CHAPTER II: Liquid-Vapor Equilibrium(LVE)

Introduction:

- The equilibrium of state change: **Liquid** ↔ **vapor** of a binary system; a mixture consisting of two pure species A and B.
- These two constituents of the system can **interact** with each other or not:
  -In the first case, it is a **real solution** (or mixture),
  -In the second, the mixture is said to be **ideal** (the gas phase is ideal, each gas is assimilated to perfect gas).

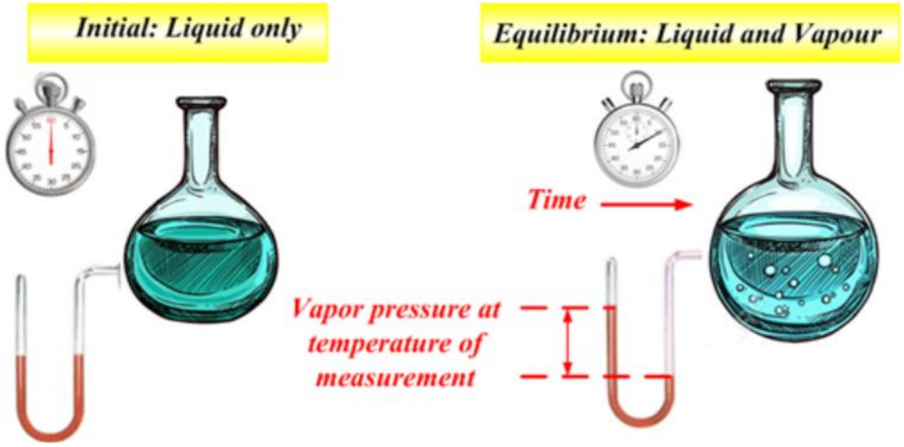
In the liquid state, A and B are:

– either **miscible**: we then have a single **homogeneous liquid phase**;

– or **immiscible** (with zero miscibility): We have **two heterogeneous** liquid phases.

II.1: Definitions

1.Liquid Vapor Equilibrium (VLE) : describes the distribution of a chemical species between the vapor phase and a liquid phase that are in equilibrium with each other



Since the system is at **equilibrium**, this implies that **the chemical potential** of each constituent **is the same in both phases**.

We recall the following some common terms inherent to this equilibrium:

- **Distinction between gas and vapor**: the two names refer strictly to the same physical state, the gaseous state. **A gas is a pure matter** existing only in the gaseous state at 1 atm and 20 °C: dioxygen and carbon dioxide are gases, not vapors. On the other hand, we speak of **ethanol vapor** (always a gaseous state) because in the conditions cited before (1atm and 20°C), ethanol exists in a **liquid state** (coexisting with ethanol vapors).

2.Change of state: the different state of water(example) are given in the diagram below. Note the use of the term **liquefaction for a gas** and **condensation for a vapor** in the case of a change of state **liquid → gas.**

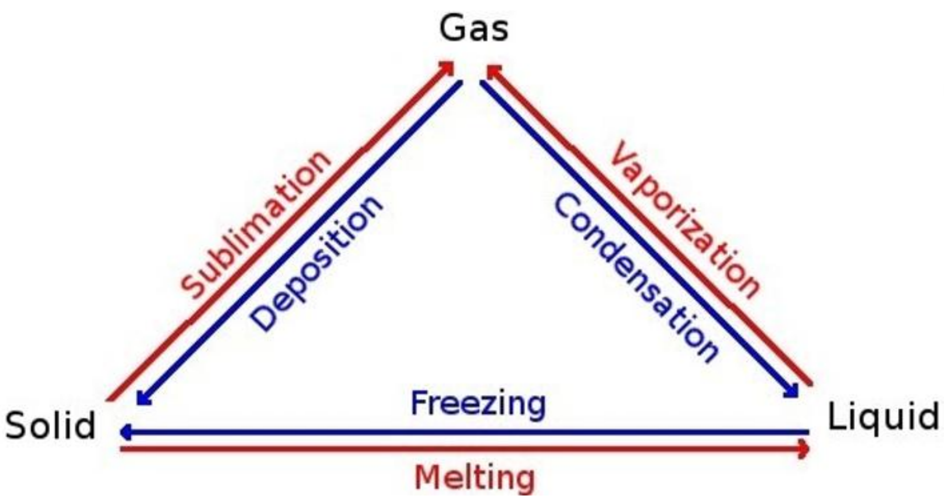


Fig.1: The change of state of a pure substance

3. Equilibrium of a system: In this state, all **the intensive properties** describing the system are constant over time:

- **The temperature** of the system is uniform (thermal equilibrium).
- **Pressure of the system** is uniform (mechanical equilibrium).
- **The chemical composition** of each phase of the system is uniform (chemical equilibrium).

4. Phase: is **the homogeneous** part of the system with identical physicochemical properties at all its points. In other words, it is a region of space where the intensive variables have values independent of the points considered.

Examples:

- Mixtures of several i**deal gases** constitute a **single phase**.
- Two or more **miscible** liquids constitute a **single phase**.
- Two or more **immiscible** liquids constitute **two phases** (oil and water).
- **Molar fraction**: In a binary mixture of 2 liquids or 2 vapors (pure substances A and B), we define in each phase (liquid or vapor) the molar fractions in A and B. We note **x** for the molar fractions in the **liquid phase** and **y** for the molar fractions in the **vapor phase.**

5.Gibb's phase rule:

$$V=2+C-\Phi$$

v: variance is the numbre of independent parameters which describes the equilibruim state
c is the number if species
φ is the number od Phases

In the case of constant pressure, we defined the **reduced variance V'**

$$V'=1+C-\Phi$$

II.2 LIQUID-VAPOR EQUILIBRIUM FOR A PURE SUBSTANCE

II.2.1 Equilibrium of a pure substance under two phases

when a system consisting of several components distributed between various phases is in thermodynamic equilibrium at a definite temperature and pressure, **the chemical potential** of each component is **the same** in all the phases.

- **If they are different (**chemical potential of A in the liquid phase and in vapor phase**)**, the component for which such a difference exists will show **a tendency** to pass from the region of **higher** to the **region of lower** chemical potential. Thus, the equality of chemical potential and the requirement of uniformity of temperature and pressure serve as the general criterion of thermodynamic equilibrium in a closed heterogeneous multicomponent system. In short, we can write at equilibrium:

$$\boxed{\begin{array}{ll} T = \text{constant}; & P = \text{constant} \\ \mu_i^{\alpha} = \mu_i^{\beta} = \ldots = \mu_i^{\pi} & \text{for} \quad i = 1, 2, 3, \ldots, C \end{array}}$$

Since the chemical potential is related to fugacity as

$$\mu_i = RT \ln \bar{f}_i + C$$

where C is a constant, an alternative and equally general criterion of equilibrium can be written in terms of fugacities as

$$\boxed{\begin{array}{ll} T = \text{constant}; & P = \text{constant} \\ \bar{f}_i^{\alpha} = \bar{f}_i^{\beta} = \ldots = \bar{f}_i^{\pi} & \text{for} \quad i = 1, 2, 3, \ldots, C \end{array}}$$

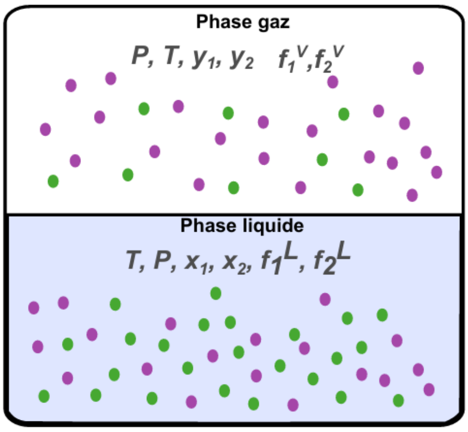


Fig.2 illustration of liquid-vapor equilibrium

From this consideration, we obtain, for example, the P-T diagram of the changes in the state of pure water. This equilibrium diagram of a pure body indicates which **phase is stable** under given conditions of temperature and pressure when this body (here H_2O) is alone present in the cylinder.

