

Diagramme Binaire : système liquide-vapeur

* Introduction :

Fraction molaire : $x_i = \frac{n_i}{\sum n_i}$

- exemple : $\begin{pmatrix} A \\ B \end{pmatrix}$

$$x_A = \frac{n_A}{n_A + n_B} ; x_A + x_B = 1$$

$$x_B = \frac{n_B}{n_A + n_B}$$

les solutions = système contient au moins 2 constituants

idéale

les interactions entre les espèces sont identiques

→ sans échange de chaleur : $\Delta H = 0$
→ sans échange de volume.

réelle

∃ interaction entre les espèces

→ $\Delta H > 0$: endothermique
→ $\Delta H < 0$: exothermique

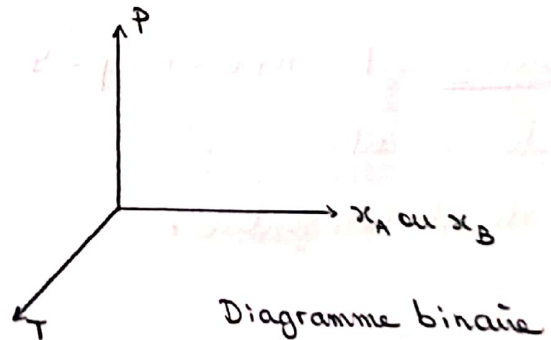
⇒ échange de chaleur + de volume.

A et B 2 corps purs

Ⓐ et Ⓑ
système binaire

$\begin{cases} T \\ P \\ x_B \text{ ou } x_A \end{cases}$

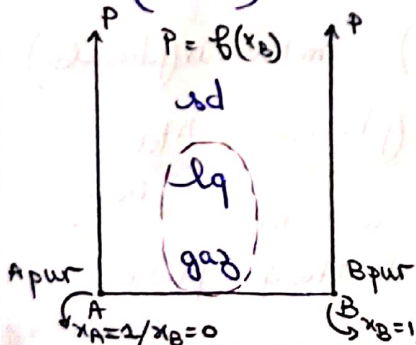
les variables



les diagrammes binaires

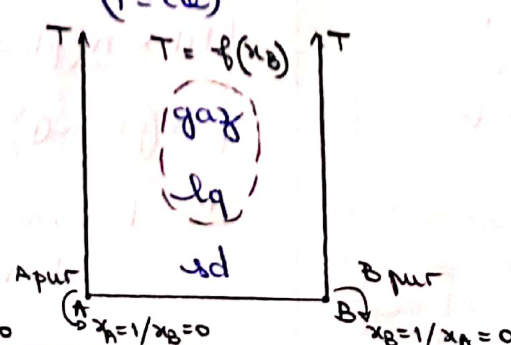
isotherme

($T = \text{cte}$)



isobare

($P = \text{cte}$)



(1)

