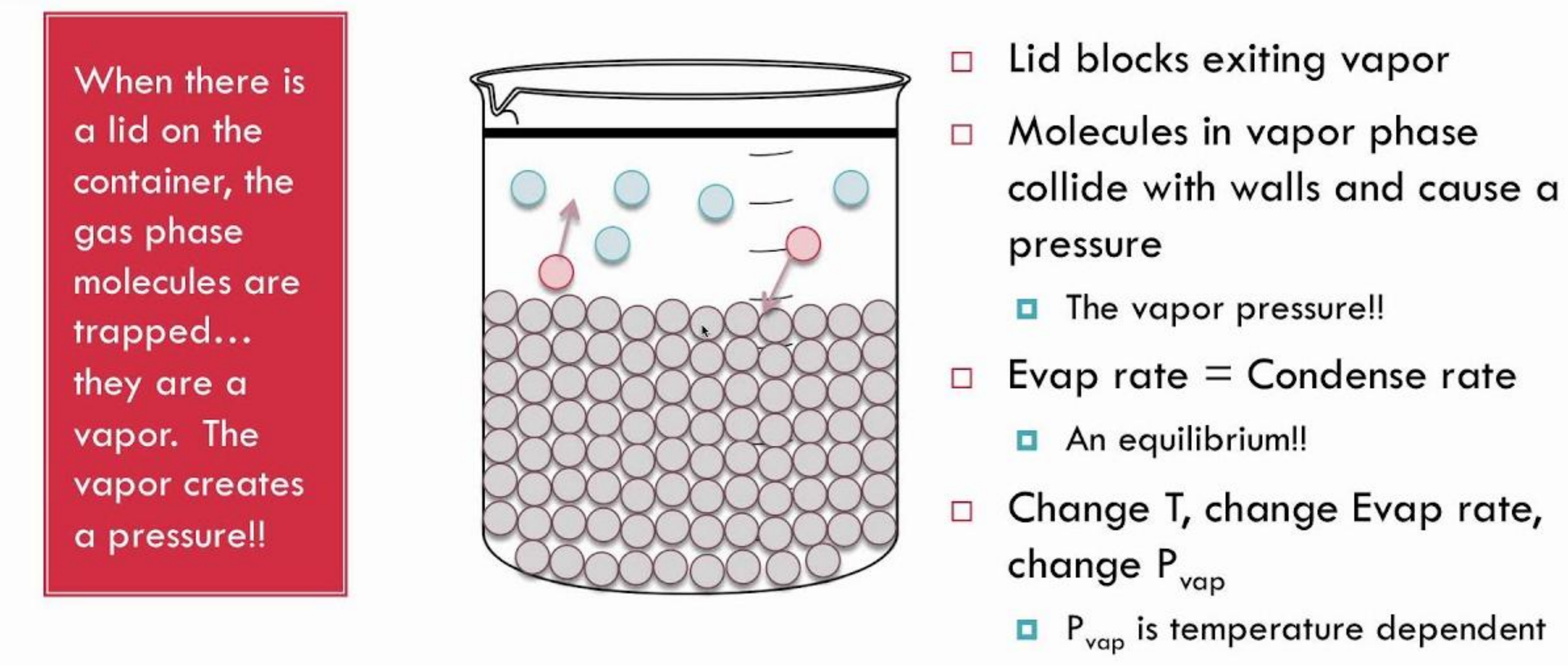
PHASE EQUILIBRIUM
(Part 3)

SOLUTIONS



Ideal Solutions	Non-Ideal Solutions
The interactions between the components are similar to those in the pure components.	The interactions between the components are different from those of the pure components.
There is no volume change and enthalpy change on mixing the components	$\Delta V \neq 0$, $\Delta H \neq 0$
Each component obey Raoult's law.	They do not obey Raoult's law.

Vapor pressure



When there is a lid on the container, the gas phase molecules are trapped… they are a vapor. The vapor creates a pressure!!

