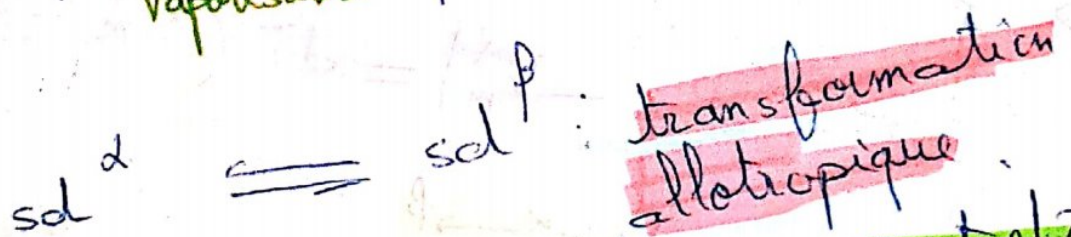
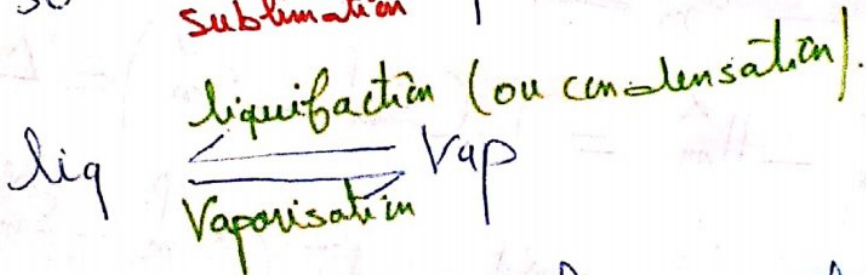
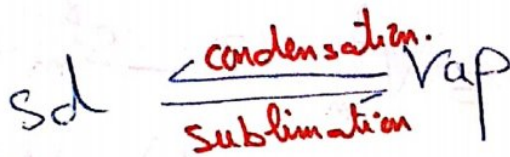
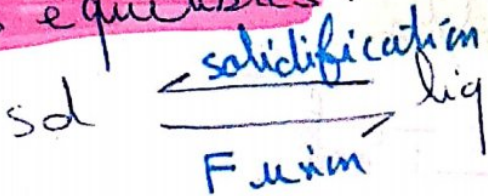


Diagramme du corps pur. (" " Unaire).

$\rightarrow c = 1$ seul constituant.

* Les équilibres :



sd^{α} et sd^{β} sont 2 phases allotropiques (2 stades ex $\text{sd}^{\alpha} \rightarrow \text{C.F.C}$ et $\text{sd}^{\beta} \rightarrow \text{C.I}$).

$$* G = H - TS$$

$$* dG = V dP - S dT$$

$$\begin{cases} \mu = H_m - TS_m \\ dp = V_m dp - S_m dT \end{cases}$$

À l'équilibre entre 2 phases on a :



$$\Delta G^{\circ} = \mu^{\circ, \beta} - \mu^{\circ, \alpha}$$

$$\mu_A^{\alpha} = \mu_A^{\beta}$$

$$d\mu_A^{\alpha} = d\mu_A^{\beta}$$

$$\left\{ \begin{array}{l} H_m^{\alpha} - TS_m^{\alpha} = H_m^{\beta} - TS_m^{\beta} \\ V_m^{\alpha} dP - S_m^{\alpha} dT = V_m^{\beta} dP - S_m^{\beta} dT \end{array} \right.$$

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

$$\left\{ \begin{array}{l} H_m^{\beta} - H_m^{\alpha} = T(S_m^{\beta} - S_m^{\alpha}) = \Delta H^{\alpha \rightarrow \beta} \\ dP(V_m^{\beta} - V_m^{\alpha}) = dT(S_m^{\beta} - S_m^{\alpha}) \end{array} \right.$$

$$\Rightarrow \left\{ \begin{array}{l} H_m^{\beta} - H_m^{\alpha} = T(S_m^{\beta} - S_m^{\alpha}) = \Delta H^{\alpha \rightarrow \beta} \\ dP(V_m^{\beta} - V_m^{\alpha}) = dT(S_m^{\beta} - S_m^{\alpha}) \end{array} \right.$$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta S^{\alpha \rightarrow \beta}}{V_m^{\beta} - V_m^{\alpha}}$$

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

→ équation de Clapeyron.

