

Chapter III: Thermodynamics of Liquid-Liquid and Liquid-Solid Equilibrium

III.1: Thermodynamic equilibrium of liquid-liquid mixtures (LLE)

INTRODUCTION

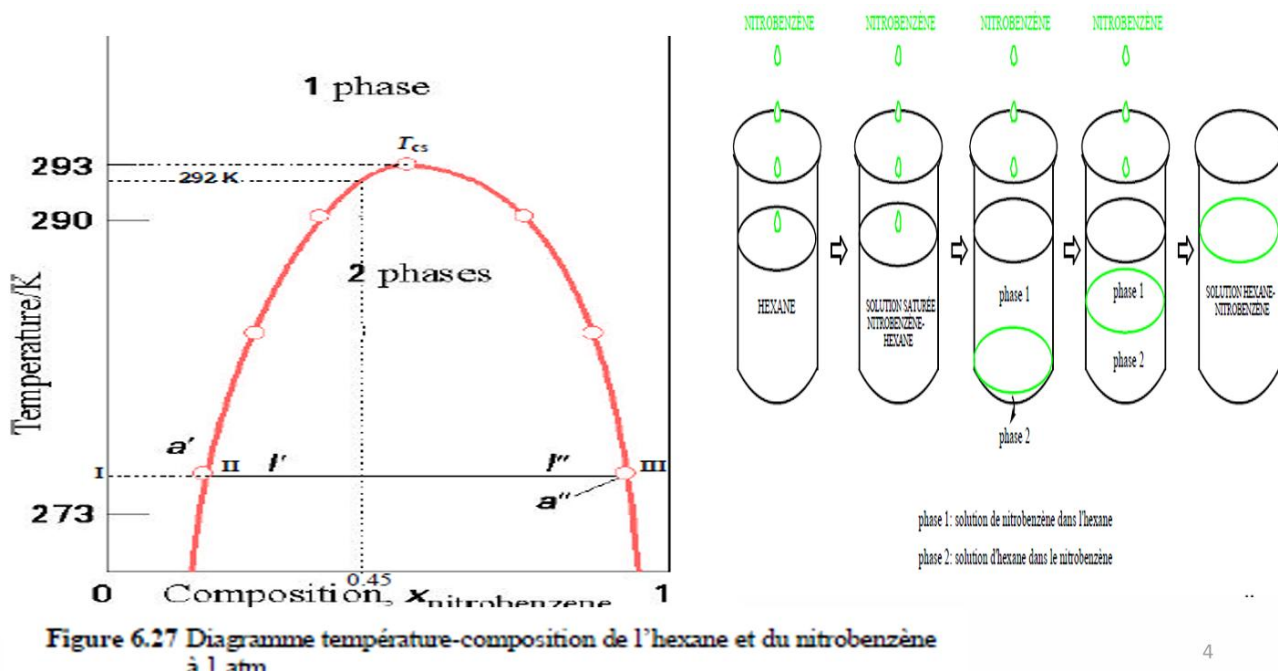
Liquid–liquid equilibrium (LLE) occurs when two immiscible or partially miscible liquids coexist in stable equilibrium

Thermodynamic Equilibrium Conditions: For two liquid phases (let's call them α and β) to be in equilibrium:

1. **Thermal equilibrium:** $T^\alpha = T^\beta$ (Both phases are at the same temperature.)
 2. **Mechanical equilibrium:** $P^\alpha = P^\beta$ (Same pressure in both phases.)
 3. **Chemical equilibrium:** For each component i , the **chemical potential** must be equal: $\mu_i^\alpha = \mu_i^\beta$ (This means there's no **driving force** for component i to move from one phase to the other.)
- Think of something like **oil and water** — they separate into **two phases**, each saturated with a little bit of the other. That's **LLE** in action.

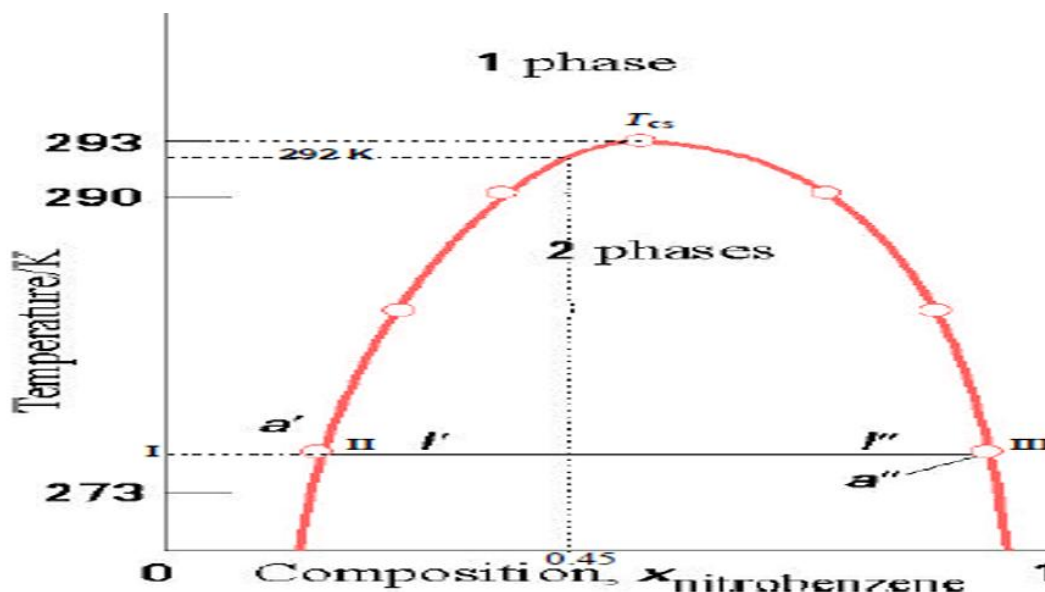
III.1.1: Liquid-Liquid Phase Diagrams: Phase diagrams can be used to analyze the composition of partially miscible liquids (liquids that do not mix in all proportions).