systeme binaire lg-vapeur

① miscibilité totale

② miscibilité nulle

③ miscibilité partielle

isobare

a/ sol idéale

b/ sol réelle

isobare

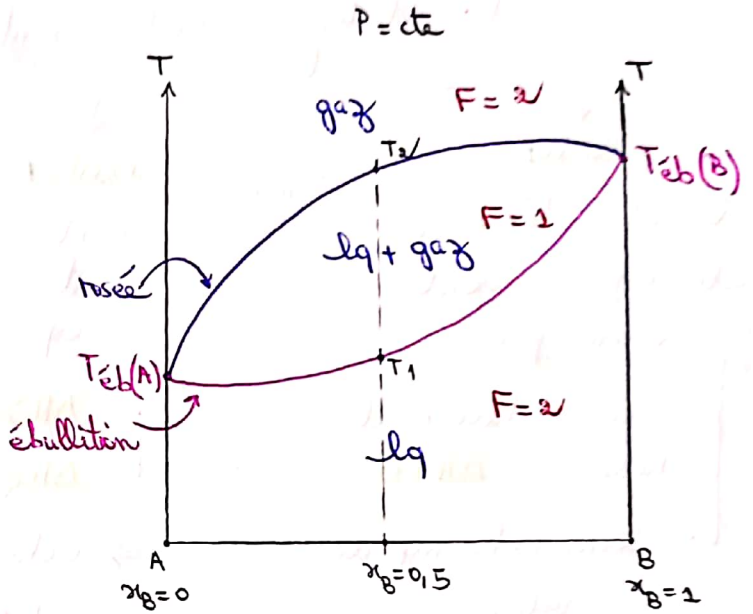
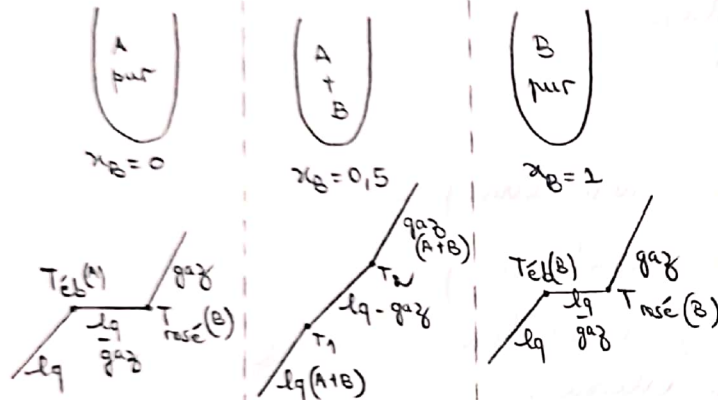
isotherme
isobare

isotherme
isobare

① Miscibilité totale :

a/ solution idéale :

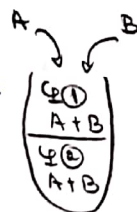
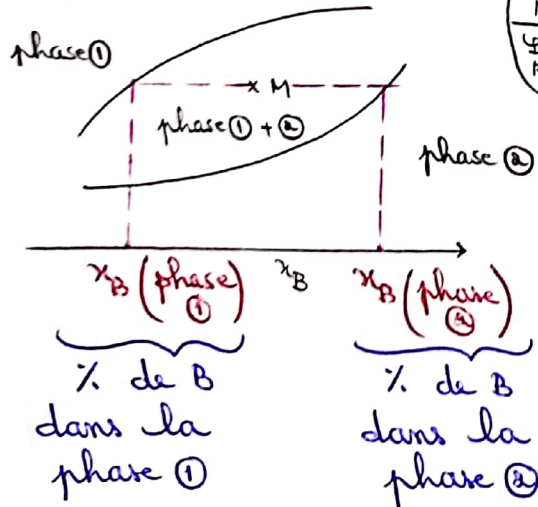
+ isobare :



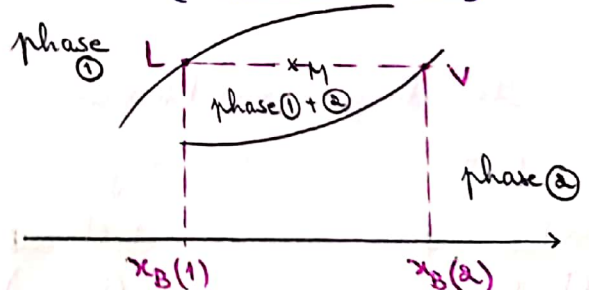
Δ = variance : $F = n + 2 - r - q - \varphi = 2 + 2 - 0 - 1 - \varphi = 3 - \varphi$

+ les lois à utiliser = !!