Rq si dans les données, on a $\Delta S^{\alpha \rightarrow \beta}$.
 et non pas $\Delta H^{\alpha \rightarrow \beta}$. donc.

$$A^{\alpha} \rightleftharpoons A^{\beta}$$

$$dP_A^{\alpha} = dP_A^{\beta} \rightarrow V_m^{\alpha} dP - S_m^{\alpha} dT = V_m^{\beta} dP - S_m^{\beta} dT$$

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

I - Equilibre liq $\rightleftharpoons$ vap.

Donnée : * $\Delta H_{\text{vap}}^{\circ}$ me donne pas de la Température

* Le gaz se comporte comme un gaz parfait c.a.d.

$$PV = nRT \rightarrow V_m^g = \frac{V}{n} = \frac{RT}{P}$$

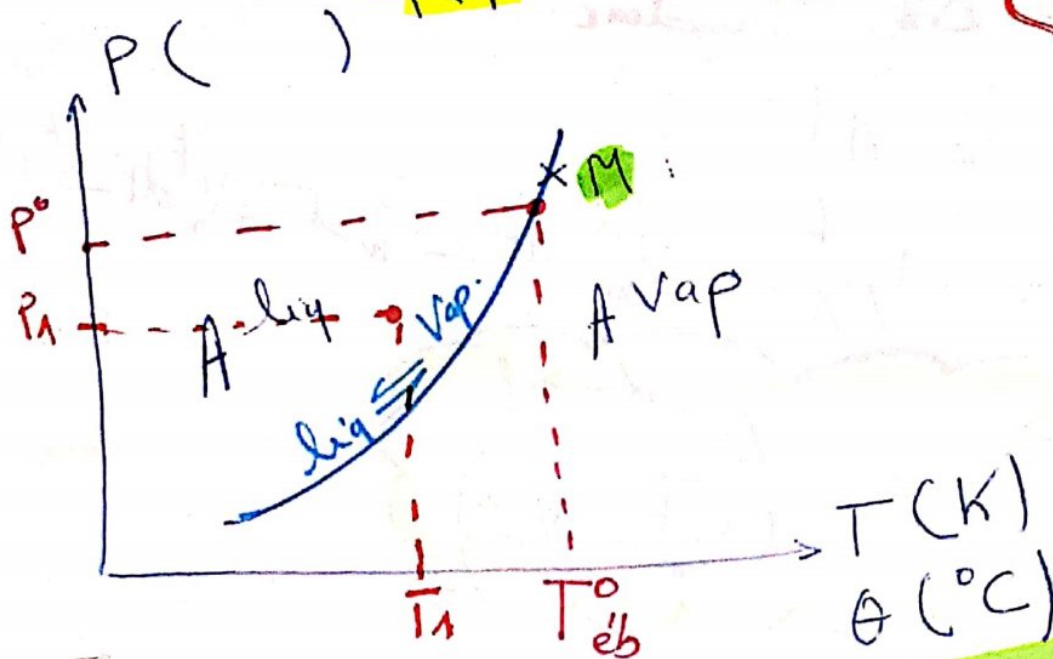
* $V_m^g \rightarrow V_m$ d'une phase condensée (sol, liq)

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}^{\circ}}{T(V_m^g - V_m^{\text{liq}})} \ll \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}^\circ}{RT^2} \times P > 0$$

$$\Delta H_{\text{fus}}^\circ, \Delta H_{\text{vap}}^\circ > 0$$

$$\Delta H_{\text{sub}}^\circ > 0$$



- * Nommer le pt M : M est un pt d'ébullition.
- * Quel est l'effet de la Pression sur les points d'ébullition ??
- Plus la Pression $\uparrow$, plus la température d'ébullition $\uparrow$.
- * Dans quel état physique se trouve le corps A à (T_1, P_1) ??
- état liquide.