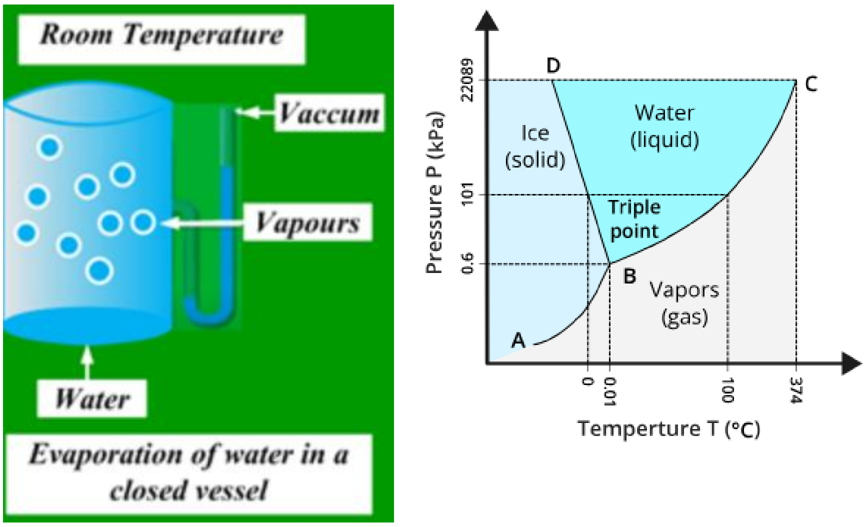


Fig.3:P-T diagram of the changes in the state of pure water.

- The state change curves delimit the stability domains. The triple point T (0.6 atm and 273.16 K) is a point for which the three phases (solid, liquid and gas) coexist.
    - The **phase rule** indicates a **zero variance** for this point: there is in fact only a single pair of conditions to describe this state.

- The **liquid ↔ vapor** state change curve (which interests us in this chapter) is called the **vaporization curve**. The points corresponding to this equilibrium (**coexistence of liquid and vapor)** are representative of a two-phase system: the variance is equal **to 1** in this case. Thus, to characterize a state of this equilibrium, knowledge of a pressure or a temperature is sufficient. This theoretical approach (phase rule) is verified experimentally by the experimental curve: we observe that a given pressure effectively corresponds to a single state change temperature value.

- The shape of the water diagram can be generalized to other pure substances, except for the melting curve which is a function which generally increases as a function of temperature.

II.3 LIQUID-VAPOR EQUILIBRIUM OF A LIQUID BINARY MIXTURE WITH TOTAL MISCIBILITY

In this case, the liquid is homogeneous (single phase) since the liquids are miscible.

II. 3.1: Phase diagrams for an ideal binary liquid mixture

1) Study of the isothermal diagram of the mixture Toluene (A)-Benzene (B) (T = Constante)

Let us consider the ideal mixture toluene (A)-benzene (B) in liquid-vapor equilibrium.

The component (B) being the most volatile (i.e. to simplify the compound having the lowest boiling point). The liquid-vapor diagrams will always be plotted using the molar fractions of the most volatile compound.

Let us try to determine the following equations:

$$P = f(x_B)\ and\ P = f(y_B)$$

1)*The composition of the liquid* $P = f(x_B)$

In the case of ideal liquid solutions we can apply Raoult's law to compounds (A) and (B):

$$p_A = x_A p_A^* \quad \text{and} \quad p_B = x_B p_B^*$$

where p_A^* is the vapour pressure of pure A and p_B^* that of pure B.

- The total vapor pressure p of the mixture is therefore

$$\boldsymbol{P = PA + PB = X_A P_A^* + X_B P_B^* = (1 - X_B)P_A^* = PA^* + (P_B^* - P_A^*)X_B}$$

- This expression shows that the total vapour pressure (at some fixed temperature) changes linearly with the composition from P_A^* to P_B^* as X_B changes from 0 to 1.
- These straight line is called: **boiling curve** which gives **the composition of the liquid phase**

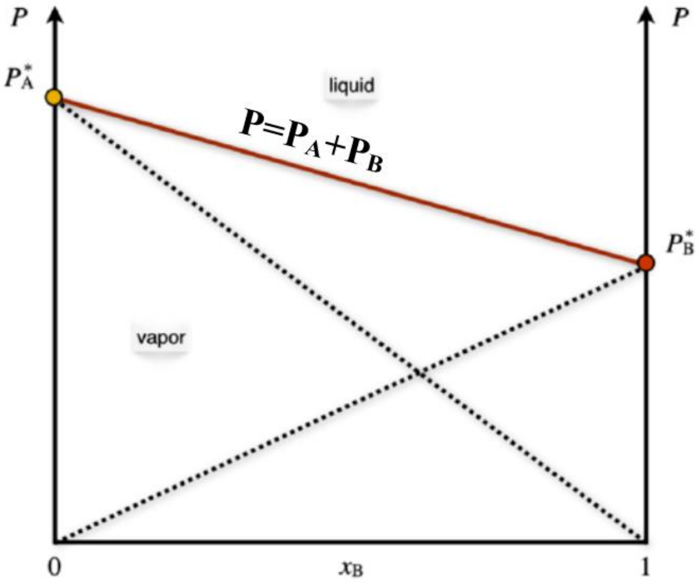


Fig.4: variation of the pressure as a function of liquid composition

2) The composition of the vapor $P = f(y_B)$

The composition of the liquid and vapour that are equilibrium are not the same. Because the vapor should be richer in the more volatile component.

The partial pressures of the components are given by the Dalton's equation. $P_A=y_AP$ and $P_B=y_BP$

$$y_A = \frac{p_A}{p} \quad ; \quad y_B = \frac{p_B}{p}$$

yA and yB are the mole fractions in the gas.Provided the mixture is ideal, the partial pressures and the total pressure may be expressed in terms of the mole fractions in the liquid by using: $PA = \boldsymbol{X_A P_A^*}$ and $\boldsymbol{PB = X_B P_B^*}$and

$$P = PA + PB = X_A P_A^* + c = (1 - X_B)P_A^* = PA^* + (P_B^* - P_A^*)X_B = \frac{P_B}{Y_B}$$

$$Y_B = \frac{X_B P_B^*}{P_A^* + (P_B^* - P_A^*)X_B}$$

And we know that : $PB = X_B P_B^* = P_B Y_B$P **so:** $X_B = \frac{Y_B P}{P_B^*}$ **and by substitution in the equation of YB we find that :** $p = \frac{P_A^* P_B^*}{P_B^* - (P_B^* - P_A^*)Y_B}$**=which is an equation of a hyperbola called the 'Dew curve',it gives the composition of the vapor phase.**