Example of a hexane and nitrobenzene mixture

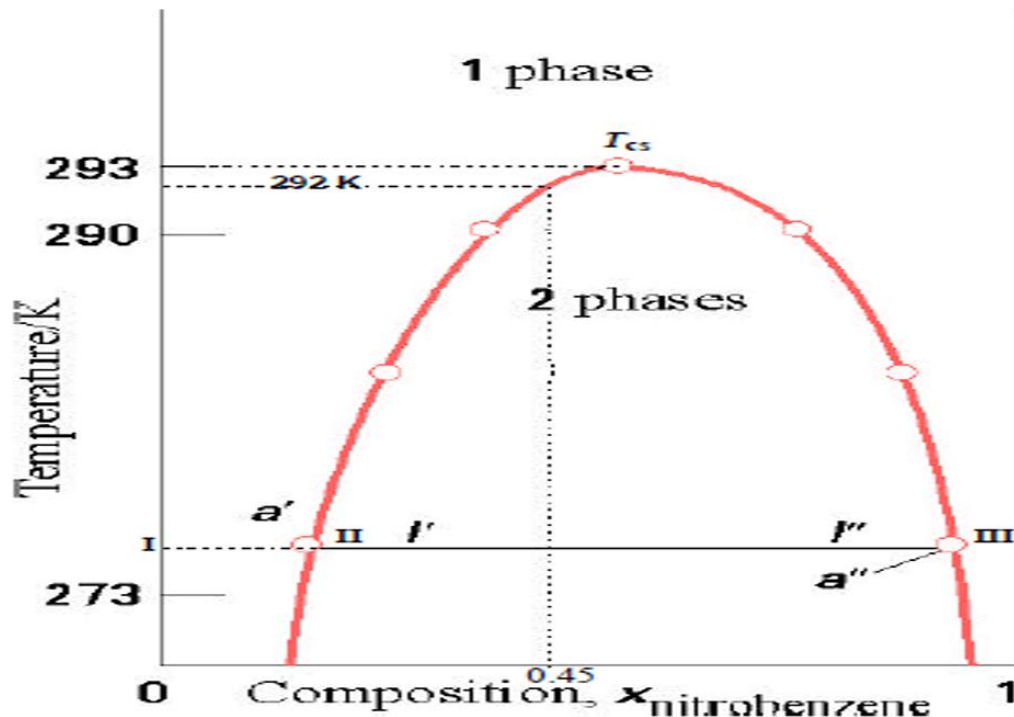


- The phase diagram shows that the solubility of nitrobenzene in hexane and that of hexane in nitrobenzene vary with temperature; therefore, the compositions and proportions of the two phases change with temperature.

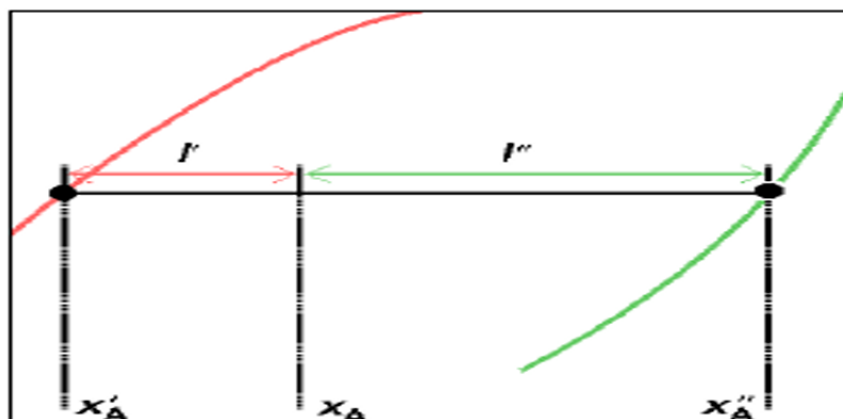
- A **temperature-composition diagram** is therefore constructed to represent the composition of the system at each temperature.
- The "∩" shaped curve is the solubility curve giving the nitrobenzene composition of the two liquid phases in equilibrium.



- Let's choose a temperature of 275 K (corresponding to point I in the Figure above). Pure hexane is present at point I. If a small amount of nitrobenzene is added to the hexane sample, it dissolves completely, leaving only one phase present. However, as more nitrobenzene is added, there comes a point where the hexane becomes saturated with nitrobenzene, and dissolution stops (point II on the phase diagram). The mixture then consists of **two phases in equilibrium** with each other. The more abundant phase is a solution of nitrobenzene in hexane, and the less abundant phase is a solution of hexane in nitrobenzene. On the temperature-composition diagram in , the composition of the majority phase is given by point a' and that of the less abundant phase is given by point a".
- For a given mixture composition, the temperature above which the system exists as a **single phase** is given by the intersection of the vertical line (drawn from the abscissa XA) with the solubility curve. For example, for $x_{\text{nitrobenzene}} = 0.45$, the phase diagram shows that this nitrobenzene-hexane mixture must be heated to 292 K to obtain a single phase (see the figure).
- This diagram will tell you below which temperature the solution will **separate**(upper critical temperature (**Tuc**)).