Règle de l'horizontale =



Règle des moments cinétiques (segment inverse)



$$\begin{cases} \overline{ML} \times n(\text{phase ①}) = \overline{MV} \times n(\text{phase ②}) \\ n(\text{phase ①}) + n(\text{phase ②}) = n_{\text{totale initiale}} \end{cases}$$

Δ : Détermination de nb de mol de chaque phase

Δ par convention :

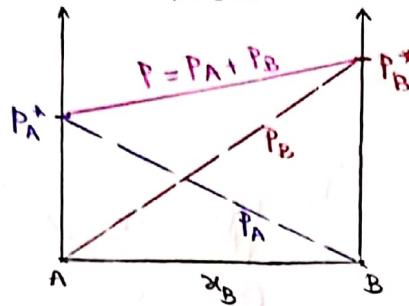
$x_B \rightarrow \text{lg}$
 $y_B \rightarrow \text{gaz}$

(2)

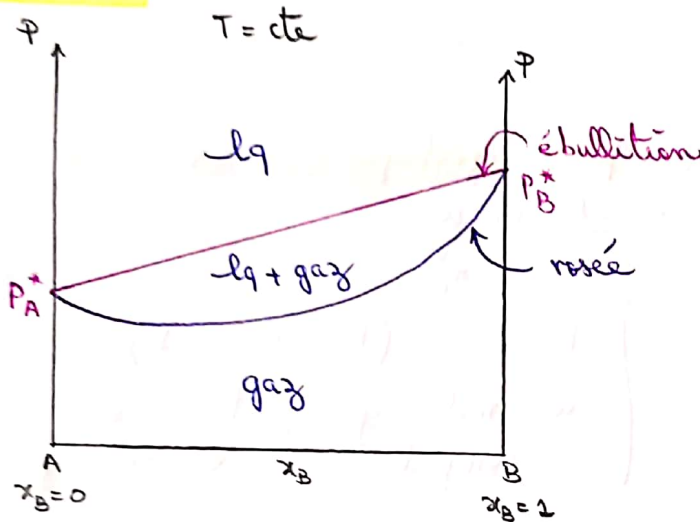
* loi de Raoult = (à utiliser avec les sol^s idéales seulement)

$P_i = x_i \cdot P_i^*$ et $P = \sum_i P_i$ ← pression partielle
pression de vapeur saturante
 $T = cte$

on a :
$$\begin{cases} P_B = f(x_B) = x_B P_B^* \\ P_A = f(x_A) = x_A P_A^* \\ P = P_A + P_B \end{cases}$$



* isotherme =



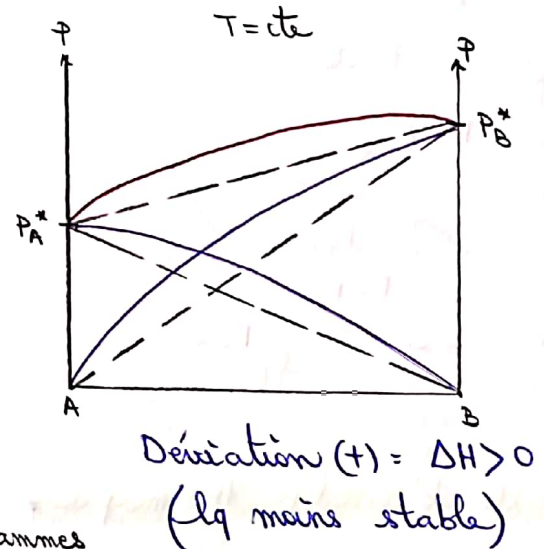
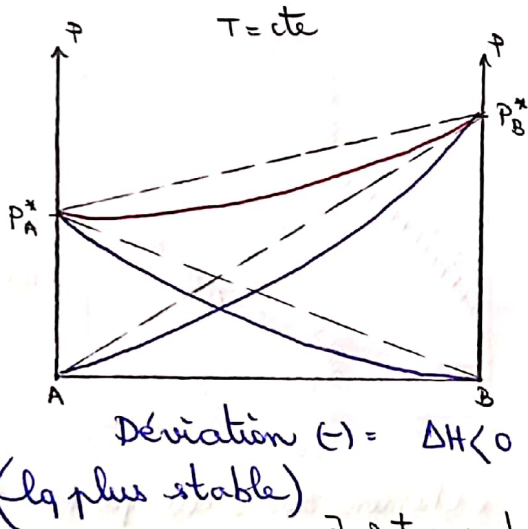
Δ = Interprétation de l'allure de courbe d'ébullition :

$$\begin{cases} P_A = x_A P_A^* = (1 - x_B) P_A^* \\ P_B = x_B P_B^* \end{cases}$$

