

* Potentiel chimique (μ) *

- potentiel chimique d'un corps pur:

$$\mu = \frac{G}{n} = G_m \quad \text{L'enthalpie libre molaire}$$

$$\mu = G_m = H_m - TS_m$$

$$* (dG = VdP - SdT) \times \frac{1}{n} \Rightarrow d\mu = V_m dP - S_m dT$$

$$V = \left(\frac{\partial G}{\partial P} \right)_T$$

$$V_m = \left(\frac{\partial \mu}{\partial P} \right)_T$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P$$

$$S_m = - \left(\frac{\partial \mu}{\partial T} \right)_P$$

$$\Delta_r S^\circ = - \left(\frac{\partial \Delta_r G^\circ}{\partial T} \right)_P$$

- Activité d'un constituant:

$$P_i = \frac{n_i RT}{V}$$

• Solup : $a_i = 1$

• gaz : $a_i = \frac{P_i}{P^\circ}$; $P^\circ = 1 \text{ atm}$; $P_i = Y_i P_t$

• Mélange de γ condensés Réel : $a_i = \gamma_i X_i$

• Mélange de γ condensés Ideal : $a_i = X_i$

• Solution de Gnc. C_i : $a_i = \frac{C_i}{C^\circ}$

Expression du potentiel chimique à T et P données:

$$T = \text{cte} \rightarrow d\mu = V_m dP$$

* Corps pur:

- à l'état gazeux: caractérisé par la pression saturation P_i^*

$$\int_{\mu_i^g}^{\mu_i^g} d\mu^g = V_m^g dP = RT \int_{P^0}^P \frac{dP}{P}$$

$$\text{donc } \mu_i^g = \mu_i^{0,g} + RT \ln \frac{P_i}{P^0}$$

- à l'état condensé: (sd / liq)

$$\int_{\mu_i^{0, \text{sd}}}^{\mu_i^{\text{sd}}} d\mu^{\text{sd}} = \underset{\text{cte}}{V_m^{\text{sd}}} \int_{P^0}^P dP \quad V_m^{\text{sd}} = \frac{M}{\rho^{\text{sd}}}$$

$$\mu_i^{\text{sd}} = G_m^{\text{sd}} = \mu_i^{0, \text{sd}} + V_m^{\text{sd}} (P - P^0)$$

$$\text{Donc } V_m^{\text{sd}} \ll \Rightarrow \mu_i^{\text{sd}} \approx \mu_i^{0, \text{sd}}$$

* Mélange de corps purs:

- à l'état gazeux: chaque constituant est caractérisé par sa pression partielle P_i

$$\mu_i^g = \mu_i^{o,g} + RT \ln \frac{P_i}{p^o}$$

- Mélange de phases condensées:

• Idéal:

$$\Delta_{\text{mél}} V = 0, \quad \Delta_{\text{mél}} H = 0, \quad I_{A-A} = I_{A-B} = I_{B-B}$$

$$a_i = X_i$$

$$\mu_i^{\text{sd}} = \mu_i^o + RT \ln X_i$$

• Réel:

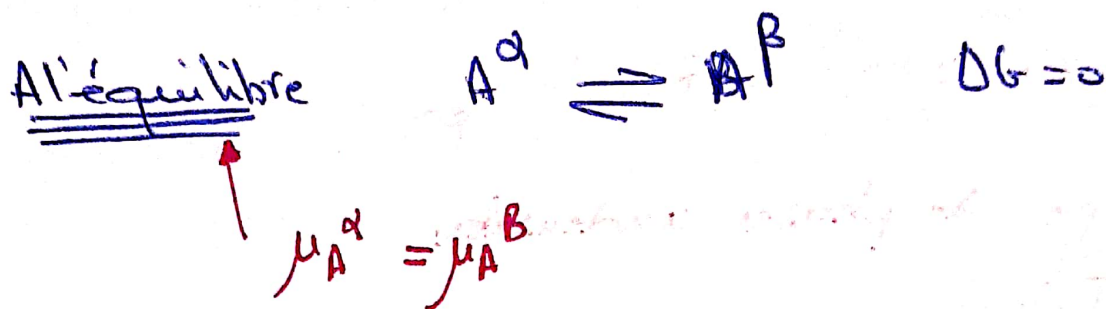
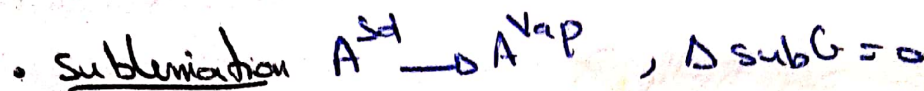
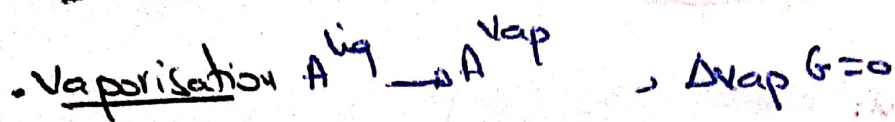
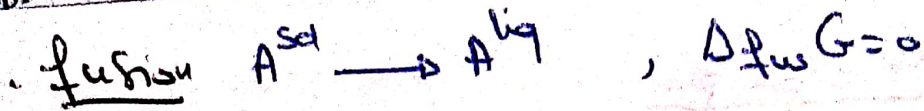
$$\Delta_{\text{mél}} V \neq 0, \quad \Delta_{\text{mél}} H \neq 0, \quad I_{A-B} \neq I_{A-A} \neq I_{B-B}$$