- Lid blocks exiting vapor
- Molecules in vapor phase collide with walls and cause a pressure
  - The vapor pressure!!
- Evap rate = Condense rate
  - An equilibrium!!
- Change T, change Evap rate, change P_{vap}
  - P_{vap} is temperature dependent

Saturated vapor pressure

Consider a hypothetical jar containing pure water with a flat surface and an overlying volume that initially contains no water vapor (a). As evaporation begins, water vapor starts to accumulate above the surface of the liquid. With increasing water vapor content, the condensation rate likewise increases (b). Eventually, the amount of water vapor above the surface is enough for the rates of condensation and evaporation to become equal. resulting equilibrium state is called **saturation and the water vapor pressure called saturation vapor pressure over a plane surface of pures water at temperature T**(c).

TWO–COMPONENT SYSTEMS OF TWO LIQUIDS

When a system consists of two liquids three causes are possible:

- completely miscible
- partially miscible
- immiscible liquids

The systems of two completely miscible liquids

In such systems both components are volatile and, hence, have a vapor pres-sure. Total vapor pressure P is in equilibrium with the solution, we must also take into consideration the partial pressures **P1** and **P2** of the components, where $\mathbf{P = P_1 + P_2}$. The partial vapor pressure of each component, by **Raoult’s law** is proportional to its mole fractions

Raoult’s Law

Vapor pressure depression takes place when a solute is added to a pure solvent. When a solute is added to a pure solvent, it depresses the vapor pressure of the solvent. The more solute added the more depressed the vapor pressure becomes. This is known as **Raoult’s Law.**

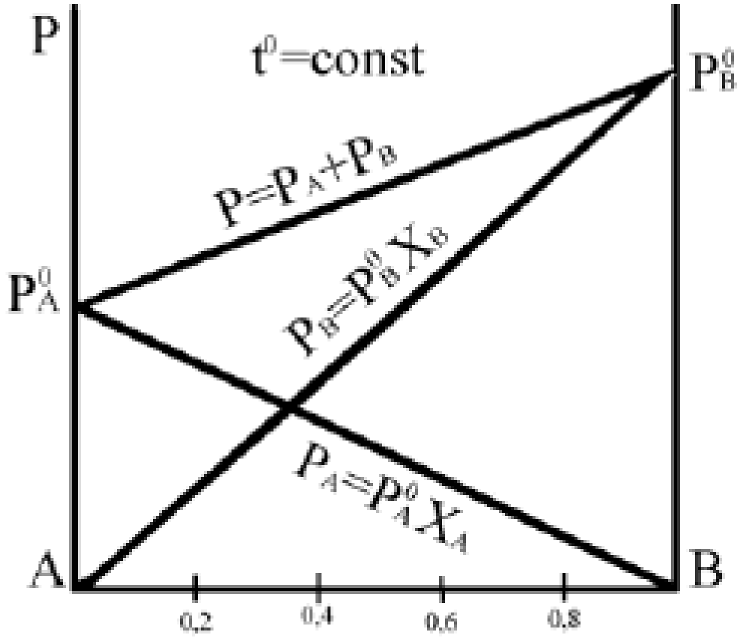
$$P_1=P^0{}_1X_1 \text{ and } P_2=P^0{}_2X_2$$

$P^0{}_1$ and P_2 are vapor pressures of pure components.

The total vapor pressure therefore is equal

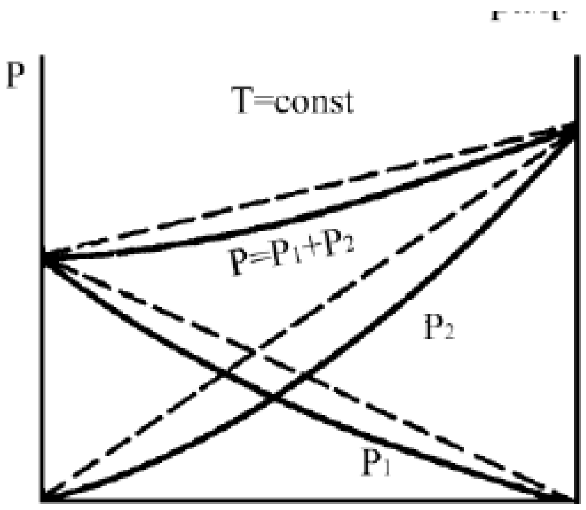
$$P = P^0{}_1X_1 + P^0{}_2X_2 = P^0{}_1(1-X_2) + P^0{}_2X_2 = P^0{}_1 + X_2(P^0{}_2 - P^0{}_1).$$