Type de concours:

on donne $\log P(\text{mmHg}) = 15,04 - \frac{5400}{T(K)}$

1) Calculer la température d'ébullition standard (ou normal) $\rightarrow P = P^0$

$$\log 760 = 15,04 - \frac{5400}{T_{eb}^0}$$

$$T_{eb}^0 = \frac{5400}{15,04 - \log 760} = \dots K$$

$$\begin{aligned} 1 \text{ atm} &\approx 1 \text{ bar} \approx 10^5 \text{ Pa} = 760 \text{ mmHg} \end{aligned}$$

2) Calculer $\Delta H_{vap}^0 = ??$

$$\frac{dP}{dT} = \frac{\Delta H_{vap}^0}{RT^2} \times P \Rightarrow \int_{P^0}^P \frac{dP}{P} = \frac{\Delta H_{vap}^0}{R} \int_{T_{eb}^0}^T \frac{dT}{T^2}$$

$$\ln \frac{P}{P^0} = \frac{\Delta H_{vap}^0}{RT_{eb}^0} - \frac{\Delta H_{vap}^0}{R \times T}$$

$$\ln x = 2,3 \log x$$

$$\log \frac{P}{P^0} = \frac{\Delta H_{vap}^0}{2,3 RT_{eb}^0} - \frac{\Delta H_{vap}^0}{2,3 \times R \times T}$$

P-5-

$$\log P = \log P^0 + \frac{\Delta H_{\text{vap}}^0}{2,3 R T_{\text{eb}}} - \frac{\Delta H_{\text{vap}}^0}{2,3 R \times T}$$

$$\log P = 15,04 - \frac{5400}{T}$$

Par identification $\Delta H_{\text{vap}}^0 = 2,3 \times R \times 5400$.

$$R = 8,314 \text{ J mol}^{-1} \text{ K}^{-1} \text{ ou } R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$$

Rq si $\ln P = a - \frac{b}{T(K)}$ $\rightarrow \Delta H$ ne dépend pas de T

ex si $\log P = 2,5 - \frac{5400}{T} - 6,56 \log T$

$\Delta H_{\text{vap}} = b(T)!$

on ne peut pas intégrer.

$$\frac{dP}{P} = \frac{\Delta H_{\text{vap}}^0}{R T^2} dT$$

donc $\ln P = 2,3 \log P$

$$= 2,3 \times \left(2,5 - \frac{5400}{T} \right) - 6,56 \times (2,3 \log T)$$

$$\ln P = 2,3 \times 2,5 - \frac{2,3 \times 5400}{T} - 6,56 \ln T$$

$$\frac{dP}{P} = \left(\frac{2,3 \times 5400}{T^2} - \frac{6,56}{T} \right) dT$$

P-6-

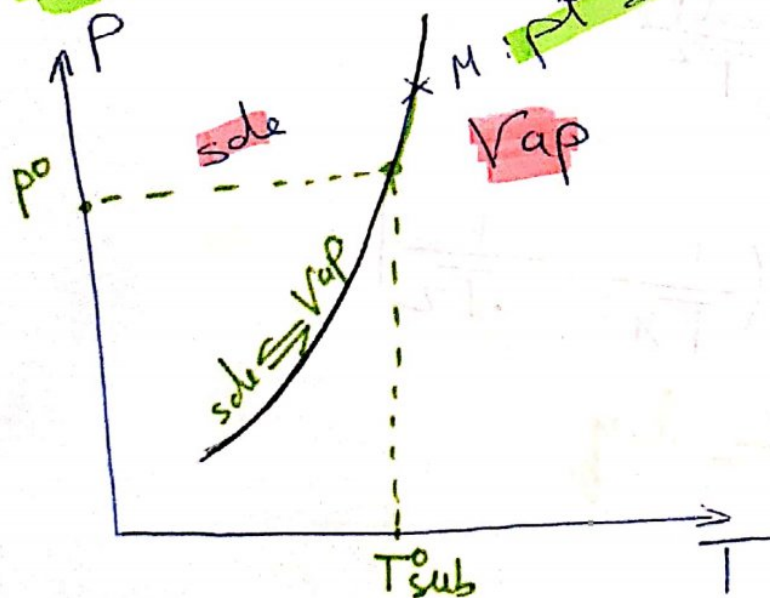
$$\Rightarrow \frac{\Delta H_{\text{vap}}^\circ}{RT^2} dT = \left(\frac{2,3 \times 5400}{T^2} - \frac{6,56}{T} \right) dT$$

$$\Rightarrow \Delta H_{\text{vap}}^\circ = RT^2 \left(\frac{2,3 \times 5400}{T^2} - \frac{6,56}{T} \right)$$