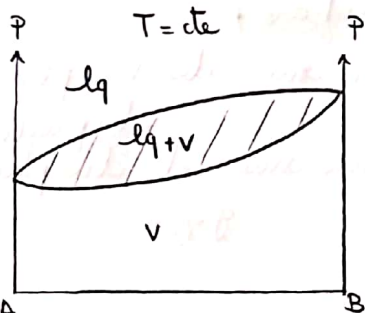
$$\Rightarrow P = P_A + P_B = (1 - x_B) P_A^* + x_B P_B^* = P_A^* + x_B (P_B^* - P_A^*)$$

Δ = sol^s idéale
courbe d'ébullition) droite affine
 $T = cte$

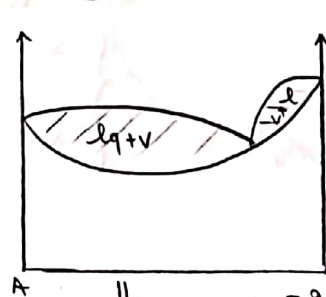
b/ Solution réelle =



∃ 2 types de diagrammes



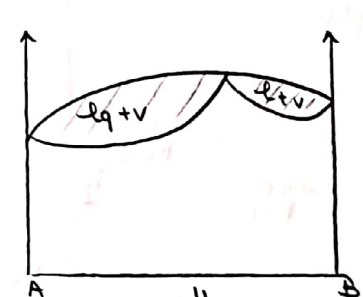
un seul fuseau =
interaction faible ~ sol^s idéale
⇒ on peut séparer A et B



écart ⊖

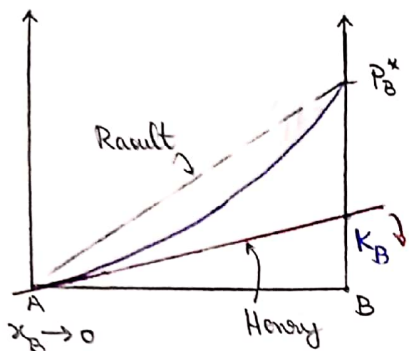
$P = cte$
ou
 $T = cte$

2 fuseaux =
on ne peut pas
séparer A et B

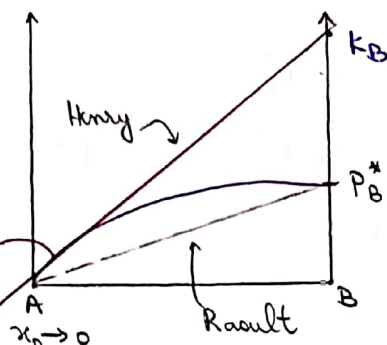


écart ⊕

Loi de Henry: $P_i = x_i K_i$
 Δ = à appliquer seulement si la solⁿ est réelle
 b constante de Henry (à déterminer lorsque $x_i \rightarrow 0$)

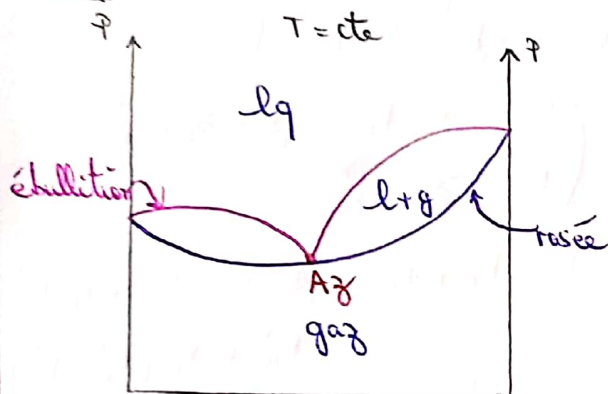


écart $\ominus$



écart $\oplus$

exemple:



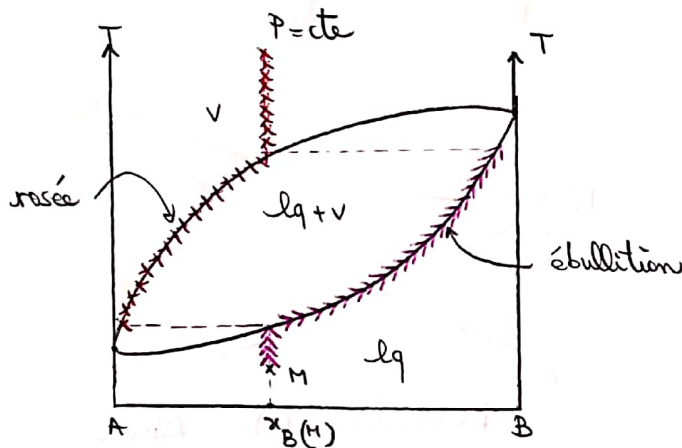
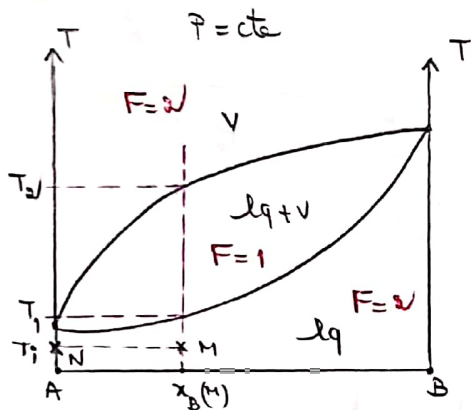
Az = point azéotrope = (les 2 phases sont présentes)

en Az on a:

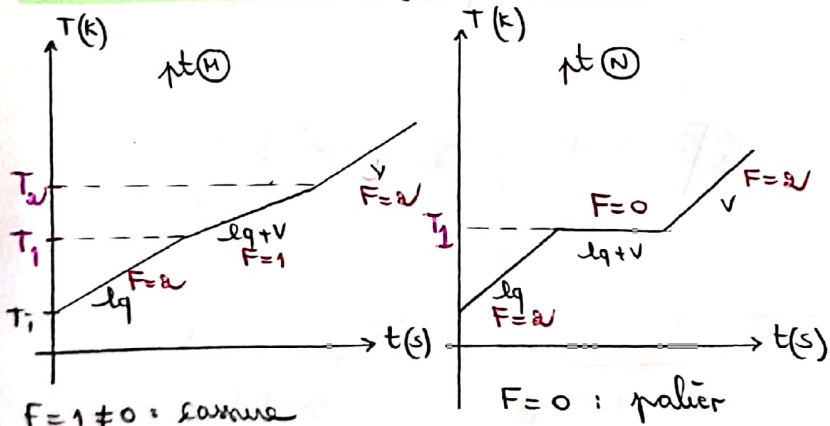
$$\begin{cases} x_B^L = x_B^V \\ F = 0 \quad (F = \Phi - 3 - 1) \end{cases}$$

un mélange azéotrope se comporte comme un corps pur

Δ : Rq:



* Courbe de l'analyse thermique =



* chemin suivi du pt M lors de chauffage isobare.

$\gg$ = chemin suivi de la phase liquide
 $\gg$ = chemin suivi de la phase gaz.