Raoult's Law. Ideal solutions

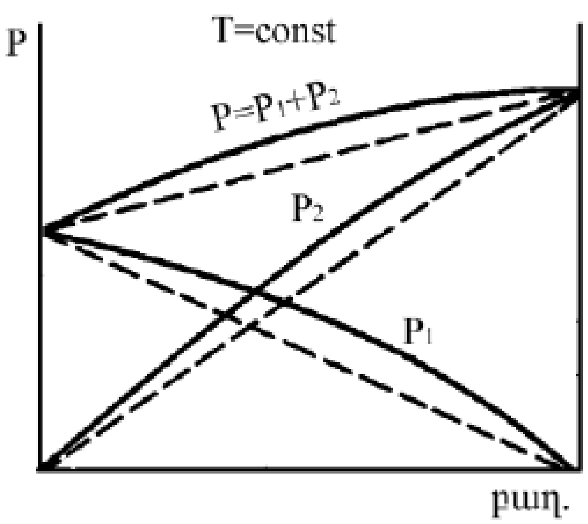


- The expression above shows the total and partial vapor pressure (at some fixed temperature) changes linearly with the composition and its graphical dependence forms straight lines
- Such systems with linear dependence between vapor pressure and composition are called **ideal solutions.**

Deviations of Raoult’s Law. Non-ideal solutions



Negative deviations



Positive deviations

- The properties of most systems, however, deviate considerably from the ideal, both in sign and magnitude.
- Deviations of these curves from a liner relation toward greater values are called **positive**, toward smaller values – **negative**.

Deviations of Raoult’s Law

The formation from the pure components of solutions showing positive deviations of the vapor pressure is accompanied for the most part by the absorption of heat and increase in volume. The formation from the pure components of solutions showing negative deviations of the vapor pressure is usually accompanied by the evolution of heat and decrease in volume

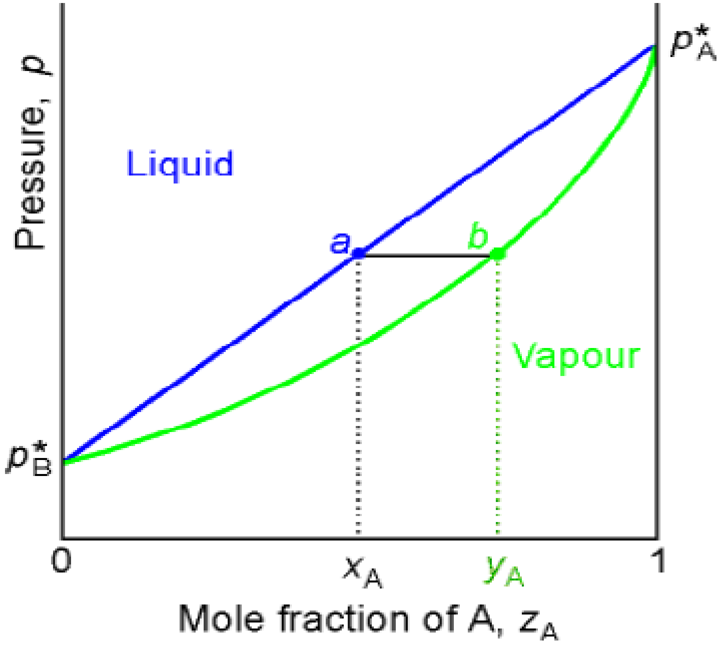
REASONS OF DEVIATIONS

- Changes in the size of particles, leads to changes in degree association and formation of compounds, which influence on the properties of the solution.
- The attraction between the molecules of the components. When the forces of attraction between not similar molecules differ a little from those between similar molecules, the system behaves as an ideal solution. But if the components are strongly dissimilar, the forces of attraction between unlike molecules will differ from those of the pure components, deviations from ideal behavior will appear.