II - Equilibre $sd \rightleftharpoons \text{vap}$

$$\frac{dP}{dT} = \frac{\Delta H_{\text{sub}}^\circ}{T(V_m^{\text{sd}} - V_m^{\text{vap}})}$$

$$\frac{dP}{dT} = \frac{\Delta H_{\text{sub}}^\circ}{RT^2} \times P > 0$$



2^{ème} type

on donne

le concours:

$$M_1(T_1, P_1)$$

$$M_2(T_2, P_2)$$

P-7

1) Calculer T_{eb} :

$$\ln \frac{P}{P_0} = \frac{\Delta H_{vap}^0}{R T_{eb}} - \frac{\Delta H_{vap}^0}{R \times T_1}$$

pour M_1 : $\ln \frac{P_1}{P_0} = \frac{\Delta H_{vap}^0}{R T_{eb}} - \frac{\Delta H_{vap}^0}{R \times T_1}$

$$\Rightarrow T_{eb} = \frac{\Delta H_{vap}^0}{R \left[\ln \frac{P_1}{P_0} + \frac{\Delta H_{vap}^0}{R \times T_1} \right]}$$

2) ΔH_{vap}^0 ??

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_{vap}^0}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

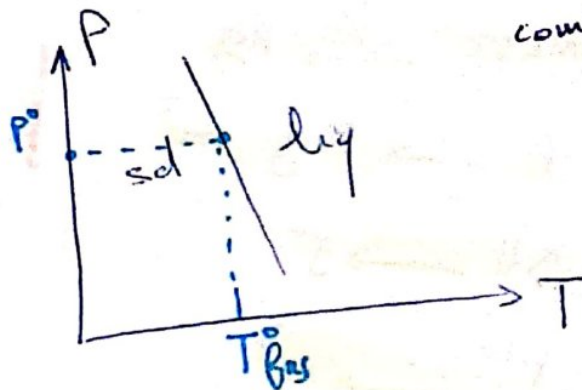
$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

III - Fusion: $sd \rightleftharpoons liq$.

$$\frac{dP}{dT} = \frac{\Delta H_{fus}^0}{T (V_m^{liq} - V_m^{sd})}$$

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

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



compte décroissant

App

Calculer la temp de fusion
de H_2O sous $P = 100 \text{ atm}$.

on a $\int_{P^0}^P dP = \frac{\Delta H_{bus}^0}{V_m^{liq} - V_m^{sd}} \int_{T_{bus}^0}^{T_{bus}} \frac{dT}{T}$

Donnée:
 $\Delta H_{bus}^0 = 10,4 \text{ kJ mol}^{-1}$

$T_{bus}^0 = 273 \text{ K}$

$\rho_{H_2O}^{sd} = 0,917 \text{ g/cm}^3$

$\rho_{H_2O}^{liq} = 1 \text{ g/cm}^3$

$M_{H_2O} = 18 \text{ g/mol}$

$\Rightarrow P - P^0 = \frac{\Delta H_{bus}^0}{M_{H_2O} \left(\frac{1}{\rho_{liq}} - \frac{1}{\rho_{sd}} \right)} \ln \frac{T_{bus}}{T_{bus}^0}$

$(P - P^0) M_{H_2O} \left(\frac{1}{\rho_{liq}} - \frac{1}{\rho_{sd}} \right) = \Delta H_{bus}^0 \ln \frac{T_{bus}}{T_{bus}^0}$

S.I $\downarrow$
 $T_{bus} = T_{bus}^0 \exp \left[\frac{(P - P^0) M_{H_2O} \left(\frac{1}{\rho_{liq}} - \frac{1}{\rho_{sd}} \right)}{\Delta H_{bus}^0} \right]$

P.9.