- If the **addition** of nitrobenzene is continued, **the hexane dissolves** in it, and the amount of matter in the second phase (the least abundant phase) increases at the expense of the first phase (the majority phase) up to point III (indicated on the curve), where the overall composition of the mixture is a. From point III onward, there is a sufficient amount of nitrobenzene present that it can dissolve all of the hexane, and the system reverts to a single phase to the right of point III. Beyond point III, further addition of nitrobenzene only dilutes the solution.
- ❖ A connecting line joining a' and a'' connects the two phases that are in equilibrium with each other. How can the relative abundance of the two phases at a given mixture composition, x_A , be determined from the connecting line (see figure below)



If n' is the number of molecules (A + B) in one phase and n'' is the number of molecules (A + B) in the other phase, the total number n of molecules in the mixture is:

$$n = n' + n''$$

The total amount of substance of A in the sample is n_XA , where XA represents the overall mole fraction of A in the sample (this is the quantity plotted on the abscissa of the temperature-composition diagram). It follows that the total number of molecules of A is also the sum of the amount of substance of A in each of the two phases, where the mole fractions are $X'A$ and $X''A$: $n_XA = n'X'A + n''XA$

Knowing that $n = n' + n''$, we can also write $n_XA = n'X'A + n''X'A$

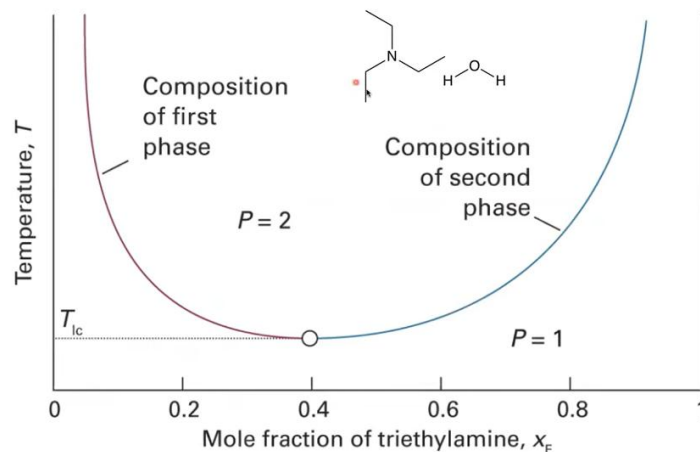
Rearranging these two expressions, we obtain: $n'X'A + n''X'A = n'X'A + n''X'A$

$$n'(XA - X'A) = n''(XA - X'A)$$

As can be seen in Figure, it follows that: $n'l' = n''l''$ or: $\frac{n'}{n''} = \frac{l''}{l'}$

➤ System with lower critical solution temperature

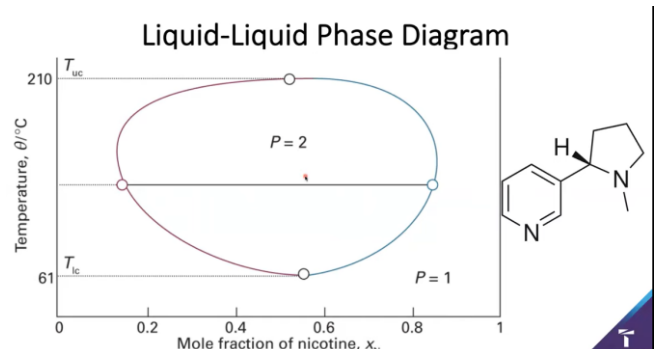
For some systems, there is a lower critical solution temperature, T_{cl} , below which they mix in all proportions and above which they form two phases. Water and triethylamine (figure below) are an example. In this case, at **lower temperatures** the two components are more miscible because they form a **weak** complex; at **higher temperatures**, the complexes **dissociate** and the components are **less miscible**.



➤ systems with upper critical temperature and lower critical temperature.

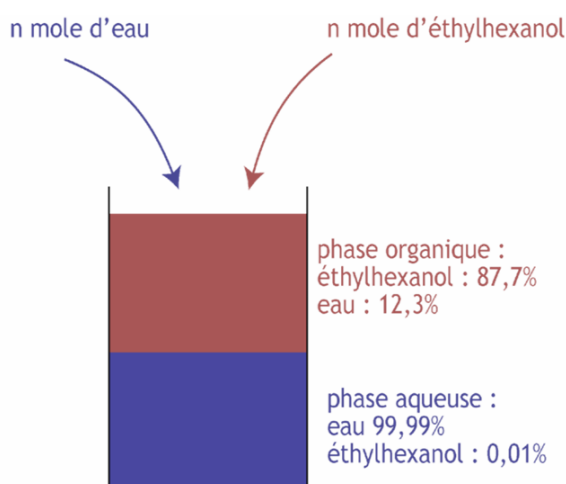
Nicotine and water are Example (see Fig below).

Temperature-composition diagram of the water and nicotine mixture



Example

- We have already discussed the partial immiscibility of two constituents in the liquid state, for example, water and butanol (The phenomenon of partial immiscibility appears particularly between water and alcohols with a longer chain length than butanol. Thus, water and 2-ethylhexanol exhibit low mutual solubility: if we create an equimolar mixture of these two substances at a temperature of 25°C, it will separate into two phases (see the following figure (below):



One, rich in water (aqueous phase), which contains only traces of ethylhexanol (around 10⁻⁴ in mole fraction)

- The other, rich in ethylhexanol (organic phase) where the mole fraction of ethylhexanol is 0.877 and that of water is 0.123
- Since water has a higher density than ethylhexanol, the aqueous phase will be found at the bottom of the container (heavy phase), while the organic phase will float (light phase).

- We can add ethanol to a mixture of water and ethylhexanol, which has the property of being miscible with each of the other two isolated constituents. We then obtain a ternary mixture; the phase diagram must be represented on a triangular diagram.