(4)

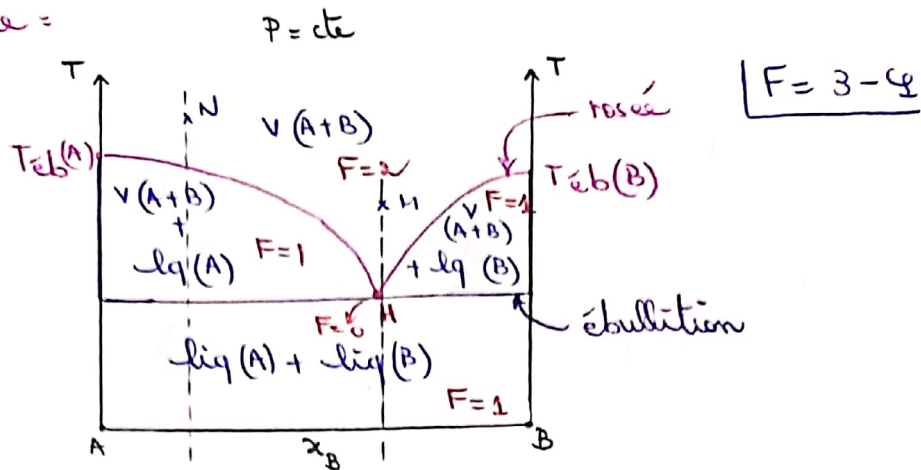
* ~~in~~ bare =


$$\text{lig}(A) + \text{lig}(B)$$

2 3 4

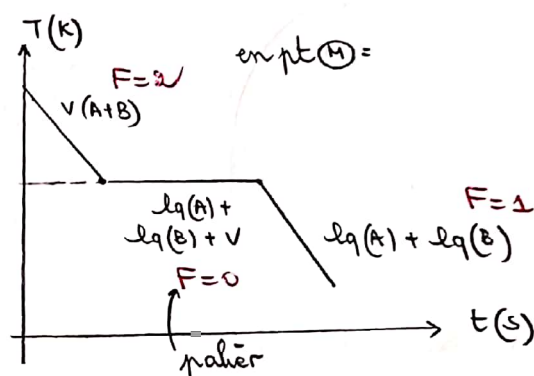
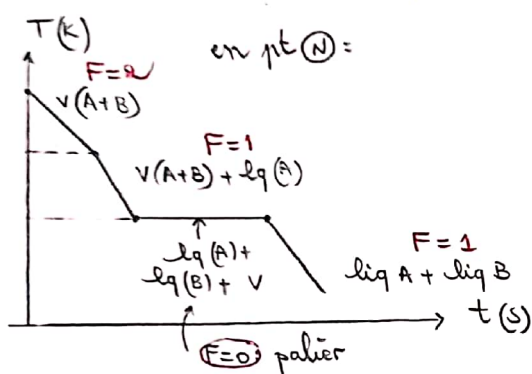
liq (A+B)

1 seal 4



H = point hétéroazeotrope = le mélange change d'état phy à $T = \text{cte}$ en ce pt avoir : $x_B^V = x_B^L$

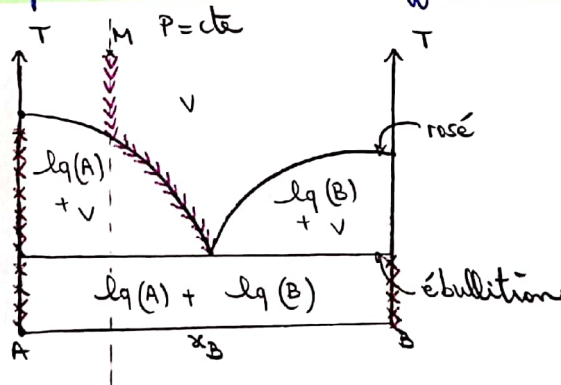
* courbe d'analyse thermique =



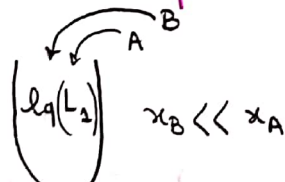
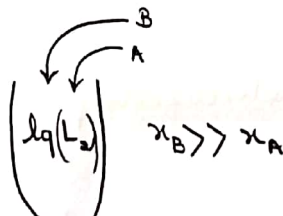
- * chemin suivi d'un pt lors d'un échauffement =