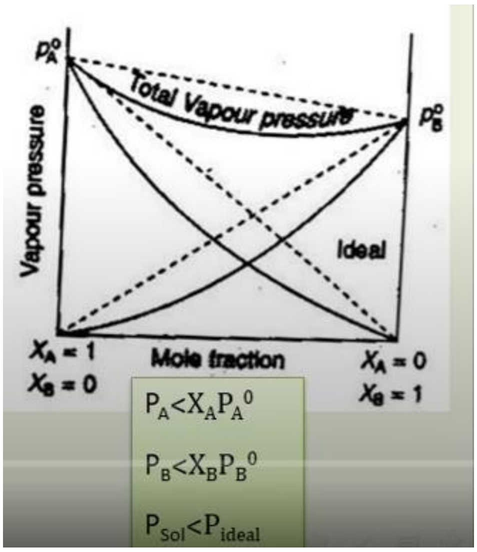


Fig.5: variation of the pressure as a function of vapor composition

Finally, we obtained the binary isotherm diagram of mixture AB as a function of composition, which is called also the P-x-y diagram

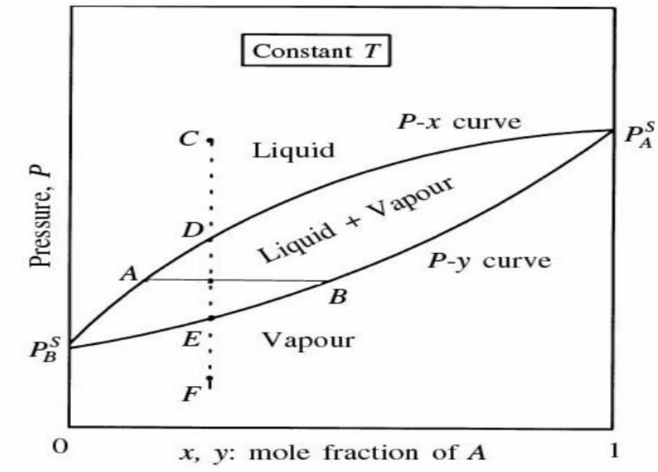


Fig. 8.6(a) *P-x-y* diagram.

Fig.6: Isothermal diagram (P=cte) of liquid-vapor equilibrium for an ideal mixture

- The two curves meet at the two ends of the diagram.
- For: x_B=0 and y_B=0 we have the liquid vapor equilibrium of component A with a pressure $\boldsymbol{P_A^*}$
- For x_B=1 and y=1 we have the liquid vapor equilibrium of component B with a pressure $\boldsymbol{P_B^*}$
- Above boiling curve, we have a single liquid phase
- Below dew curve we have a single vapor phase
- Between the two curves we have two phases in equilibrium

Example of Application:

Calculate the mole fraction in the vapor phase of a liquid solution composed of 67% of toluene (A) and 33% of benzene (B).

P_A^*=0.03 bar and $P_B^* = 0.1\ bar$

we have:

$$Y_B = \frac{P_B}{P} = \frac{X_B P_B^*}{X_A P_A^* + X_B P_B^*} = \frac{0.033}{0.0201 + 0.033}$$

se we obtain: Y_B=0.6215

2)Constant-pressure Equilibria

2.1) Study of the isobaric diagram of the binary mixture AB (P = Cte)

Component A is assumed to be more volatile than B, i.e. the vapour pressure of A is **greater than** that of B at any given temperature. For a binary liquid mixture in equilibrium with its vapour, according to the Gibbs Phase rule, **the number of degrees of freedom is two (variance=2)**. When **the pressure is constant**, only one variable (reduced variance: **v'=1**), say liquid phase composition, can be changed independently and other properties such as the temperature and the vapour phase compositions get uniquely determined. Vapor–liquid equilibrium data at constant pressure are usually represented using either the temperature-composition diagrams (the T-x-y diagrams or the boiling point diagrams) or the distribution diagrams (x-y diagrams or equilibrium curves).

T-x-y diagram or boiling point diagram: The boiling point diagrams are plotted of temperature as a function of composition of liquid and vapour as abscissa.

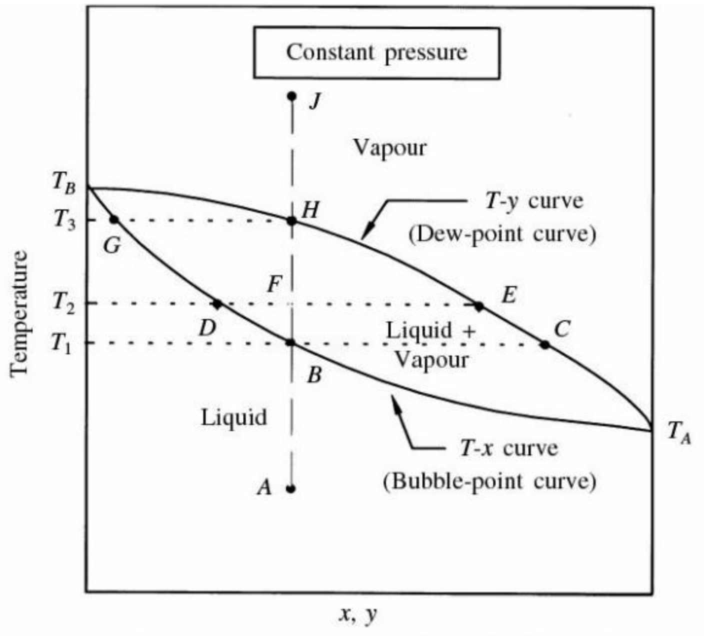


Fig. 8.2 *T-x-y* diagram (boiling-point diagram).

- To make these points clearer, consider a mixture whose temperature and composition (x1) are such that it is represented by point A in the above figure Since **the point A** lies **below the bubble**-point curve, the solution is entirely **liquid**.
- The mixture is heated slowly so that its temperature increases along the vertical line passing through point **A** till point **B** on the bubble-point curve is reached. The temperature **T1** corresponding to point **B**, is **the bubble point** of the **original mixture**
- **The first bubble** of the vapour is **produced** at this temperature and it will have the composition (**y1**) represented by point C on the upper curve. The vapour is richer in the more volatile component. **Therefore y1 > x1,** and the dew-point curve lies above the bubble-point curve. The mixtures at points **B** and **C** are **the liquid** and **vapou**r at **equilibrium** at the system pressure and temperature **T1**. Since both are at the same temperature, they can be joined by a horizontal line **BC**, known as a **'tie line'.**
- **Further heating** will result in the vaporization of more liquid, and at temperature **T2** the system will consist of saturated liquid represented by point **D** and saturated vapor represented by point E, which are in equilibrium. Since the vapor formed is not removed from the system, the overall composition of the combined mixture of liquid and vapor will be same as **x1**, the composition of the original mixture. However, the relative amounts of the liquid and the vapor change as the temperature is changed. These relative amounts are given by the ratio in which the point representing the combined mixture (in this case, point **F**) divides the tie line DE. Using the **chemical moment theorem**, it can be easily verified that

$$\frac{\text{Amount of liquid}}{\text{Amount of vapour}} = \frac{\text{Line } EF}{\text{Line } DF}$$

- If heating is continued, eventually a temperature **T3** is reached when almost all liquid is **vaporized**. The last drop of liquid getting vaporized at this temperature has a composition denoted by point **G** and **the equilibrium vapour** has the composition at **H** same as the original mixture. Temperature **T3** is **the dew point of the original mixture**. The mixture temperature increases along the vertical line **HJ** on further heating. **On cooling** the superheated mixture at point **J**, the first drop of condensate appears when the temperature drops to **T3**, the dew point of the mixture and the composition of the liquid is given by point **G**. We have seen that the mixture at point **A** has vaporised over a temperature range from **T1** (the bubble point) to **T3** (the dew point), unlike a pure substance, which vaporises at a single temperature known as the boiling point of the substance. For a solution, the term '**boiling point'** has no meaning, because, at a given pressure the temperature during vaporisation of a solution varies from the bubble point to the dew point.