III.1.2: Application to Liquid - Liquid Extraction

- Liquid-liquid extraction involves the separation of the constituents (solutes) of a liquid solution by contact with another insoluble liquid.
- Solutes are separated based on their different solubilities in different liquids.
- Separation is achieved when the substances constituting the original solution is transferred from the original solution to the other liquid solution.
- So in this operation. the solvent-rich product of the operation as an extract, and the **residual** liquid from which solutes have been removed, as **raffinate**, is obtained.
- Hence, the liquid-liquid extraction involves a ternary (i.e. 3-component) system.
- So, to describe the concentrations and amounts of these ternary mixtures equilateral triangular coordinate system is used

III.1.3: Extension to the Ternary System (one pair partially soluble)

This is the most common type of **Extraction**

Example

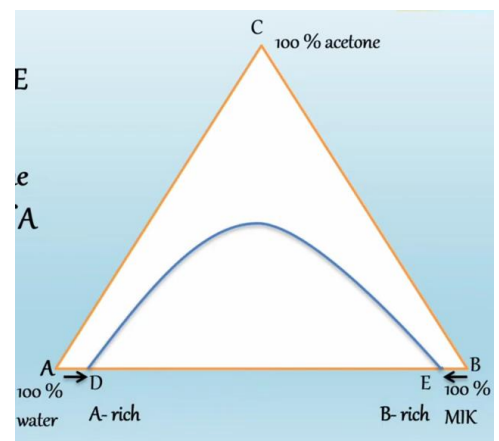
- System of water(A), methyl isobutyl ketone(B) and Acetone(C)
- System of Water(A), Chloroform(B) and acetone(C)
- System of Benzene(A), water(B) and acetic acid(C)

In the above examples, A is the carrier and B is the solvent for extracting the solute C.

- Such that the solute C is completely miscible with the two solvents A and B but the two solvents A and B are partially miscible with each other.

Triangular coordinate system

- apex C represents 100 % acetone and apexes A represents 100% water and B and 100% methyl isobutyl ketone (MIK).
- In this ternary system, Liquid C dissolves completely in A and B, but A and B dissolve only to limited extent in each other

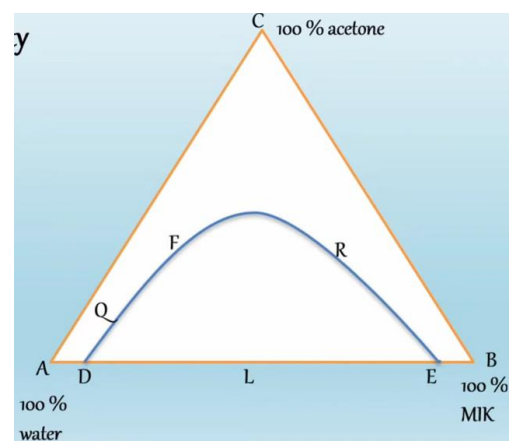


-Distance between points D and E represents a binary mixture of MIK and water of composition in the form of two liquid layers.

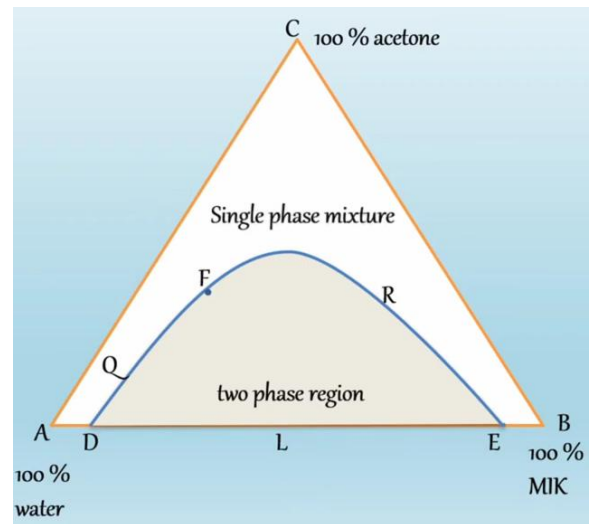
-Point L anywhere between D and E, represents a binary mixture, will separate into two insoluble liquid layers of compositions at D and E.

-Curve DQFRE is the binodal solubility curve, which indicates the change in solubility of the A-rich and B-rich phases due to addition of C.

Equilibrium compositions of two phases lie on this curve.



- The area under the binodal solubility curve represents a two-phase region.
- All points outside the binodal solubility curve represent a homogeneous solution of one liquid phase(single phase mixture).
- The curved line ERF indicates the composition of the saturated MIK layer, and the curved line DQF indicates the composition of the saturated water layer.



III.2: liquid solid binary mixture

We are interested in the equilibrium properties of a system composed of two (metallic) components denoted A and B. We assume that components A and B:

- form a single phase in the liquid state (**total miscibility**)
- are distributed into one or two phases in the solid state.
- ❖ The behavior of the system depends a priori on the species present as well as the state variables: temperature and pressure. For condensed phases, the influence of pressure is weak. We limit ourselves in the following to isobaric diagrams.
- ❖ **Miscibility of solids:** The study of the miscibility of solids, as for liquids, reveals three possibilities:

1. Total solubility:

Examples: * Silicon-Germanium

* gold-Copper

2. Partial solubility

Examples: * Chromium-Nickel

Sn(tin)-Pb(plomb)

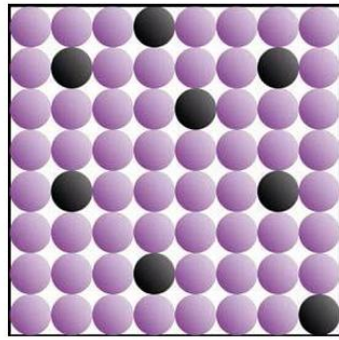
3. Zero solubility

Examples: * Cd(cadmium)-Bi(Bismuth)

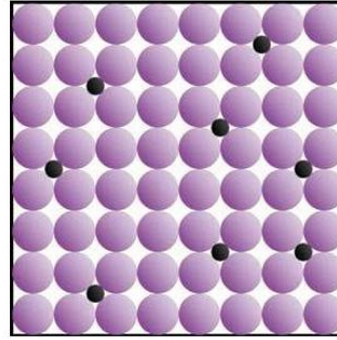
III.3.1 Miscibility total in the Solid State

Two crystalline solids are completely miscible (form a single solid solution) when they have:

- Identical crystal structures.
- Similar atomic radius (difference < 15%).
- Very similar physical and chemical properties.