Liquid-vapor diagrams

We can describe the liquid-vapor equilibrium in systems of two immiscible liquids by two types of diagrams: **pressure-composition** and **temperature-composition**, which is a reflection of each other for the same system.

PRESSURE-COMPOSITION. VAPOR PRESSURECOMPOSITION DIAGRAM FOR TWO COMPONENT LIQUID SOLUTION



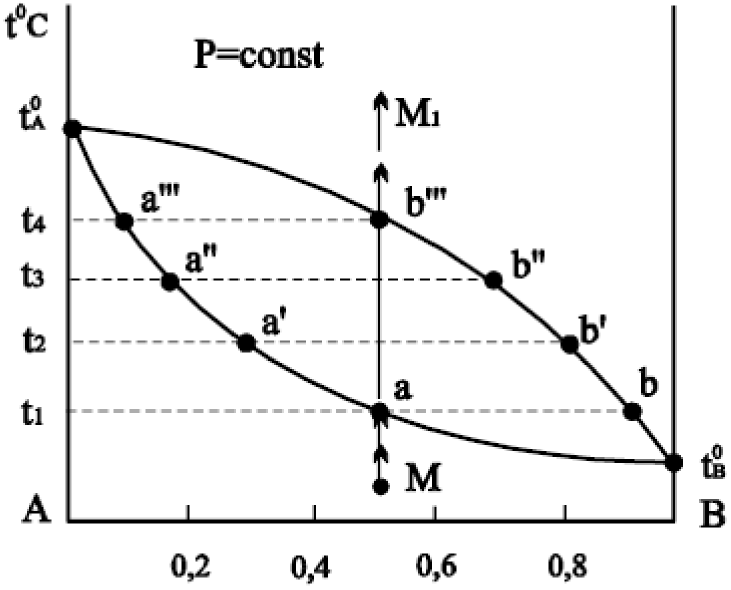
Point a indicates the vapor pressure of a mixture of composition xA, and point b indicates the composition of the vapor **yA** that is in equilibrium with the liquid at that pressure.

- Points P*A and P*B are the vapor pres-sures of the pure liquids A and B. (f=1–2+1=0)
- Above the higher curve there is only a liquid phase (f=2–1+1=2)
- lower curve the system contains only a vapor phase (f=2–1+1=2)
- Points that lie between the two lines cor-respond to a system in which two phases are present – a liquid and a vapor (f=2–2+1=1)
- The horizontal line joining the two phases in equilibrium at certain temperature is called **tie lin.**

KONOVALOV'S FIRST LAW

The composition of the vapor phase differs from that of the liquid phase, and this difference is the greater the greater the difference between the vapor pressures over the pure components. It is expressed in **Konovalov's first law**: ***in a binary system in equilibrium the vapor has a higher relative content of that component, the addition of which to the system leads to an increase in the total vapor pressure, i.e., to a lowering of the boiling point of the system at the given pressure.***