- The temperature and pressure of a pure component are related by **Antoine equation**:

$$\log_{10} P^* = A - \frac{B}{C+T} \qquad P : mm\ de\ Hg \qquad T : {}^\circ C$$

A, B and C are constants characterizing the nature of the pure compound used.

II.3.2 Case of a non-ideal (real) liquid mixture: azeotropy

1) The deviation from ideality of the solutions (i.e. in the case of a real solution) can lead to the obtaining of **azeotropes**. The situation of azeotropy is quite frequent and has important practical implications.

A system is said to be **azeotropic** (or also **homoazeotropic**) when the liquid-vapor equilibrium is not selective. This means that the binary azeotropic mixture:

- ❖ is a homogeneous liquid boiling at constant temperature: the change of state takes place at constant temperature.
- ❖ is defined mathematically for a constituent j by an equality of the liquid and vapor compositions (Gibbs–Konovalov theorem):

$$\boxed{x_j^{liq} = x_j^{vap}} \quad \text{ou} \quad \boxed{x_j = y_j}$$

- ❖ At the equilibrium of the change of state we have 2 phases, the variance is therefore v = 2. The pressure is fixed. Furthermore, the molar fraction of the constituent j is the same in the two phases. This additional relationship between intensive parameters means that the reduced **variance is 0**: the change of state of the azeotrope therefore takes place at constant temperature.

1)Minimum-boiling azeotropes. Solutions showing positive deviation from ideality in certain cases may lead to the formation of azeotropes of the minimum-boiling type. The P-x-y, T-x-y and x-y curves for the minimum-boiling azeotropes are shown in the Figure below

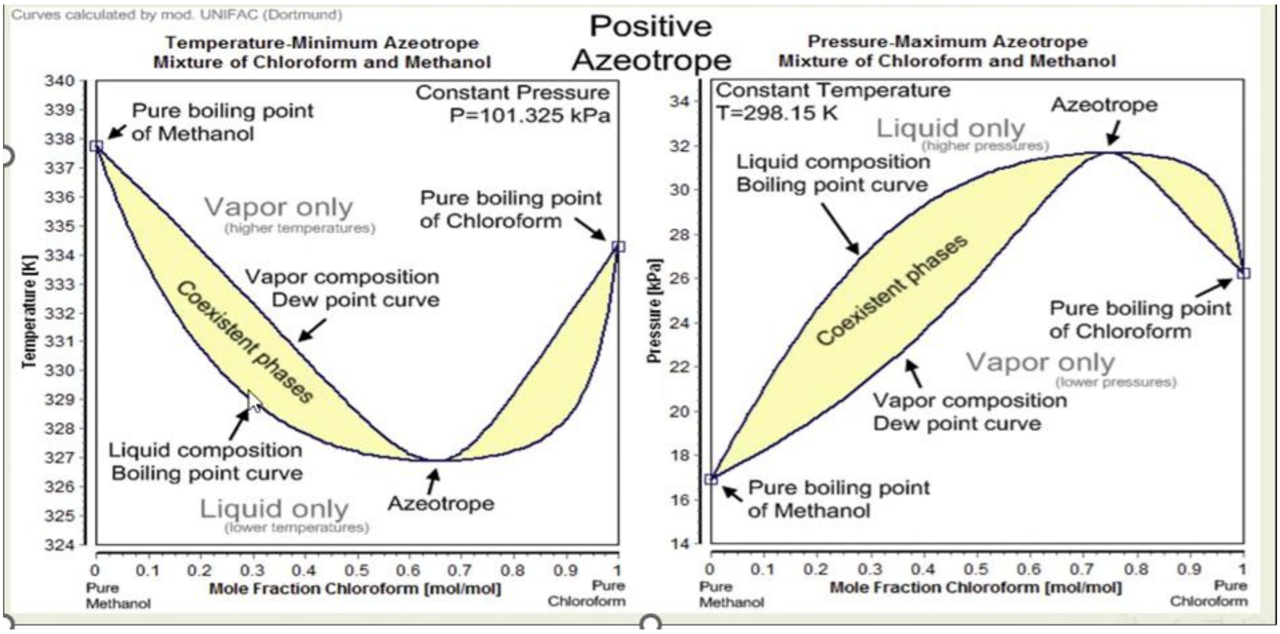


Fig.7: Non-ideal liquid-vapor binary diagram of mixture with minimum boiling temperature

2)Maximum boiling Azeotropes:

When the total pressure of the system at equilibrium is less than the ideal value, the system is said to exhibit negative deviation from ideality. When the difference in vapour pressures of the components is not too great, and in addition, the negative deviations are large, the curve for total pressure against composition passes through a minimum. This condition results in a maximum in the boiling temperature and a condition of azeotropes at point **Z**