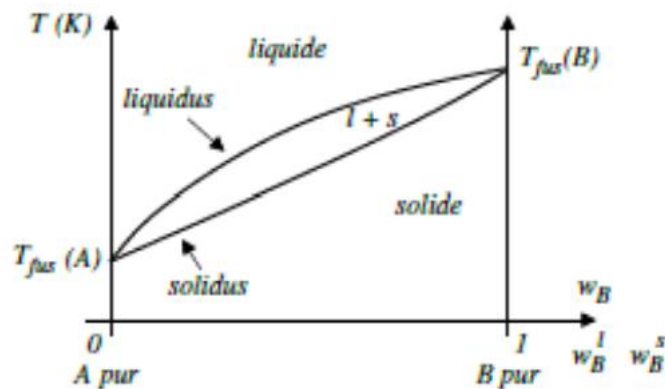
(a) Solution solide de substitution



(b) Solution solide d'insertion

III.3.2 Binary Diagram for an Ideal Solid Mixture

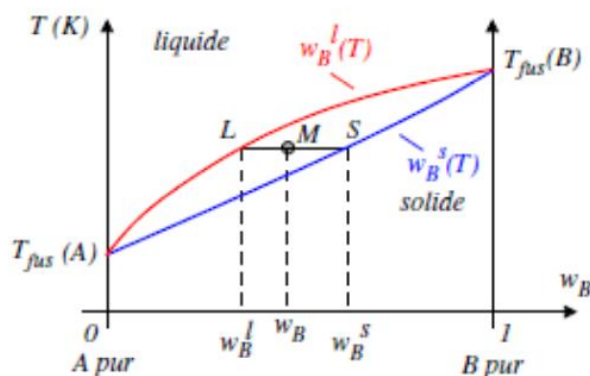
In the case of the copper-nickel alloy, since the crystal lattices are identical and the metallic radii are similar, the mixture is ideal, and the shape of the binary diagram is shown in the figure below.



- The curve separating the solid domain from the {solid + liquid} domain is called **the solidus curve**, and it allows us to determine the composition of the solid phase. The curve separating the liquid domain from the two-phase domain is called the **liquidus curve**, and it allows us to determine the composition of the liquid phase.

- Two-phase system

A mixture where the liquid and solid phases coexist is represented by point M:



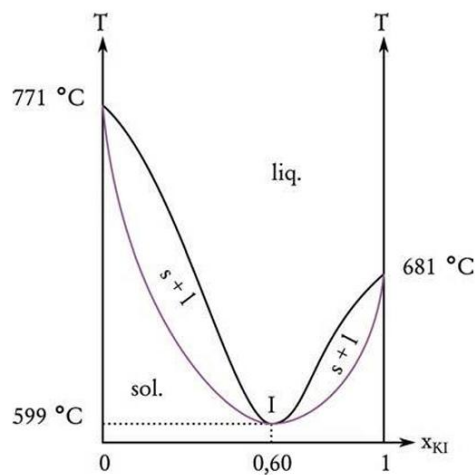
- Projecting M onto the x-axis gives the mass fraction of B in the mixture: w_B .
- Projecting point S of the solidus onto the x-axis gives the mass fraction of B in the solid phase: w_B^s .

- The projection of the liquidus point L onto the abscissa axis gives the mass fraction of B in the liquid phase: w_B^L

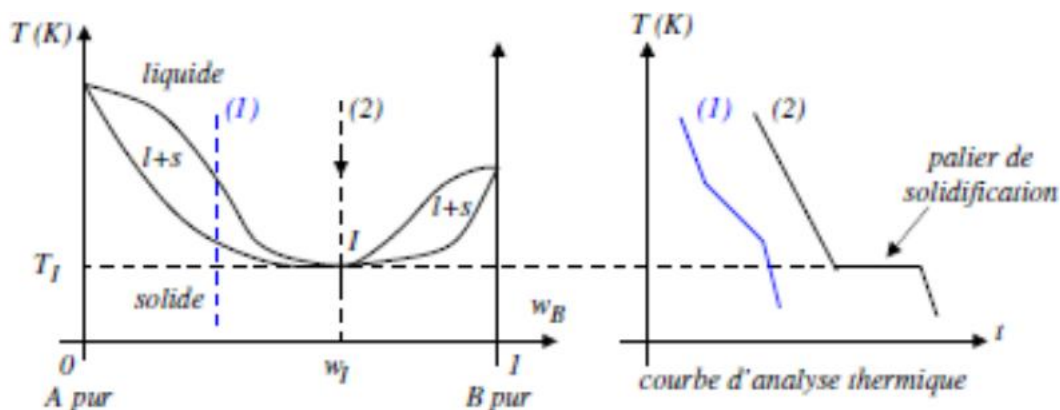
Chemical Momentum Theorem (inverse segment rule): for a two-phase system, the mass of the liquid phase m^L and m^S , the mass of the solid phase, verify the equality. $\frac{m^L}{m^S} = \frac{MS}{ML}$

III.2.3 Binary Diagram for a Non-Ideal Solid Mixture

As with liquid-vapor binary diagrams, when **the solid mixture is non-ideal**, an **extremum** appears on the diagram, similar to **an azeotrope**. For a solid-liquid diagram, this point is called **the indifferent point**. The solid-liquid binary diagram KI KCl, shown below, has one at 599 °C.



At point I, the liquid and solid phases coexist with the same composition. This is the case, for example, with the **Gold/Copper diagram**. These diagrams read and use exactly like the single-zone diagrams.