S.I

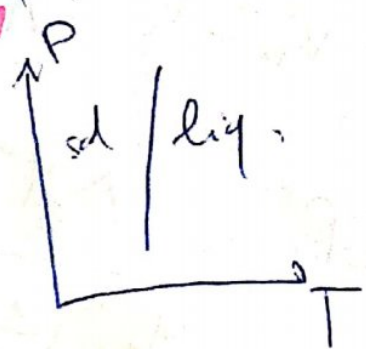
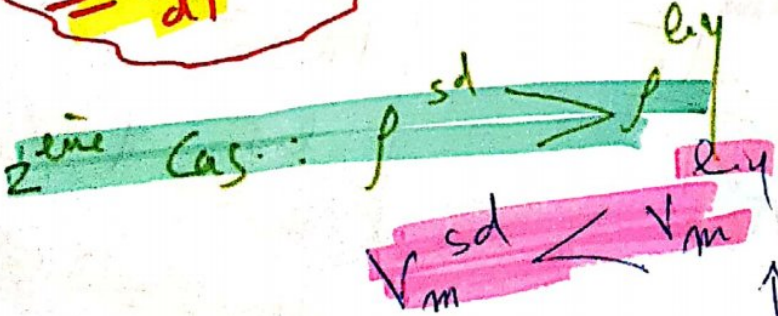
$\left\{ \begin{array}{l} \text{Pressim} \rightarrow \text{Pa} \\ \text{masse} \rightarrow \text{kg} \\ \rho \rightarrow \text{kg/m}^3 \\ \Delta H \rightarrow \text{J} \\ V \rightarrow \text{m}^3 \end{array} \right.$

!

$$T_{\text{fus}} \approx 272,6 \text{ K.}$$

$$\left\{ \begin{array}{l} f_{\text{sd}} < f_{\text{liq}} \\ V_{\text{m sd}} > V_{\text{m liq}} \\ \Rightarrow \frac{dP}{dT} < 0 \end{array} \right.$$

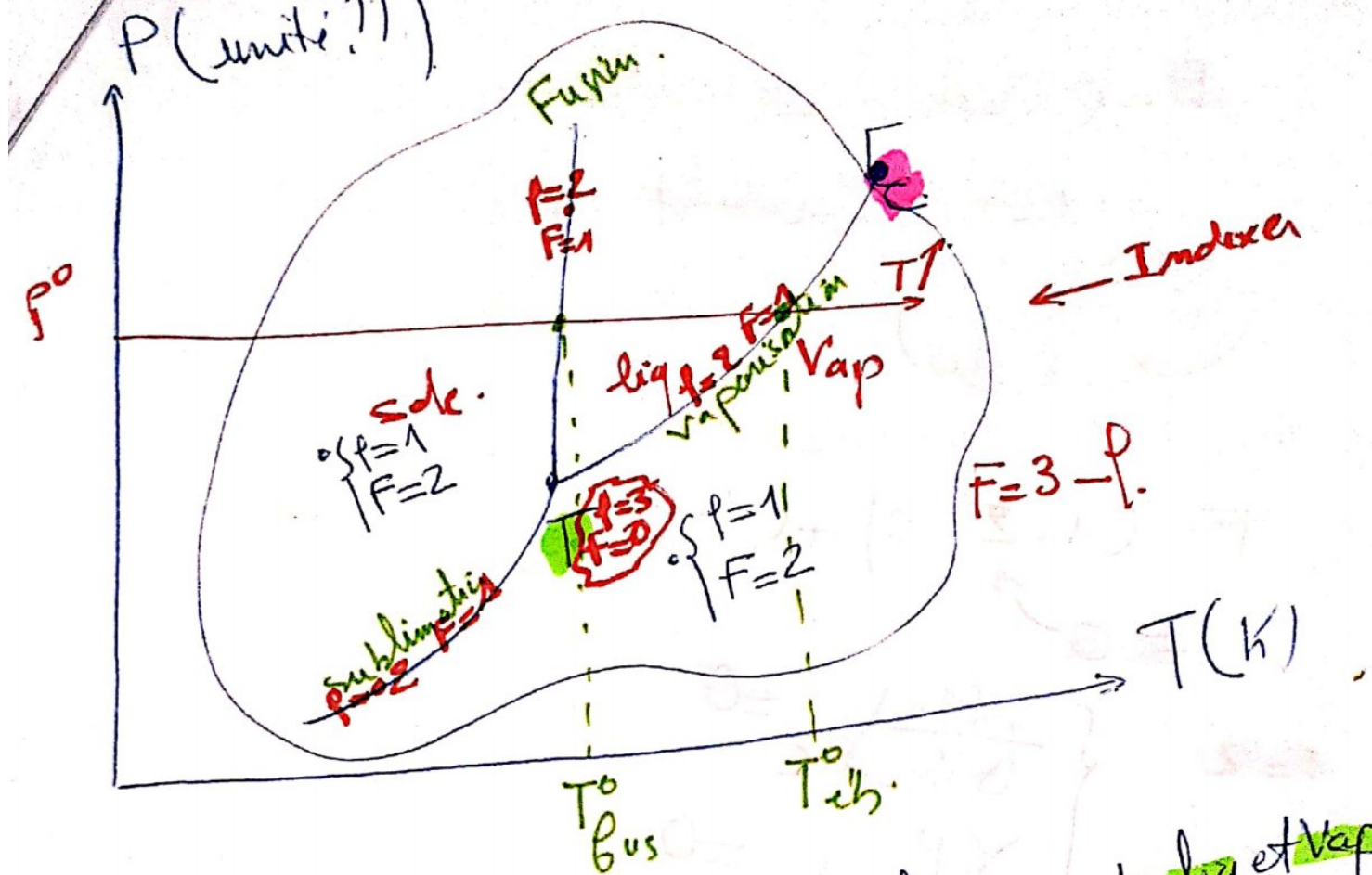
$$\theta_{\text{fm}} = \theta_{\text{fus}}^0 - \varepsilon$$