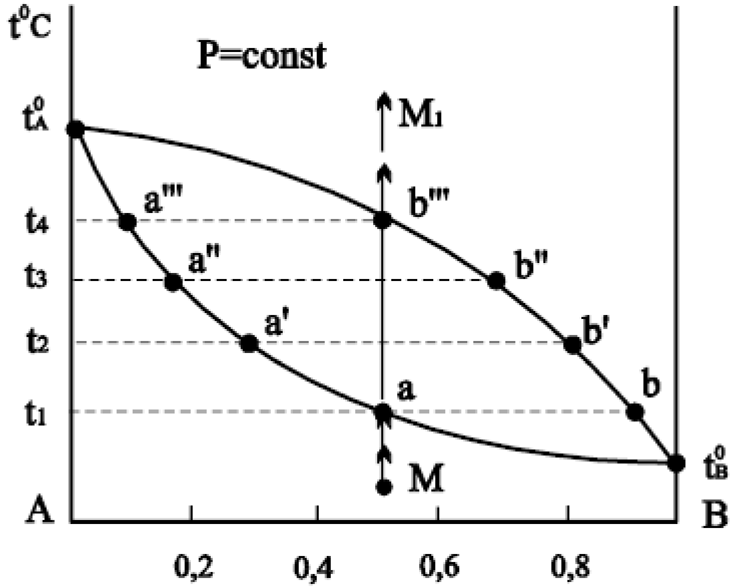
TEMPERATURE-COMPOSITION DIAGRAM



Changes occurred in solution during heating

- The compositions of the phases that are in equilibrium at various temperatures (P=const).
- The liquid phase now lies in the lower part of the diagram.
- If we heat a system of composition corresponds of point M, it will start boiling at the temperature t1 and vapor will first appear at that point. The composition of a liquid phase corresponds to point **a, and the composition of a vapor – to point b.**
- The vapor is richer in the more volatile (with lower boiling temperature) component B **according to the Konovalov's first law**

TEMPERATURE-COMPOSITION DIAGRAM



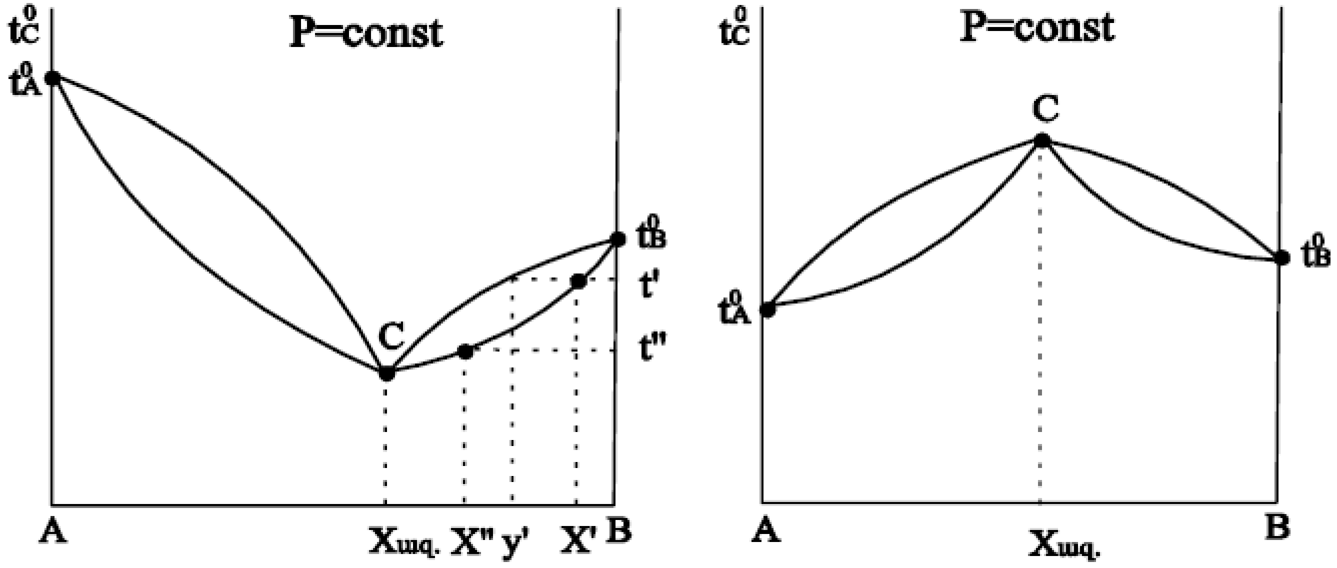
- As with following solution vaporizes, the remainder is enriched in component A and a solution of thus composition boils at higher temperature t2, at which it is in equilibrium with a vapor of composition b′. If the process is continued, the composition of the both a liquid and a vapor, as well as the boiling temperature are changed up to t4, where the composition of the vapor becomes equal to the composition of the initial liquid (point b′′′), because all the liquid transits to the vapor.