$$a_i = \gamma_i X_i$$

$$\mu_i = \mu_i^o + RT \ln \gamma_i X_i$$

$$V_m^{\text{sd}} = \frac{n}{\rho^{\text{sd}}}$$

$$V_m^{\text{liq}} = \frac{n}{\rho^{\text{liq}}}$$



$\rightarrow \Delta_i = \mu_A^\circ - \mu_B^\circ < 0 \quad \text{à } T = \dots$

$\Rightarrow$ La phase A est plus stable à T et à P = P°

Diagramme linéaire (corps pur)

$$C=1$$

un seul constituant

$Sd^\alpha \rightleftharpoons Sd^\beta$: transformation allotrope

Sd^α et Sd^β ont 2 phases $\neq$

* Equation de Clapeyron

$$\frac{dP}{dT} = \frac{\Delta H^{\alpha \rightarrow \beta}}{T(V_m^\beta - V_m^\alpha)}$$

Dém.



All'eq: $\mu_A^\alpha = \mu_A^\beta$ (1)

$$H_m^\alpha - T S_m^\alpha = H_m^\beta - T S_m^\beta$$

$$T(S_m^\beta - S_m^\alpha) = H_m^\beta - H_m^\alpha$$

$$T \Delta_{\alpha \rightarrow \beta} S_m = \Delta_{\alpha \rightarrow \beta} H$$

$$\Rightarrow \Delta_{\alpha \rightarrow \beta} S_m = \frac{\Delta_{\alpha \rightarrow \beta} H}{T} \quad (*)$$

Or $\mu_i = G_i^m = H_i^m - T S_i^m$

$$d\mu_i = V_i^m dP - S_i^m dT$$

$d\mu_A^\alpha = d\mu_A^\beta$ (2)

$$V_m^\alpha dP - S_m^\alpha dT = V_m^\beta dP - S_m^\beta dT$$

$$(V_m^\beta - V_m^\alpha) dP = (S_m^\beta - S_m^\alpha) dT$$

$$\left. \frac{dP}{dT} \right|_{\alpha \rightarrow \beta} = \frac{\Delta_{\alpha \rightarrow \beta} S_m}{\Delta_{\alpha \rightarrow \beta} V_m} \quad (*)$$

Rq:

*) 1^{er} cas: on suppose que S_m^B et S_m^d sont indépendantes de T

$$MP^{2012} \frac{dP}{dT} = \frac{S_m^B - S_m^d}{V_m^B - V_m^d} = \frac{\Delta_{vap} S_m}{\Delta_{vap} V_m}$$

*) 2^{em} cas: on suppose que $\Delta_{vap} H_m$ indépendante de T

$$MP^{2013} \frac{dP}{dT} = \frac{\Delta_{vap} S_m}{\Delta_{vap} V_m} = \frac{\Delta_{vap} H_m}{T \Delta_{vap} V_m}$$

*) Equilibre $A_{liq} \rightleftharpoons A_{vap}$: courbe de vaporisation:

*) $\Delta_{vap} H^\circ$ ne dépend pas de T.