compte croissant.

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

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



* **T: pt triple**: coexistence de 3 phases sde, liq et vap en équilibre.

au pt triple: $\Delta H_{\text{sub}}^0 = \Delta H_{\text{fus}}^0 + \Delta H_{\text{vap}}^0$!

ΔH_{sub}^0 (sde $\rightarrow$ Vap)
 ΔH_{fus}^0 (liq $\rightarrow$ Vap)
 ΔH_{vap}^0 (liq $\rightarrow$ Vap)

* **C: pt Critique**: au delà de ce pt on ne peut plus distinguer entre la phase liq et la phase Vap: une seule phase fluide ($p=1$)

$$F = (c - r - k) + (P - p)$$

$$= (1 - 0 - 0) + (2 - p)$$

$$F = 3 - p$$

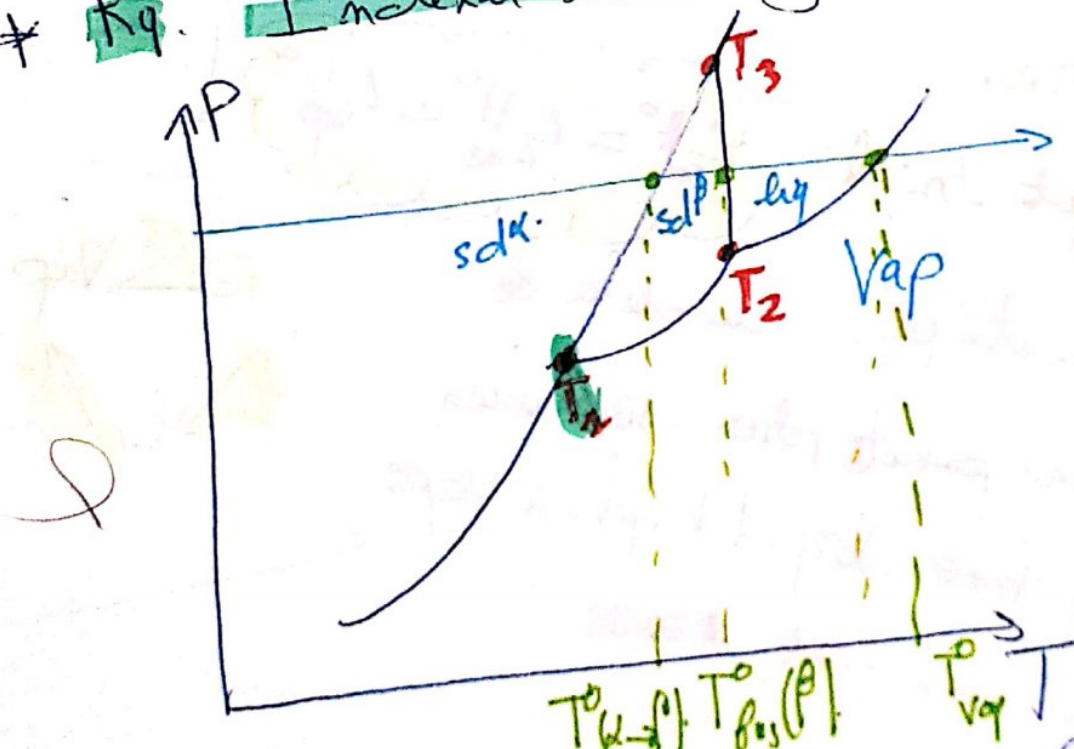
* Point Critique C.