» = chemin suivi par la phase gaz

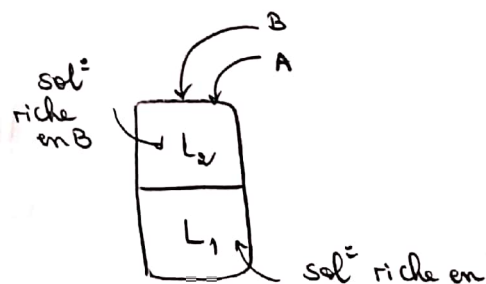
xxx = chemin suivi
par la phase lg



③ Miscibilité partielle =

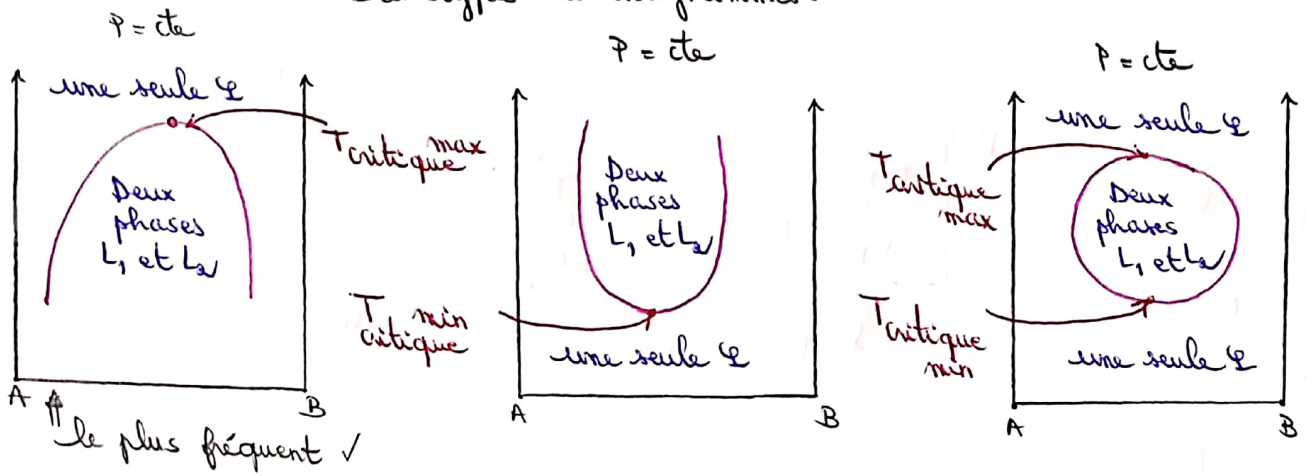

$$(L_1) = \text{sol}^e \text{ lg riche en } A$$


(L₂): sol⁺ lg riche en B



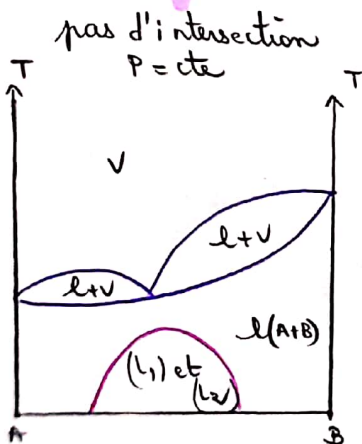
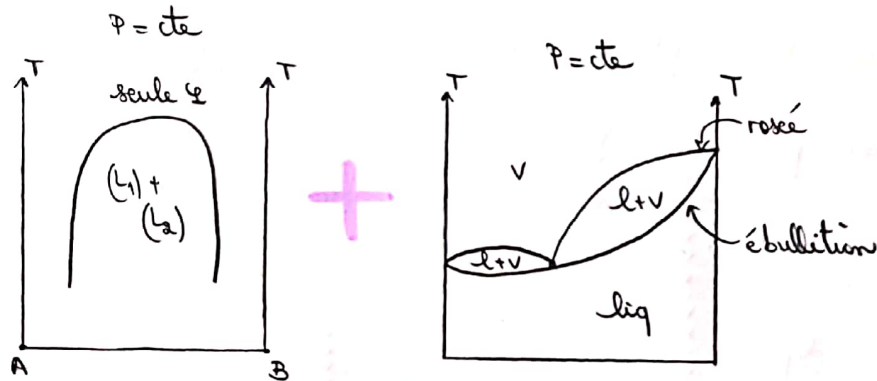