$$*) V_m^g = \frac{V}{n} = \frac{RT}{P}$$

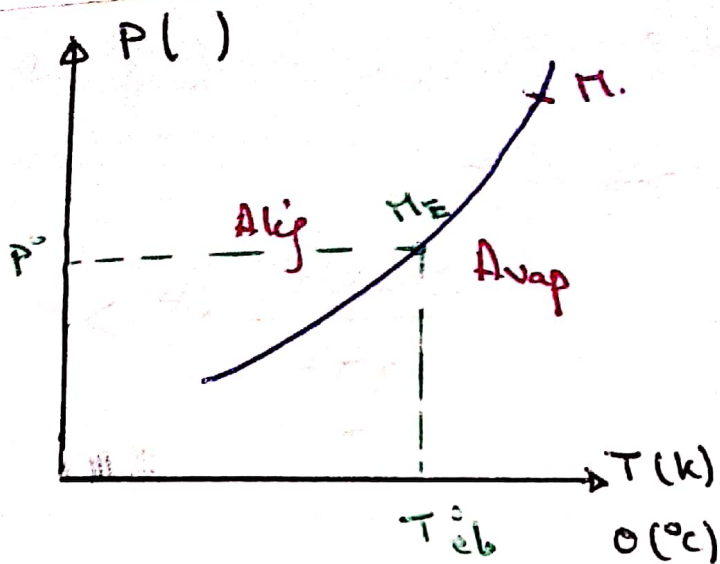
*) $V_m^g \gg V_m$ (phase condensée, liq, sol)

$$\frac{dP}{dT} = \frac{\Delta_{vap} H^\circ}{T(V_m^g - V_m^{liq})} = \frac{\Delta_{vap} H^\circ}{RT^2} \quad P. > 0 \Rightarrow \text{courbe } \nearrow \text{ ascendante.}$$

$\frac{RT}{P}$ $\ll$

$$\frac{dP}{dT} = \frac{\Delta_{vap} H^\circ}{RT^2} \quad P \Rightarrow \int_{P^0}^P \frac{dP}{P} = \frac{\Delta_{vap} H^\circ}{R} \int_{T_{vap}}^T \frac{dT}{T^2}$$

$$\boxed{\begin{aligned} \ln\left(\frac{P}{P^0}\right) &= \frac{\Delta_{vap} H^\circ}{RT_{vap}} - \frac{\Delta_{vap} H^\circ}{RT} \\ \log\left(\frac{P}{P^0}\right) &= \frac{\Delta_{vap} H^\circ}{2,3 RT_{vap}} - \frac{\Delta_{vap} H^\circ}{2,3 RT} \end{aligned}}$$



Rq: ⚠

• M est un pt d'ébullition:

• M_E est un pt d'éq.

→ si $P \nearrow \Rightarrow T \nearrow$

• Si on donne: $\ln P = a - \frac{b}{T} \Rightarrow \Delta H$ ne dépend pas de T

Rq ⚠

Si on donne V_t et n_t , cherchons n^{liq} et n^{vap} ?

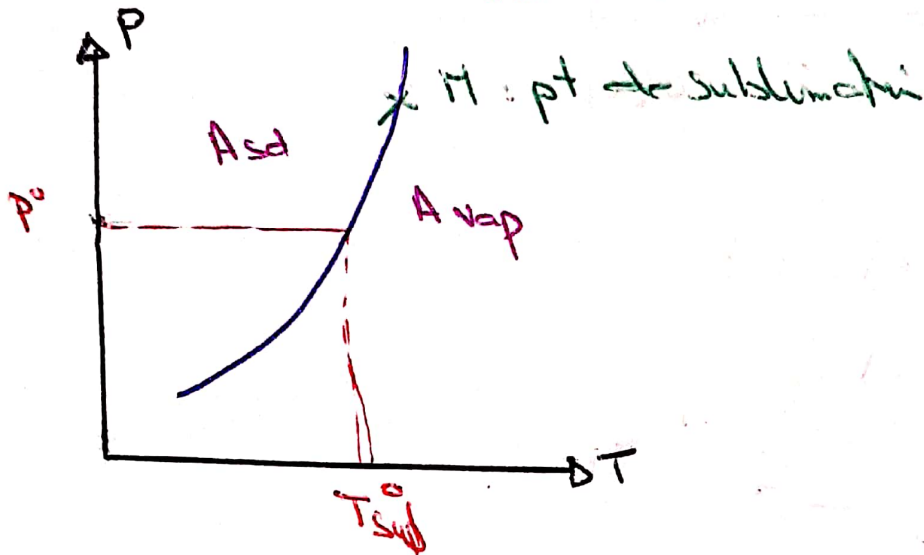
$$\text{on a } V = \sum_i n_i V_{ni} \Rightarrow \begin{cases} V_t = n^{liq} V_m^{liq} + n^{vap} V_m^{vap} \\ n_t = n^{liq} + n^{vap} \end{cases}$$

* Equilibre $A_{sd} \rightleftharpoons A_{vap}$: courbe de sublimation.