AZEOTROPES

The solution at the maximum point has a higher boiling temperature, than the less volatile component, and the solution at the minimum point has a lower boiling temperature, than the more volatile component. The solution of such com-position is boiled at a constant temperature and the composition of a liquid is nod changed since vaporization is over. Such solutions are called an **azeotrope** and **for them Konovalov's second law states.**

KONOVALOV’S SECOND LAW

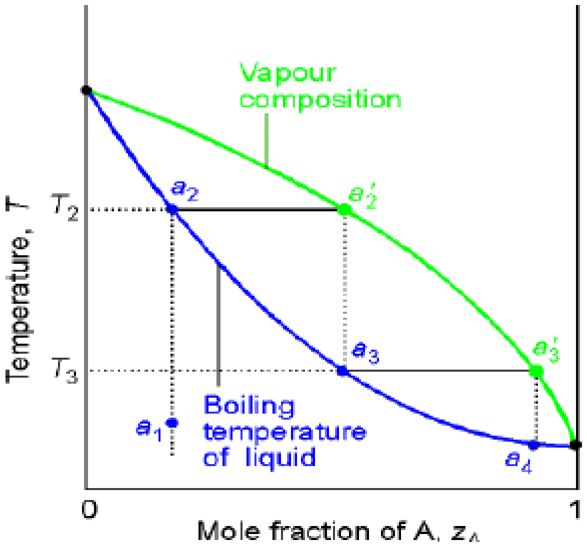
The minimum and maximum points on the boiling phase diagrams correspond to solutions for which the liquid and vapor have the same composition.



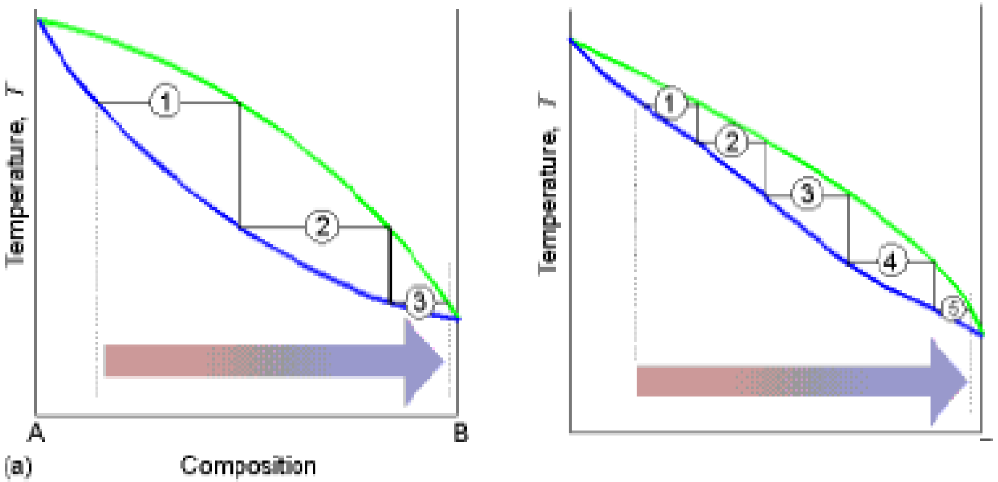
DISTILLATION

- **Distillation** is a process of separating a solution into its components by boiling them off and collecting their condensates.
- **Simple distillation** is mainly applied for solutions with non-volatile solute (for instance, salt solution). In boiling process all vapor is drawn off and at the end one has solid residual and vapor, which is condensed in original liquid
- **The fractional distillation** is based on the difference between the compositions of the equilibrium liquid and vapor and in general proceeds more easily, the greater this difference is.