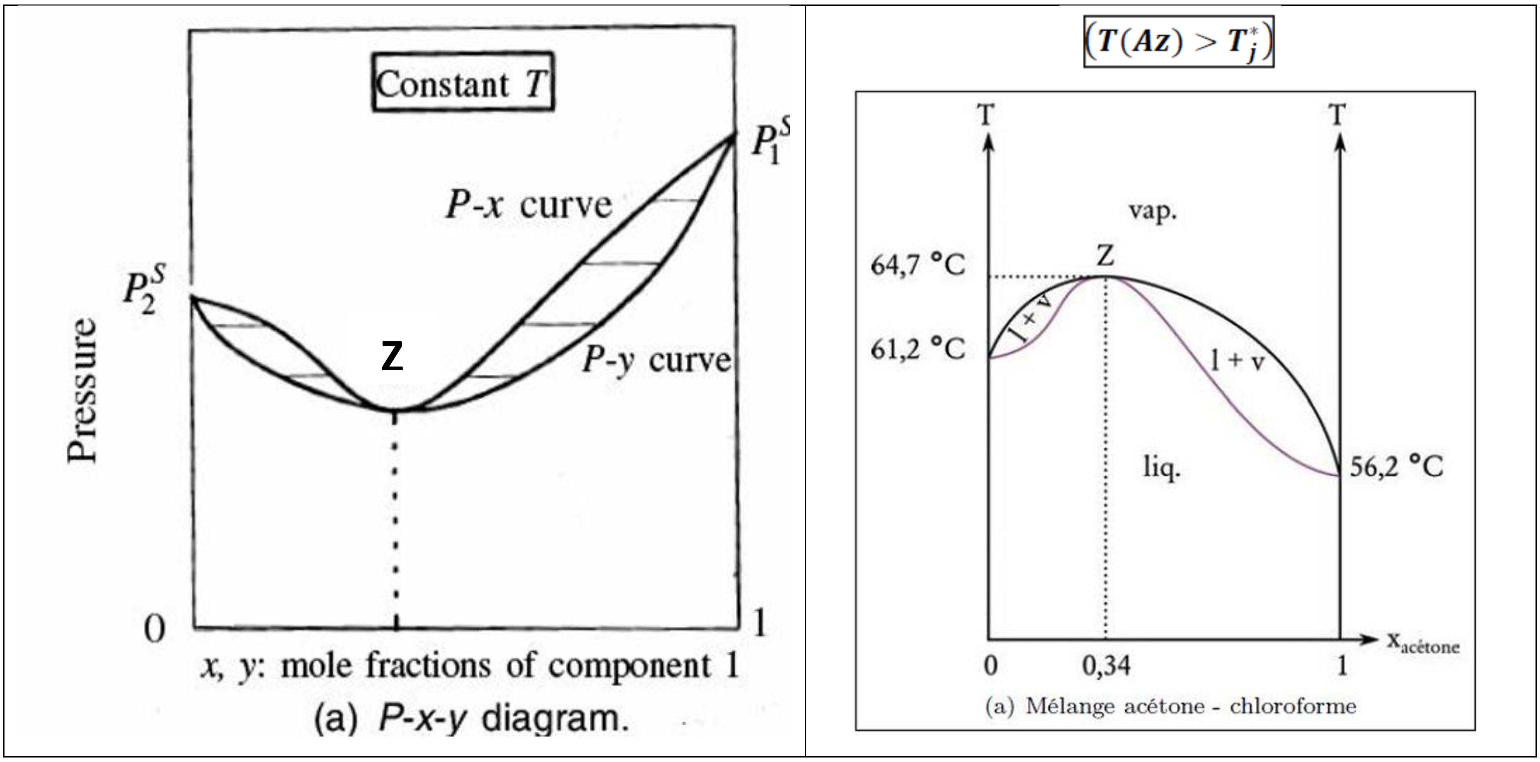


Fig.8: Vapor-liquid equilibrium for solution forming maximum-boiling azeotrope.

Thermal analysis curve:

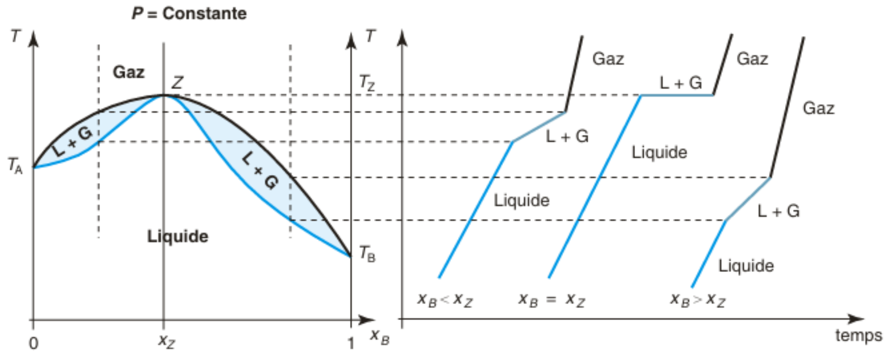


Fig.9: Thermal analysis curve of some points on the binary diagram (G is the vapor phase)

II.3.3: Some properties of azeotropes:

- It is not possible to separate the constituents of an azeotropic mixture by liquid-vapor distillation, under azeotropic conditions, the two phases have the same composition, and the two constituents have the same volatility (the same tendency to pass into the vapor phase)
- on other side of the azeotrope in terms of composition, the relative volatilities of the constituents are reversed: thus, in a propanol-water mixture with 10 mol% propanol, it is propanol that is the most volatile (it is the one that preferentially passes into the vapor phase, the vapor phase is richer in propanol than the liquid phase).

  On the other hand, in a mixture with 90% propanol, it is the opposite, and water appears as more volatile than propanol.
- in the case of a **positive azeotrope**, the azeotropic mixture boils at a **temperature lower** than the temperature of each of **the pure substances**. This property is sometimes used to vaporize a solvent at low temperature, by adding a component with which it forms an azeotrope.
- The azeotropic mixture is a solution that has the appearance of a pure substance when boiling and liquefying but in composition varies with temperature and pressure.
- When the pressure changes, the temperature and **composition of the azeotrope change**. For example, the coordinates of the ethanol-water azeotrope are:

$$\boxed{\left|\begin{array}{l} x_{\text{eau}} = 0{,}11 \\ \theta = 78\ °\text{C} \end{array}\right. \text{sous } P = 1 \text{ bar}} \qquad \boxed{\left|\begin{array}{l} x_{\text{eau}} = 0{,}07 \\ \theta = 48\ °\text{C} \end{array}\right. \text{sous } P = 0{,}25 \text{ bar}}$$

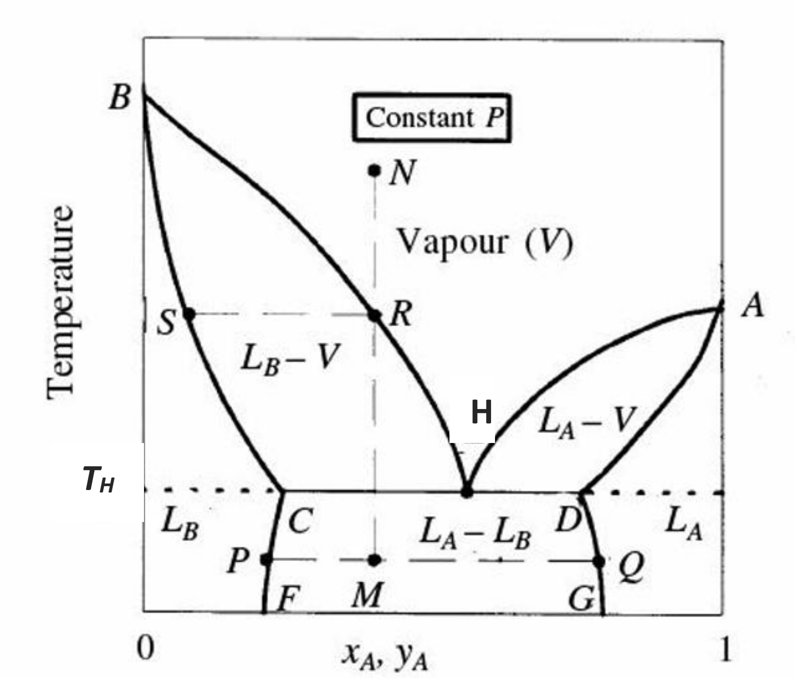
II.4 LIQUID-VAPOR EQUILIBRIUM OF A LIQUID BINARY MIXTURE WITH LIMITED MISCIBLITY-HETEROAZETROPIC MIXTURES

Introduction: We have considered so far that the two constituents were completely miscible in the liquid state. This is not the case for all binary mixtures. We will now study the appearance of binary diagrams in the case of non-miscible mixtures. There are two types of heteroazeotropic mixtures that are easy to visualize on simple isobaric diagrams depending on the partial or zero solubility of the two phases in each other.

Definition: **A heteroazeotrope** is a liquid **heterogeneous** system (2 phases) in equilibrium with its vapor.

II.4.1 Partially Miscible Systems

The binary diagram for a mixture with partial miscibility is shown below:



Temperature-composition diagram
for a partially miscible binary mixture.