* $\Delta_{sub}H^\circ$ ne dépend pas de T

$$\frac{dP}{dT} = \frac{\Delta_{sub}H^\circ}{T(V_m^{sd} - V_m^{sd})} = \frac{\Delta_{sub}H^\circ}{RT^2} \times P > 0$$

$< \infty$



* Equilibre $A_{sd} \rightleftharpoons A_{liq}$: courbe de fusion:

$$\frac{dP}{dT} = \frac{\Delta_{fus}H^\circ}{T(V_m^{liq} - V_m^{sd})}$$

$$\Delta_{fus}V_m = V_m^{liq} - V_m^{sd}$$

$$= n \left(\frac{P_{liq} - P_{sd}}{P_{liq} + P_{sd}} \right)$$

$$P_{sd} = \frac{n}{V_m^{sd}}$$

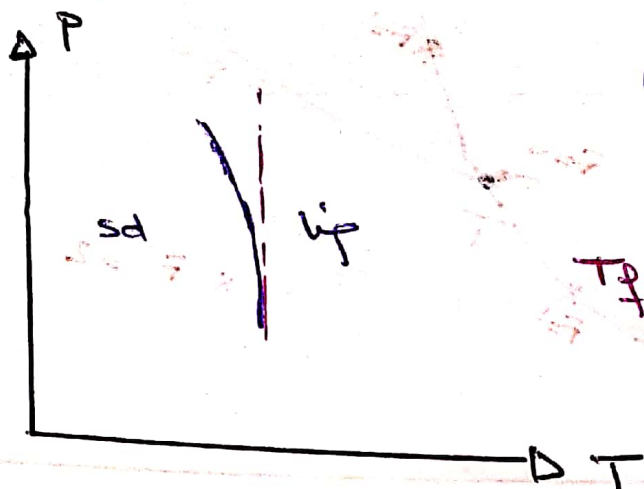
$$P_{liq} = \frac{n}{V_m^{liq}}$$

* 1^{er} cas

$$\rho^{sd} < \rho^{liq} \rightarrow V_m^{sd} > V_m^{liq}$$

(fusion avec contraction du volume)

$$\frac{dP}{dT} < 0$$



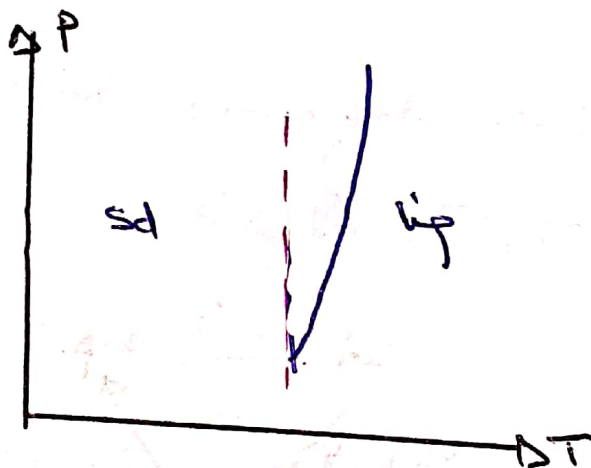
(H₂O).