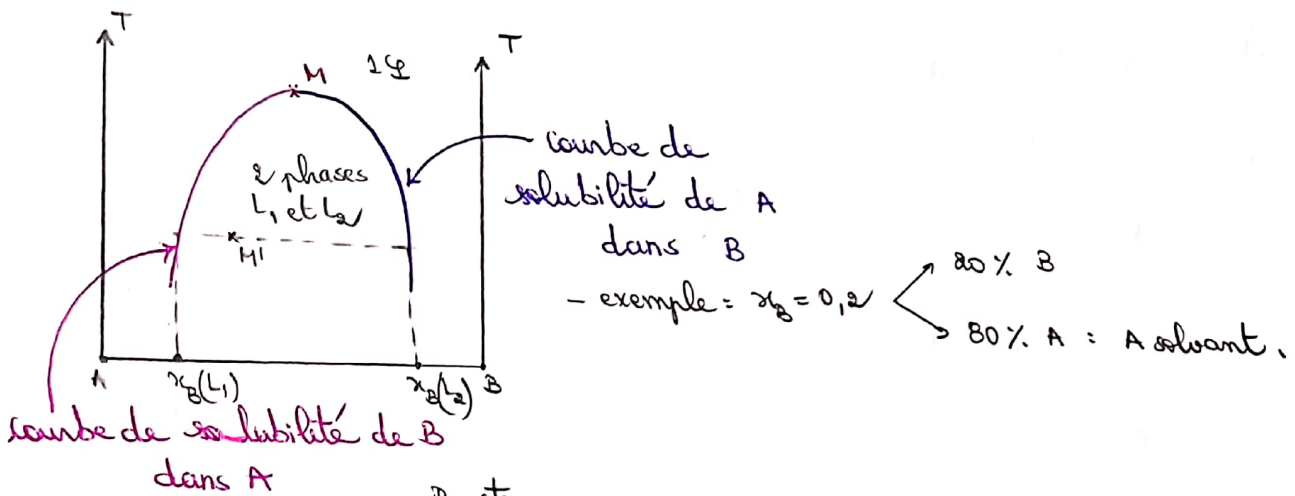
* isobare

les types des diagrammes =



$T_{critique}$ = à partir de cette température $\exists$ une seule phase.

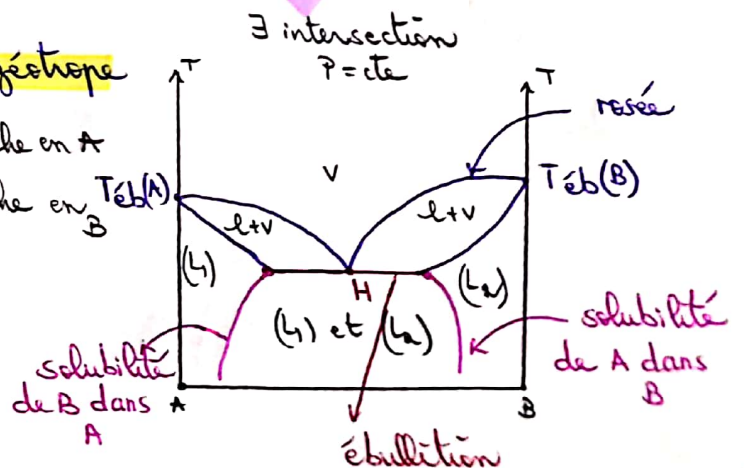
Δ intérieur de la courbe = 2 phases.



H = pt hétéroazéotrope

(L_1) : sol^c liq riche en A

(L_2) : sol^c liq riche en B



(6)