Below T_H, the system is entirely liquid. It may exist as a homogeneous system, or, as a heterogeneous system consisting of two saturated liquid phases, depending upon its overall composition.

- within the region bounded by the curves **FC** and **GD** below temperature **T_H** , the mixture cannot exist as a single phase. It separates into two saturated liquid phases, a A-rich phase (LA) represented by the curve GD and a B-rich phase (LB) represented by the curve FC.
- For a point **M** exist in the two liquid region (**LB –LA**), the mixture separates into a **B-rich** phase represented by point **P**, and a **A-rich** phase represented by point **Q**. The mutual solubility of A and B increases with an increase in temperature as shown by the curves **FC** and **GD** .
- The change in the solubility of liquid A in liquid B with temperature is along **FC** and that of B in A is along **GD**.
- Suppose that the mixture at **M** is heated at constant pressure. Its temperature increases till T_H is reached. AtT= T_H, the temperature remains constant until ine of the liquid phases disappears
- At $T>T_H$ the system can exist either as two phases(L-V) or as a single-phase V depending in the composition
- At point R the mixture is entirely vapor

II.4.2:binary diagram of immiscible mixture

When liquids are completely immiscible, each liquid is pure in its phase.

- At the change of state :we start with a mixture of the two liquids(two phases) and one vapor phase($x=x_H$) so variance is equal to 1 and since the pressure is constant, we defined the redyced variance v'=0.
- The composition of the vapor in equilibrium with pure liquids at 3phases temperature is given by point H (**Heteroazeotrope),** the corresponding temperature is noted **T_H**

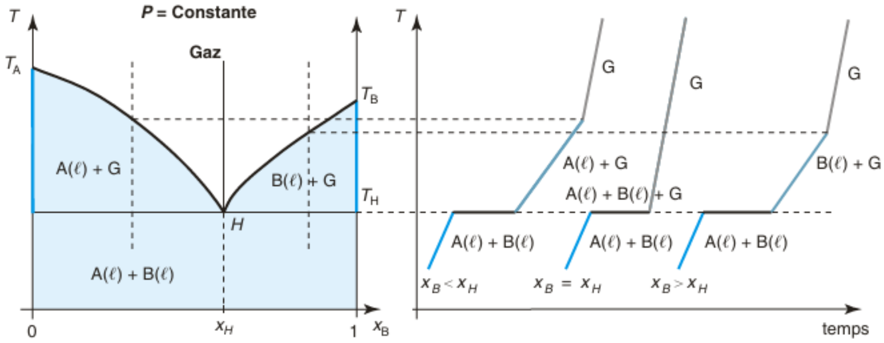


Fig.10: Binary diagram and thermal analysis curve of a mixture with partial miscibility

<u>LECTURE OF THE BINARY DIAGRAM</u>:

- The only single-phase region is the vapor (in the figure mentioned as Gaz) above the dew curve,
- Two liquid-vapor phases in equilibrium appear on the diagram
- On the left for ($x<x_H$): we can see the presence of A pure liquid phase in equilibrium with the vapor phase
- On the right ($x>x_H$): compound B pure liquid in equilibrium with the vapor
- AT $T=T_H$:3 phases in equilibrium(A(l)+B(l)+vapor phase
- AT $T<T_H$: two liquid phases A and B
- At $T>T_H$: one liquid phase in equilibrium with vapor phase

<u>II.5 Using binary diagram</u>

The binary diagram allows us to:

✓ Determine the boiling (or condensation) temperature of a homogeneous mixture,

✓ The composition of the first vapour bubbles formed (or first drops of liquid formed),

✓ Which of the two species is more volatile,

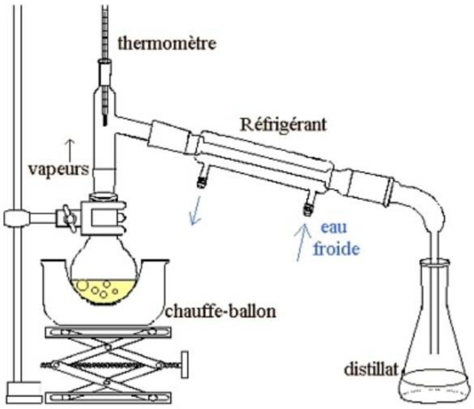
✓ The nature of the distillate and the residue.

II.6: Application to distillation

Definition: The **distillation** of a liquid mixture, whether homogeneous or heterogeneous, is an operation aimed at separating the constituents of this mixture, or at purifying one of them

1)Case of a simple distillation (without column)

Consider an **ideal mixture** of two completely miscible **liquids A and B** with respective boiling points TA and TB. At constant pressure, the temperature at which the mixture of compounds A and B changes state depends on their respective proportions (Figure 12). This figure shows that at a temperature of **T = 90°C,** the composition of the liquid mixture is given on the boiling curve at point (L1), i.e., 20% A and 80% B. The composition of the vapor is given at point (V1) on the dew point curve, i.e., 50% A and 50% B. Thus, we see that the proportion of A is greater in the vapor phase than in the liquid phase since A is more volatile than B. The phase diagram shows that the vapor phase is always richer in the more volatile compound, regardless of the temperature of the mixture.



The setup used for sample distillation

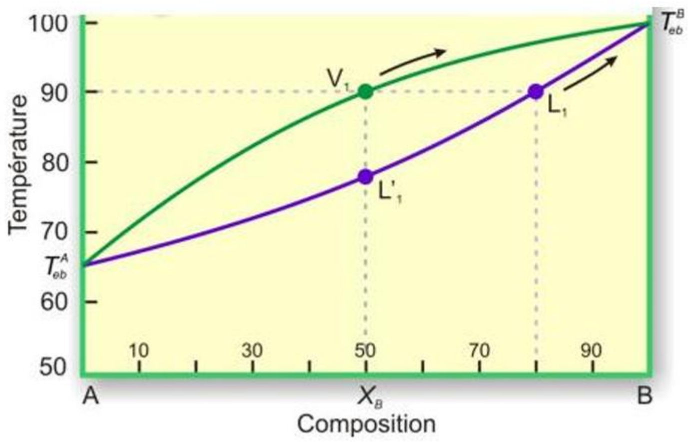


Figure 11: Evolution of the composition of the mixture during a simple distillation.

When this vapor (V1) condenses in the distillation head (L’1), it produces a distillate whose first drops will of course, have the same composition as the vapor which gave rise to it, i.e. 50% A and 50% B. We can thus see that the distillate has become enriched in compound A and the boiler has become depleted in compound A and enriched in B. Therefore, the mixture has a new composition and its boiling point will increase, producing a new vapor with a lower proportion of A than previously. The process continues in this way until A is exhausted, after which B eventually distills alone. This progression can be visualized on the phase diagram: as the mixture distills, we move towards higher temperatures and a higher proportion of B (The direction of evolution of the mixture in the boiler is indicated by arrows in the figure).