$$T_{fus} = T_{fus}^0 - \varepsilon$$

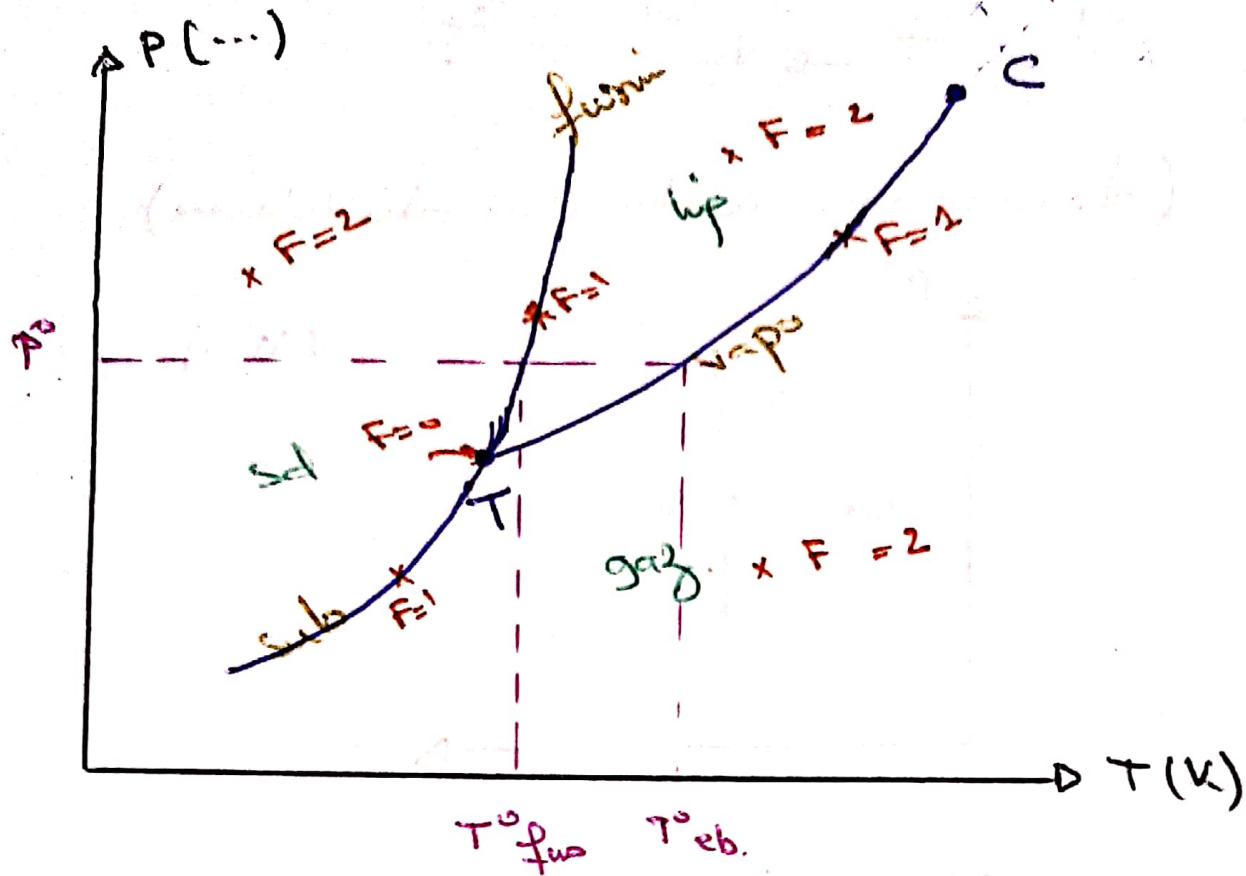
* 2^{ème} cas:

$$\rho^{sd} > \rho^{liq} \rightarrow V_m^{sd} < V_m^{liq}$$

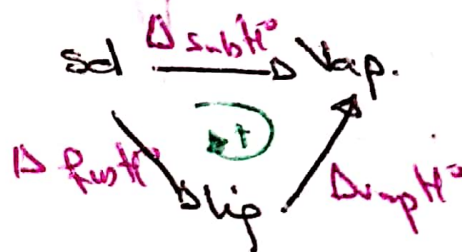
$$\frac{dP}{dT} > 0$$



$$T_{fus} = T_{fus}^0 + \varepsilon$$



T: pt triple : coexistence des 3 phases, sd, lip et vap
 en équilibre, en T^0 : $\Delta_{sub}H^0 = \Delta_{fus}H^0 + \Delta_{vap}H^0$



C: pt critique : on ne peut pas distinguer
 entre la phase lip et la phase vap
 → une seule phase : fluide

$$\begin{aligned}
 F &= (C - r - k) + (P - e) \\
 &= (1 - 0 - 0) + (2 - 1)
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} F &= (C - r - k) + (P - e) \\ &= (1 - 0 - 0) + (2 - 1) \end{aligned}} \right\} \Rightarrow F = 3 - 4$$

* Apt critique c

$$\begin{aligned}
 F &= (C - r - k) + (P - e) \\
 &= (1 - \overset{\uparrow}{2} - 0) + (2 - 1) = 0
 \end{aligned}$$