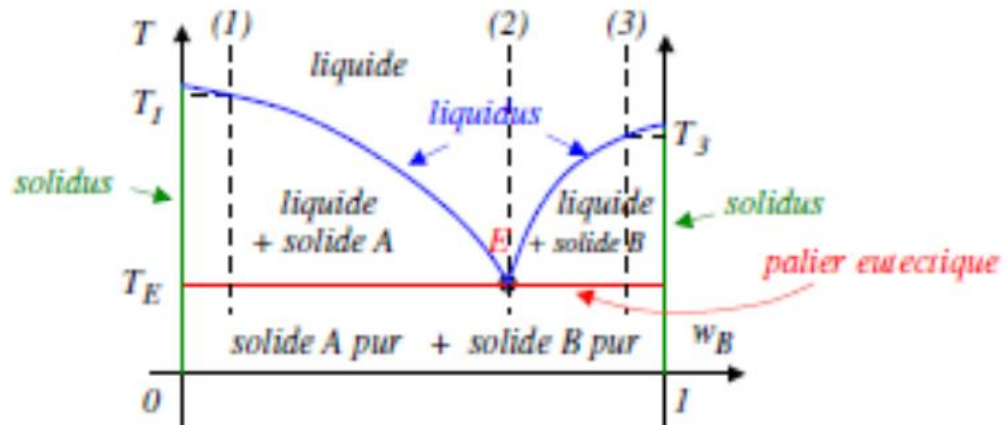


Note: An indifferent mixture (composition of the indifferent point) behaves like a pure substance.

III.2.4 Immiscible Liquid-Solid Mixture (or Zero Miscibility of Solids): Eutectic Point

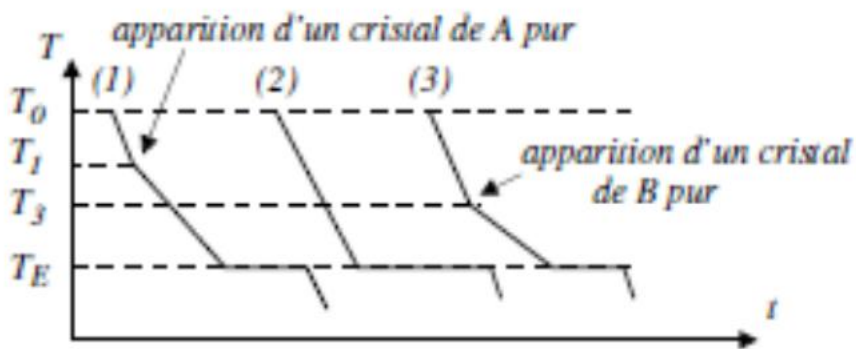
Immiscibility in the solid state is a very common situation. In these systems, the coexistence of three phases (two immiscible solids and the liquid phase) results in the existence of a characteristic point called the eutectic (E), which "melts well."

- The three-phase equilibrium temperature T_E is **the eutectic temperature**, and a mixture with the composition of the liquid phase of a three-phase system is a eutectic mixture.



❖ Equilibrium at eutectic level **E**: $\text{Liq} \Leftrightarrow \text{A(solid)} + \text{B(solid)}$

- Thermal analysis curve



Experiment 1: When the temperature reaches T_1 , pure crystals of A appear. The system enters the biphasic domain (pure solid A and liquid A). When the temperature reaches T_E , the liquid composition is that of the eutectic, and solid B appears. We observe the simultaneous crystallization of pure solids A and B. Throughout the process, the temperature remains at T_E .

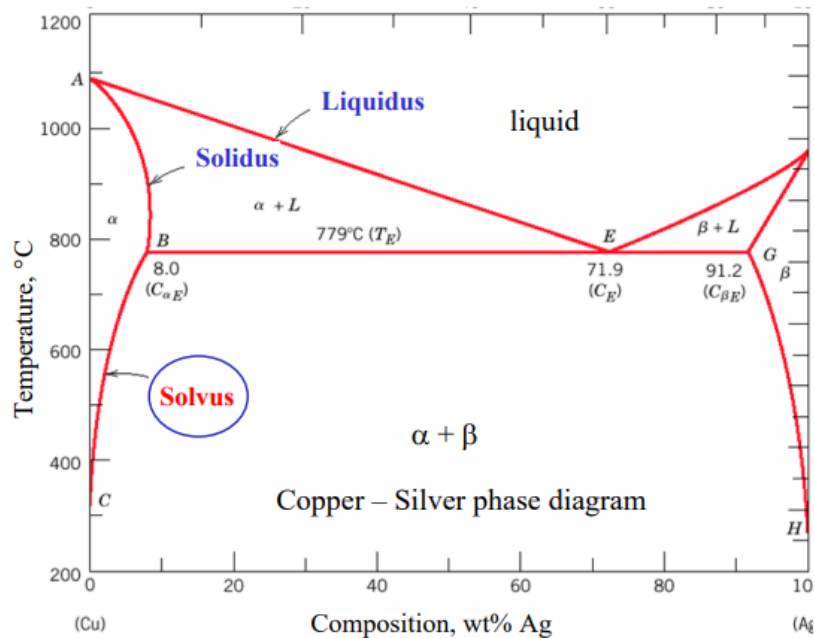
Experiment 2: The liquid has the eutectic composition; it cools to the eutectic point. The two solids crystallize at the eutectic composition. A temperature plateau is observed. Once crystallization is complete, the solids simply cool.