2)Fractional Distillation

To completely separate the mixture, several successive distillations are required. In fractional distillation, the process of successive vaporization and condensation is carried out in a fractionating column. The figure below is the schema of the fraction distillation

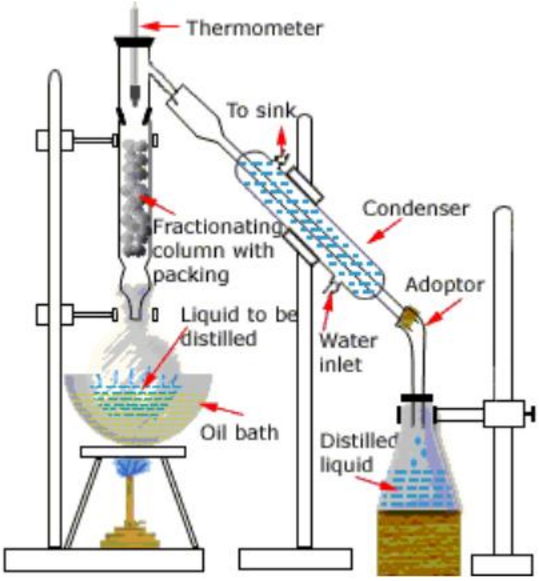


Fig.12: illustration of the fractional distillation

Example of a benzene and toluene liquid mixture

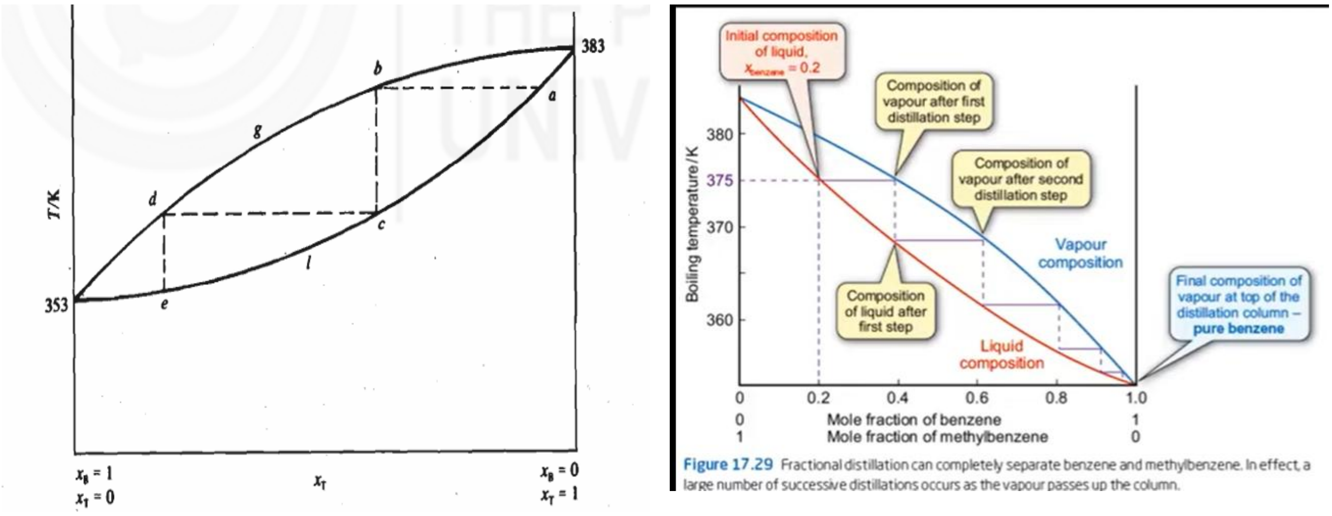


Figure 17.29 Fractional distillation can completely separate benzene and methylbenzene. In effect, a large number of successive distillations occurs as the vapour passes up the column.

Fig.13: binary diagram of fractional distillation of benzene-toluene mixture

The vapor in equilibrium is richer in the more volatile component (benzene) and will have the composition **b**. This vapor may be condensed by lowering the temperature along the line **bc**. If a small fraction of this condensate is vaporized, the vapors formed will have composition **d**. Finally, by repetition of vaporization

II.8: Extension to the Ternary System

So far, we have studied the liquid-vapor equilibria of binary (two-component) mixtures. Binary mixtures have the advantage of simple graphical representations in the plane, since a single axis graduated from 0 to 1 is sufficient to represent the mole fractions.

- However, nature is essentially composed of multi-component mixtures, and knowledge of the liquid-vapor equilibria of these mixtures is, of course, essential in classical chemical or petrochemical processes: it is generally only in the final stages of a separation process that mixtures that can be considered binary are obtained.

- The behavior of ternary mixtures can also be represented graphically in three-dimensional space (or in the form of plane sections or projections of diagrams in three dimensions).

Example of a ternary mixture of an ideal mixture:

We begin by considering the mixture methanol (1) - ethanol (2) - propanol (3): this mixture, formed of three alcohols, behaves roughly like an ideal mixture.

The liquid-vapor equilibria of this mixture are described by the temperature T, the pressure P, the composition of the liquid phase (x1, x2, x3), and the composition of the vapor phase (y1, y2, y3).

We immediately note that the composition of the liquid phase is described by only two independent variables, for example, x1, x2, since x1 + x2 + x3 = 1. The same is true for the vapor phase. The variance of such an equilibrium can be defined by:

$$\mathbf{v=c+2-\varphi}$$

Where: c is the number of constituents and φ is the number of phases.

A ternary liquid-vapor equilibrium therefore has a variance = 3.

We can therefore, for example, independently choose the temperature T and the composition of the liquid phase x1, x2. But once this choice is made, there will be only one pressure at which a liquid-vapor equilibrium can occur (bubble pressure**), and the composition of the vapor in equilibrium with the liquid will also be fixed.

In the case of our ideal liquid mixture, and assuming that the vapor phase can be considered an ideal gas, the equilibrium equations are:

$$x_1 P_1^{(s)}(T) = y_1 P$$

$$x_2 P_2^{(s)}(T) = y_2 P$$

$$x_3 P_3^{(s)}(T) = y_3 P$$

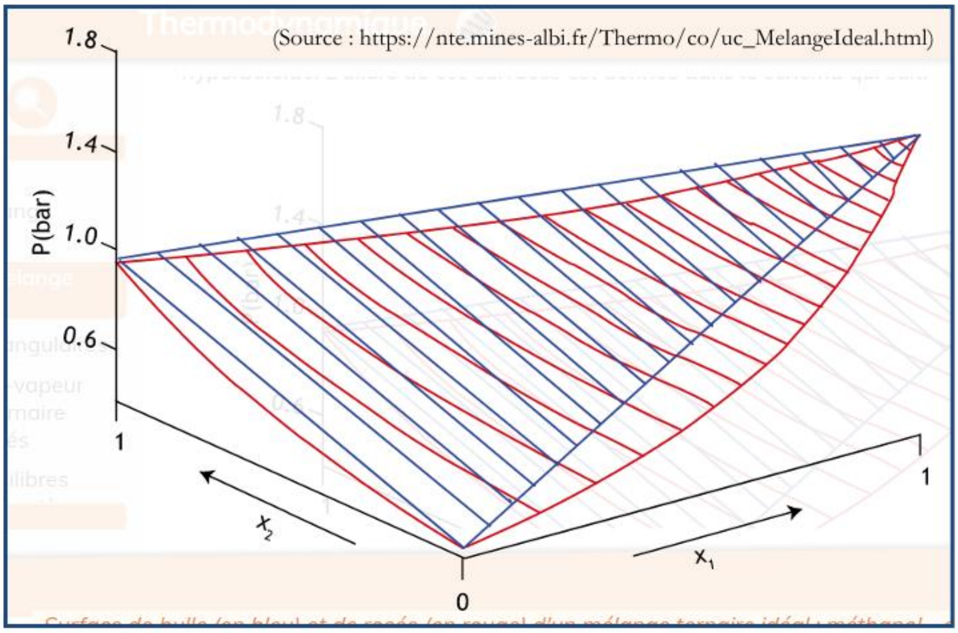
We see that if T, x1 and x2 are fixed, we can find the equilibrium pressure analytically:

$$P = x_1 P_1^{(s)}(T) + x_2 P_2^{(s)}(T) + (1-x_1-x_2)\, P_3^{(s)}(T)$$

and the composition of the steam is immediately deduced:

$$y_1 = P_1^{(s)}(T)/Py_2 = P_2^{(s)}(T)/P$$

We can thus plot a bubble surface: P as a function of x1 and x2, which is a plane here, and a dew surface*: P as a function of y1 and y2, which, for an ideal mixture, is a hyperboloid. The shape of these surfaces is given in the following diagram.