$$F = (1 - 2 - 0) + (2 - 1)$$

$$= 0$$

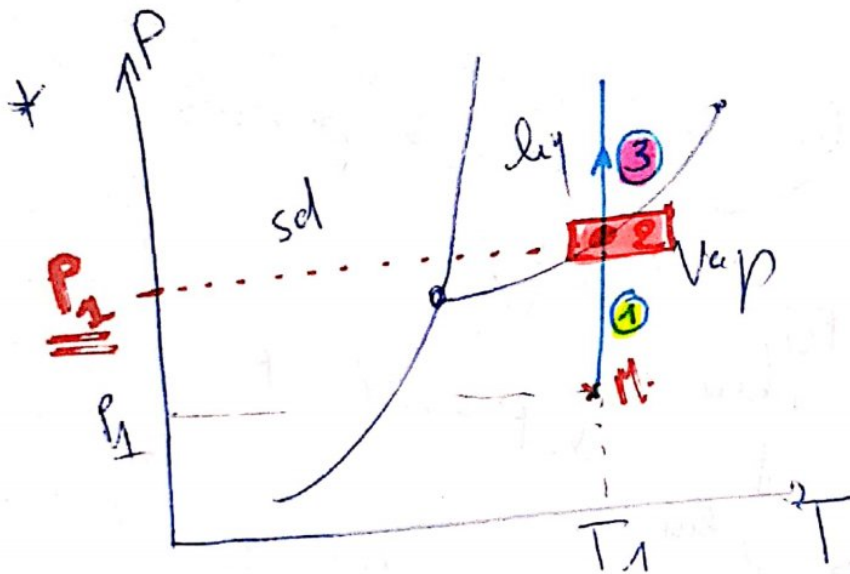
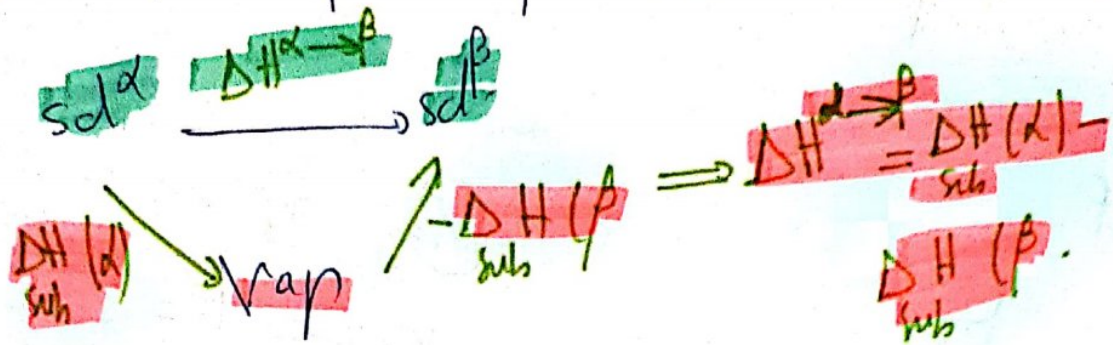
$$r = 2 \quad \left\{ \begin{array}{l} \frac{\partial P}{\partial V_m} \Big|_{T_c} = 0 \\ \frac{\partial^2 P}{\partial V_m^2} \Big|_{T_c} = 0 \end{array} \right.$$