III.2.5 systems (alloys) with limited solubility in the solid state

This is the case of two substances that are **completely miscible in the liquid state** but **poorly soluble in the solid state**. In this case, several representations are possible:

1) Binary Eutectic Systems

The figure below shows the binary diagram of a solid-liquid mixture with partial miscibility in the solid state



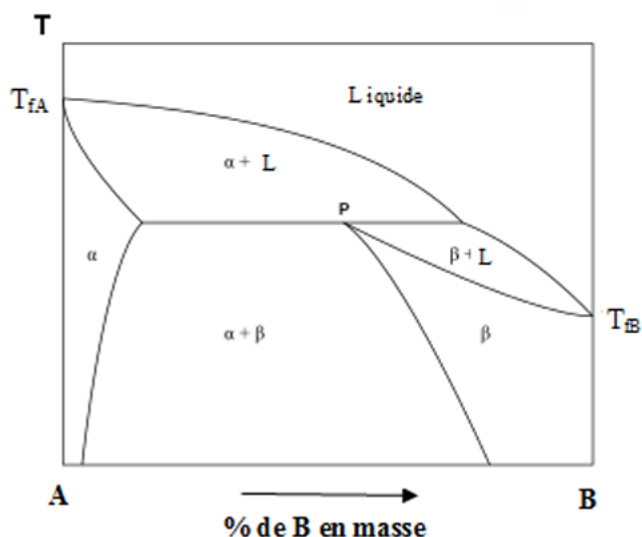
- **Three single-phase regions:** (α - solid solution of Ag in Cu, β = solid solution of Cu in Ag, L - liquid)
- **Three biphasic regions** ($\alpha + L$, $\beta + L$, $\alpha + \beta$) Solvus line separates one solid solution from a mixture of solid solutions. The solvus line shows the limit of solubility
- **At Eutectic or invariant point (E):** Liquid and two solid phases co-exist in equilibrium at the eutectic composition CE and the eutectic temperature TE (temperature at eutectic point).
- **Eutectic isotherm** is the horizontal solidus line at TE.

Eutectic reaction is the **transition** between a **liquid** and a mixture of **two solid phases**, $\alpha + \beta$ at eutectic composition CE. The melting point of the eutectic alloy is lower than that of the components (eutectic = easy to melt in Greek). At most two phases can be in equilibrium within a phase field. Three phases (L, α , β) may be in equilibrium only at a few points along the eutectic isotherm. Single-phase regions are separated by 2-phase regions.

2) Binary equilibrium diagram of A-B showing a peritectic point

Peritectic Reactions: A peritectic reaction is when a solid phase and liquid phase will together form a second solid phase at a **particular temperature** and composition **upon cooling**, e.g. $L + \alpha \leftrightarrow \beta$ These reactions are rather slow as the product phase will form at the boundary between the two reacting phases thus separating them, and slowing down any further reaction.

- This reaction occurs at a **constant temperature**, and at **the peritectic point**, three phases coexist in equilibrium.



3) Binary system with the formation of a compound.

- **DEFINED COMPOUNDS**

Example: In the solid state, compounds A and B of the binary mixture can combine to form new chemical species **AB** with properties very different from those of **the two pure substances**.

a) Binary system with congruently melting compounds :

This phase diagram can be treated as two parts divided by **a vertical line** which represents the compound **AB**. The left part of the line can be considered as **the eutectic system of A and AB**, and the right part of the line can be treated **as the eutectic system of AB and B**. The characteristic feature of this system is that the maximum of the liquidus curve represents the melting point of AB. By **cooling** down a liquid mixture with the composition **AB** the **compound AB** crystallizes. In other words, the compound **AB melts congruently**.

Consider the binary s/l diagram of the aniline A/phenol B mixtures. It should reveal a defined compound **A_xB_y** (here $x = y = 1$), with the same properties in the solid state and for its phase change as a pure substance.

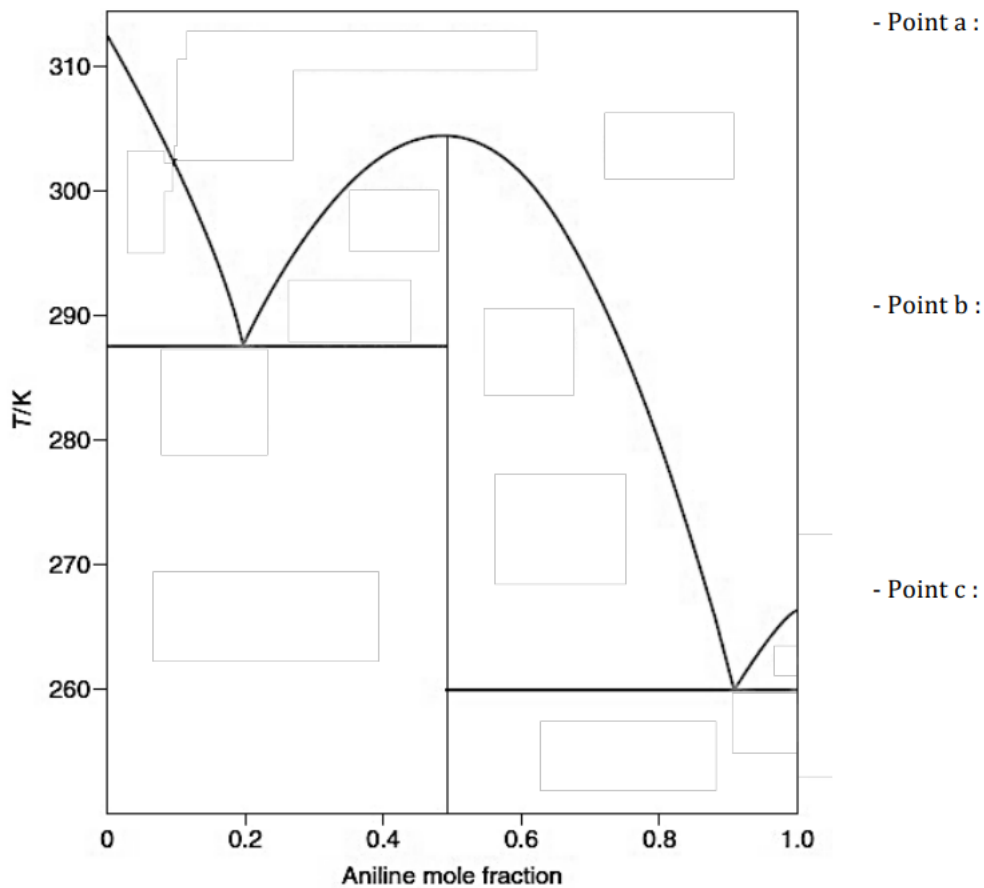
Note:

- The binary s/l diagrams of **A/B mixtures** involving a defined compound A B are constructed and read as the juxtaposition of the two binary **diagrams A/A_x-B_y**, and **A_x-B_y/B**.