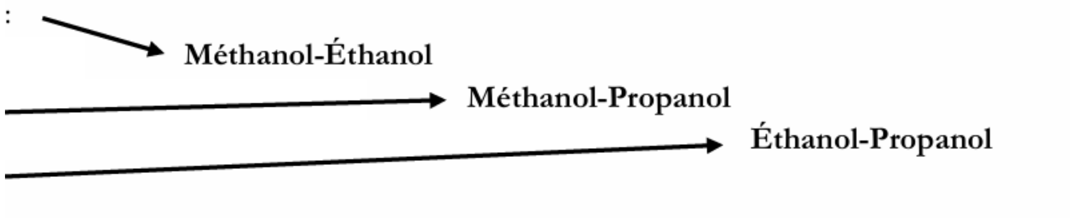


(Source : https://nte.mines-albi.fr/Thermo/co/uc_MelangeIdeal.html)

Fig.14:Bubble surface (in blue) and dew point (in red) of an ideal ternary mixture: methanol - ethanol - propanol at 350 K.

On the faces of this graph, we can clearly see the equilibrium lenses of

the binary subsystems:



But if we take any composition of the liquid on the bubble surface, we cannot, from this simple diagram, find the composition of the vapor in equilibrium: all we know is that it is found on the dew point surface at the same pressure: the locus of possible points is therefore a curve. This diagram should be completed with straight line segments, connecting the points representing the liquid (on the bubble surface) to the points representing the vapor in equilibrium (on the dew point surface). Such a diagram will quickly become illegible. This is why ternary mixtures are most often represented by sections at different pressures of these isothermal surfaces. On these sections at fixed T and P, we see a bubble curve separating a homogeneous liquid domain from a liquid-vapor domain, and a dew curve separating the liquid-vapor and vapor domains. On these diagrams, we can easily show the conodals: segments that connect the points representing the liquid and vapor phases at equilibrium.

- **Triangular diagrams:**

- A constant-pressure cross-section, as described, of the isothermal phase diagram of a mixture will have the shape of a right triangle: a diagram with two orthonormal axes at x1 and x2, varying from 0 to 1, and bounded by the line (hypotenuse) x1 + x2 = 1: beyond this line, the mole fraction x3 would be negative.
- Each point in this domain corresponds to a composition, and each vertex to a pure substance. The mole fractions x1 and x2 are read directly by projection onto the axes. We obtain a reading of the mole fraction x3 by lowering, from the point representing the mixture, the height MH to the hypotenuse: it is easily shown that MH= $\sqrt{2}x_3$.

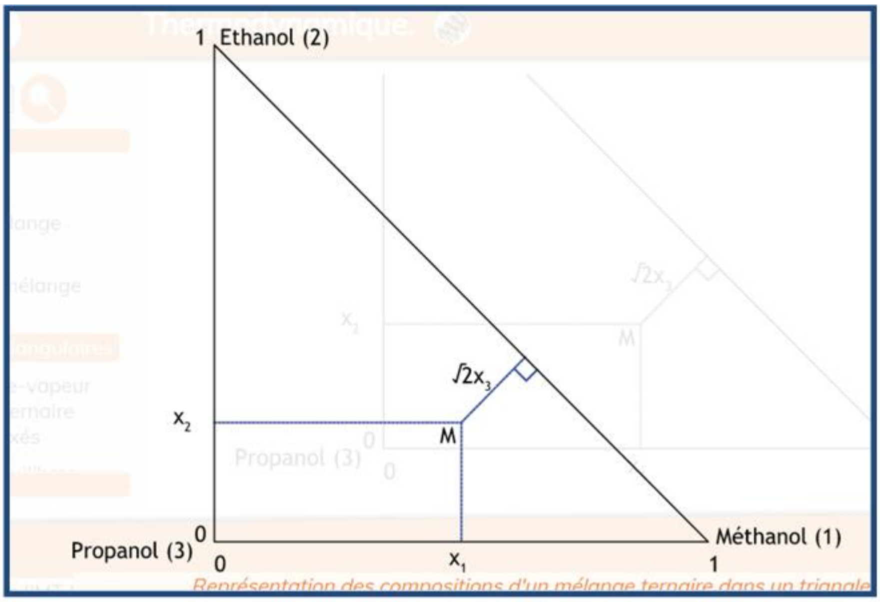


Fig.15:Representation of the compositions of a ternary mixture in a right triangle

This representation based on two orthogonal composition axes introduces an asymmetry between the constituents and the ways of interpreting mole fractions. It is often preferred to use an equilateral triangle, i.e., to start with axes forming an angle of π/3 between them. The height of this triangle is standardized to unity. A mixture is represented by a point inside the triangle, and the mole fraction of a constituent is given by the height reduced from this point on the side of the triangle opposite the vertex corresponding to the constituent in question.

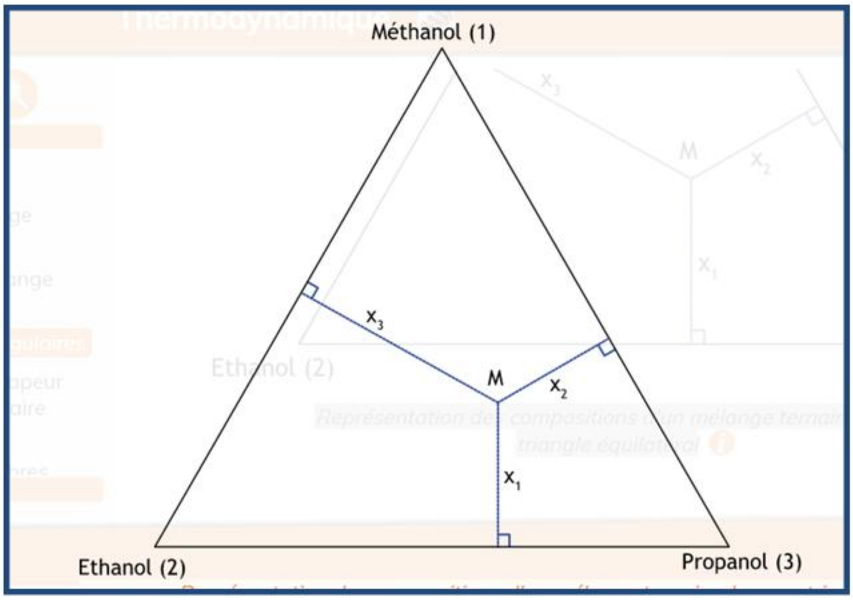


Fig.16:Representation of the compositions of a ternary mixture in an equilateral triangle