* Rq. Indexer le diagramme du soufre

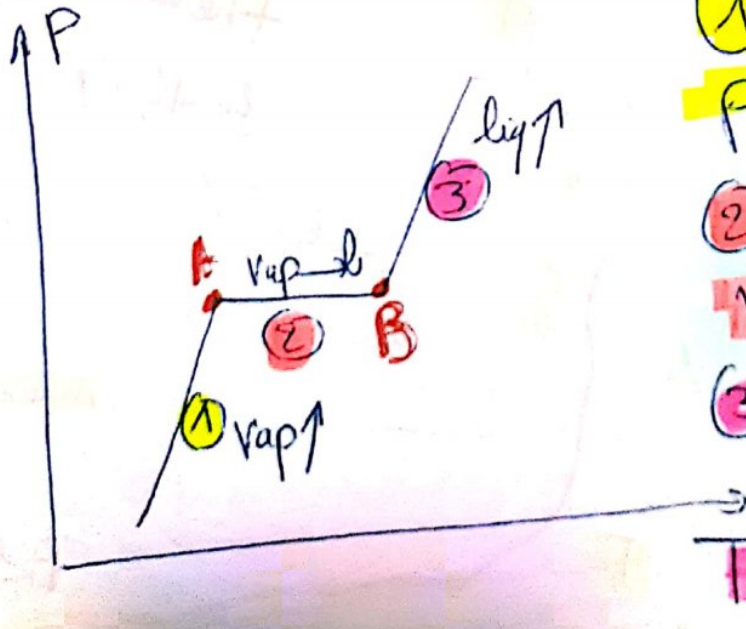


temp de transformation

T_1 : pt triple : coexistence des 3 phases
 sol ^{α} , sol ^{β} , et vap en équilibre



on fait la compression d'un système $H(T_1, P_1)$
 Tracer la courbe d'analyse de Pression.



- ① compression de la phase vapeur
- ② équilibre liq-vap
 $\text{vap} \rightleftharpoons \text{liq}$
- ③ compression de la phase liq

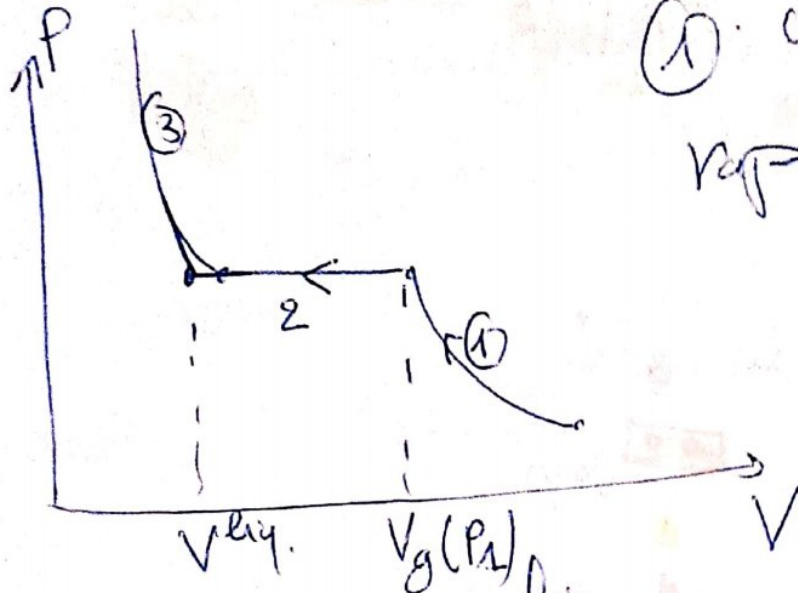
Temps

P-13

A : Apparition de la 1^{re} gte de liquide

B : Disparition de la dernière Bulle de Vapeur

② Tracer la courbe $P=f(V)$.



① compression de la
vapeur $P = \frac{nRT}{V}$
hyperbole.

② Vap $\xrightarrow{\quad}$ liq
 $\downarrow$ $\downarrow$
 $V_g(P_2) \rightarrow V_{liq}$
la $P = \text{cste} = P_2$.

③ la Pression n'influence pas sur le Volume
d'une phase condensée.