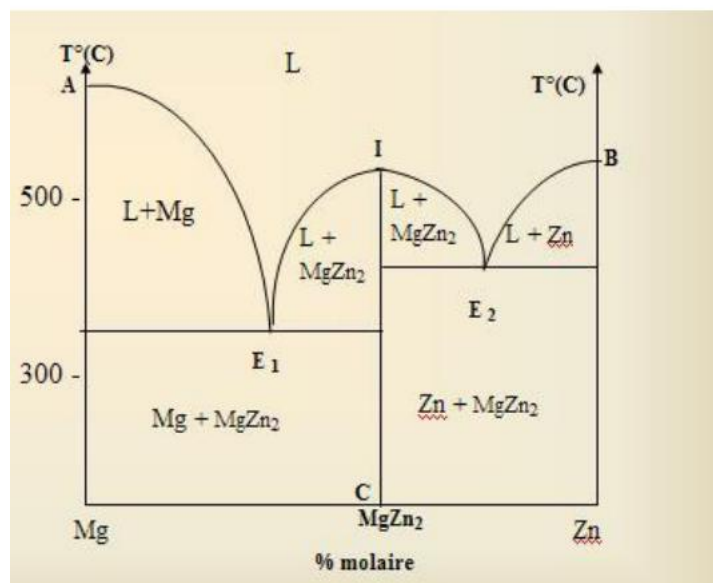
- These two diagrams each have **eutectic mixture**.

Indeed, the pure substances A and B have very different structures from the defined compound, so there is never complete miscibility in the solid state.

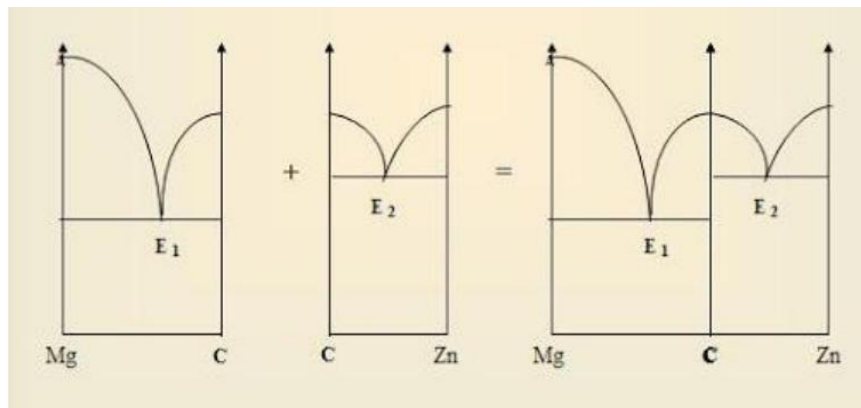
+ Reading the binary solid liquid diagram of the aniline A/phenol B mixture:



Example: let's take an example of Mg Zn mixture:

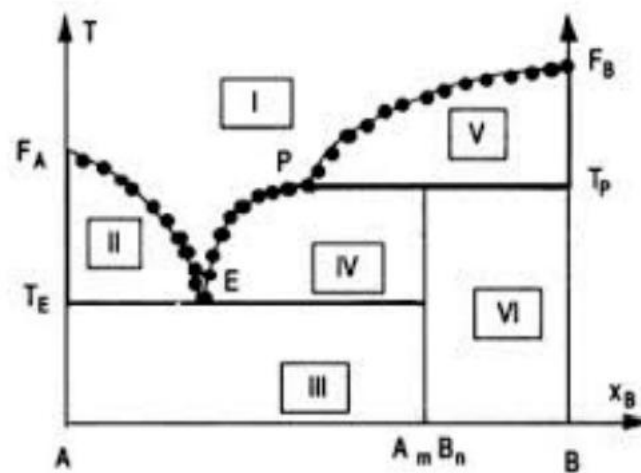


The existence of vertical line C indicates the presence of a **defined compound** with a composition of 66.67% Zn and 33.33% Mg. Its formula is therefore $\text{Mg}_{0.33}\text{Zn}_{0.66}$ (MgZn_2). This compound is similarly melting since its vertical line reaches the liquidus (AE1IE2B). Point I is called the indifferent point and corresponds to the melting point of the defined compound. This diagram can be considered as the **juxtaposition of two simple solid-liquid diagrams** (Mg-MgZn₂) and (MgZn₂-Zn).



b) Defined compound with incongruent melting

In the case where the vertical line indicating the presence of a defined compound does not reach the liquidus, the defined compound **decomposes before melting** at a temperature called the **incongruent melting temperature**.



Description of the diagram:

I : Liquide ($V = 2$)

II : Liquide + $A_{(sd)}$ ($v = 1$)

III : $A_{(sd)} + A_m B_n(sd)$ ($v = 1$)

IV : Liquide + $A_m B_n(sd)$ ($v = 1$)

V : Liquide + $B_{(sd)}$ ($v = 1$)

VI: $B_{(sd)} + A_m B_n(sd)$ ($v = 1$)