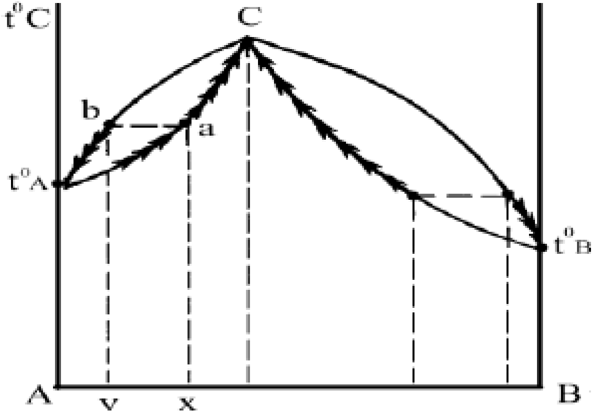
DISTILLATION



Changes in composition of the liquid and vapor during heated of solution



The process of fractional distillation

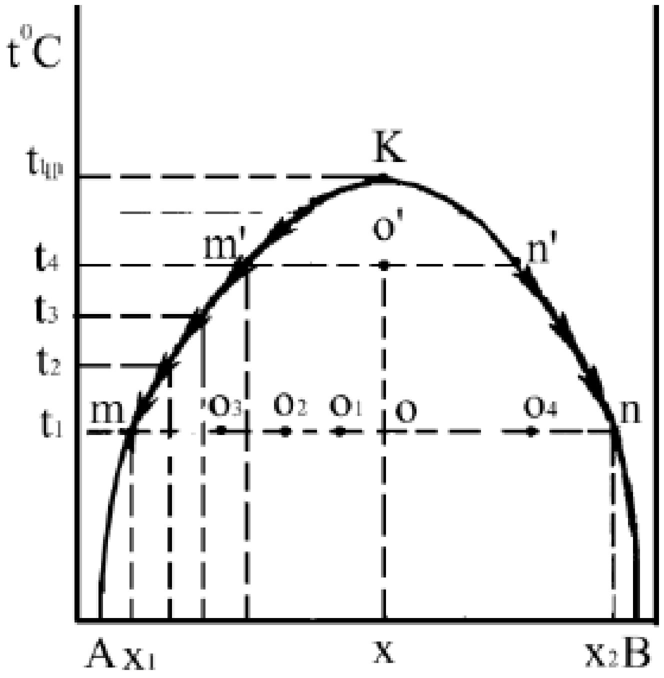


Distillation of system with azeotrope

The systems of two partially miscible liquids (water - phenol)

When a certain amounts of two liquids are shaken together at room temperature, one obtains a system of two liquid phases in equilibrium. Each contains both components, but in different amounts: one layer is the saturated solution phenol in water and the other layer is the saturated solution water in phenol. Further adding of water or aniline into the system does not change the composition of layers

The systems of two partially miscible liquids (water -phenol)

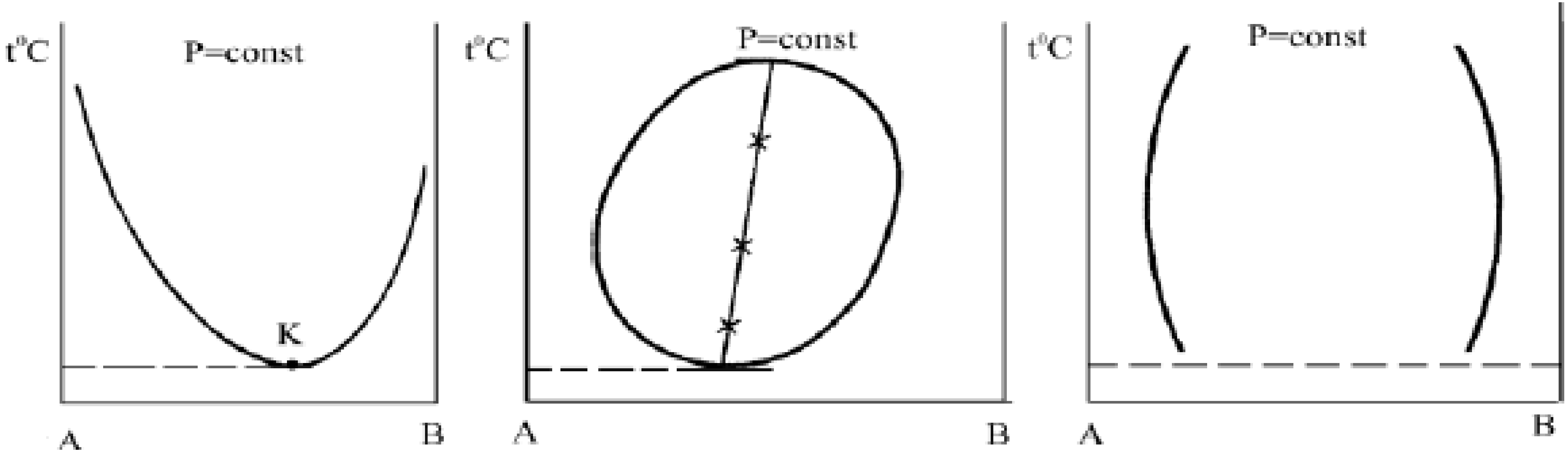


- Curve AK shows solubility solute B in solvent A with temperature rising
- curve KB shows solubility solute A in solvent B.
- At temperature t1 we have two saturated solutions in points m and n in equilibrium. The point’s m and n are maximum solubility of these liquids in each other at temperature t1.
- Between points m and n two phases (two layers) are present in equilibrium.
- The overall composition is reflecting by point O.
- The temperature, at which complete miscibility sets, is called the **critical solution temperature**

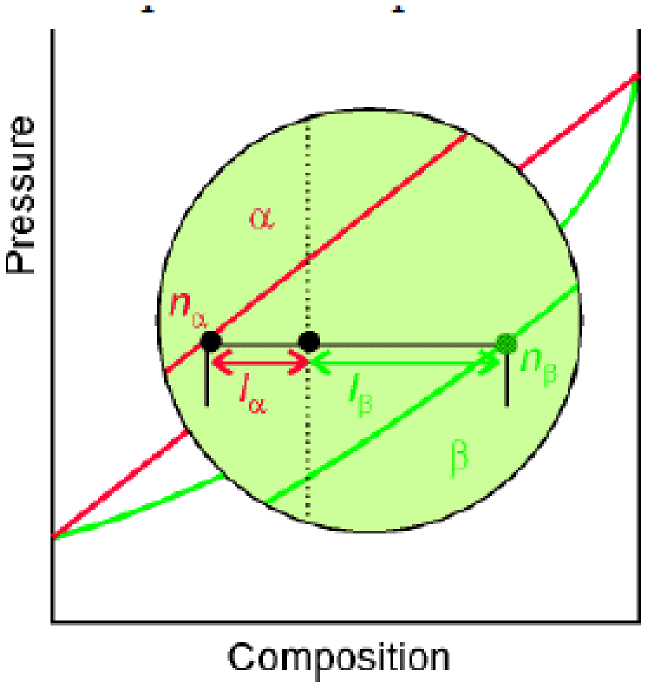
The systems of two partially miscible liquids (water -phenol)

- If the overall composition is changed (points along the line mn) the compositions of two phases in equilibrium is not changed at certain temperature (points m and n). This is the **first rule of Konovalov for such systems.**
- **According the second rule of Konovalov** in unchanged overall composition (point 0′) changing of the temperature lead to the change in the compositions of two phases (points m′ and n′).

THE SYSTEMS WITH DIFFERENT CRITICAL BOILING POINT



THE LEVER RULE



The point corresponding to the composition of a heterogeneous binary system lies on the straight line connecting the points that represent the coexisting phases, and divides this line into segments that are inversely proportional to the amounts of the two phases:

$$n_\alpha l_\alpha = n_\beta l_\beta$$