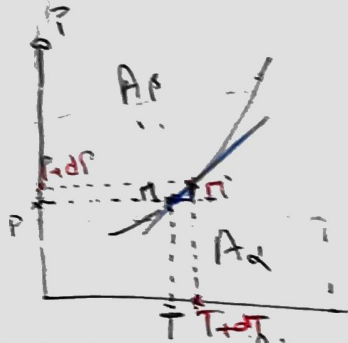


II - Relação de Clapeyron

$$A_\alpha \xrightleftharpoons[T=\bar{T}]{P=\bar{P}} A_\beta \quad (n=2)$$



$\pi(P, T)$ - para 2 fases

$$DG = 0$$

$$G_\beta - G_\alpha = 0$$

$$\mu_{A,\beta}^{x,\beta}(P, T) - \mu_{A,\alpha}^{x,\alpha}(P, T) = 0$$

$$\mu_A^{x,\beta}(P, T) = \mu_A^{x,\alpha}(P, T) \quad (1)$$

$$H_{A,\beta}^{x,\beta} - T S_{A,\beta}^{x,\beta} = H_{A,\alpha}^{x,\alpha} - T S_{A,\alpha}^{x,\alpha}$$

$$(H_{A,\beta}^{x,\beta} - H_{A,\alpha}^{x,\alpha}) = T(S_{A,\beta}^{x,\beta} - S_{A,\alpha}^{x,\alpha})$$

$$D_{\alpha \rightarrow \beta} H_A^x = T D_{\alpha \rightarrow \beta} S_A^x$$

$$D_{\alpha \rightarrow \beta} S_A^x = \frac{D_{\alpha \rightarrow \beta} H_A^x}{T} \quad (1')$$

$$\mu_{A,\beta}^{x,\beta}(P, T) + d\mu_{A,\beta}^{x,\beta} = \mu_{A,\alpha}^{x,\alpha}(P, T) + d\mu_{A,\alpha}^{x,\alpha}$$

$$d\mu_{A,\beta}^{x,\beta} = d\mu_{A,\alpha}^{x,\alpha} \quad (2)$$

$$(\mu_{A,\beta}^{x,\beta} dP - S_{A,\beta}^{x,\beta} dT) = (\mu_{A,\alpha}^{x,\alpha} dP - S_{A,\alpha}^{x,\alpha} dT)$$

$$(H_{A,\beta}^{x,\beta} - H_{A,\alpha}^{x,\alpha}) = T(S_{A,\beta}^{x,\beta} - S_{A,\alpha}^{x,\alpha})$$

$$D_{\alpha \rightarrow \beta} H_A^x = T D_{\alpha \rightarrow \beta} S_A^x$$

$$\left(\frac{dP}{dT} \right)_{\alpha \rightarrow \beta} = \frac{D_{\alpha \rightarrow \beta} S_A^x}{D_{\alpha \rightarrow \beta} V_A^x} \quad (2')$$

$$\left(\frac{dP}{dT} \right)_{\alpha \rightarrow \beta} = \frac{D_{\alpha \rightarrow \beta} H_A^x}{T D_{\alpha \rightarrow \beta} V_A^x}$$

$$\left(\frac{dP}{dT} \right)_{\alpha \rightarrow \beta} = \frac{D_{\alpha \rightarrow \beta} H_A^x}{T D_{\alpha \rightarrow \beta} V_A^x}$$

$$\left(\frac{dP}{dT} \right)_{\alpha \rightarrow \beta} = \frac{D_{\alpha \rightarrow \beta} H_A^x}{T D_{\alpha \rightarrow \beta} V_A^x}$$

$$\left(\frac{dP}{dT} \right)_{\alpha \rightarrow \beta} = \frac{D_{\alpha \rightarrow \beta} H_A^x}{T D_{\alpha \rightarrow \beta} V_A^x}$$

$$\left(\frac{dP}{dT} \right)_{\alpha \rightarrow \beta} = \frac{D_{\alpha \rightarrow \beta} H_A^x}{T D_{\alpha \rightarrow \beta} V_A^x}$$

Relação de Clapeyron

$$\mu_{A,\beta}^{x,\beta}(P, T) = \mu_{A,\alpha}^{x,\alpha}(P, T)$$

$$d\mu_{A,\beta}^{x,\beta} = V_{A,\beta}^{x,\beta} dP - S_{A,\beta}^{x,\beta} dT$$

$$\left(\frac{\partial \mu_{A,\beta}^{x,\beta}}{\partial P}_T \right) = V_{A,\beta}^{x,\beta}$$

$$\left(\frac{\partial \mu_{A,\beta}^{x,\beta}}{\partial T}_P \right) = -S_{A,\beta}^{x,\beta}$$

$$\left(\frac{\partial \mu_{A,\beta}^{x,\beta}}{\partial P}_T \right) = V_{A,\beta}^{x,\beta}$$

$$\left(\frac{\partial \mu_{A,\beta}^{x,\beta}}{\partial T}_P \right) = -S_{A,\beta}^{x,\beta}$$

$$\mu_{A,\beta}^{x,\beta}(P, T) = \mu_{A,\alpha}^{x,\alpha}(P, T) \quad (1)$$

$$d\mu_{A,\beta}^{x,\beta} = d\mu_{A,\alpha}^{x,\alpha} \quad (2)$$

$$d\mu_{A,\beta}^{x,\beta} = d\mu_{A,\alpha}^{x,\alpha} \quad (2)$$

Relação de Clapeyron

III - Construction du diagramme.

casine (P,T)
 A supposer $D_{c,e} H_m^*$ indépendante de T
 c.e. chargement d'état physique
 1) Equilibre de sublimation
 $A_{\text{sol}} \xrightleftharpoons[T]{P} A_{\text{g}} \quad (n=1)$

$$\left(\frac{dP}{dT}\right)_{\text{sub}} = \frac{D_{\text{sub}} H_m^*}{T \Delta V_m^*}$$

$$\Delta V_m^* = V_m^{*g} - V_m^{*l} \approx V_m^{*g} = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{D_{\text{sub}} H_m^*}{RT^2} \cdot ?$$

$$\int_{P_0}^{P_{\text{sat}}} \frac{dP}{P} = \int_{T_{\text{sub}}^0}^T \frac{D_{\text{sub}} H_m^*}{RT^2} dT$$

P_{sat} : pression de vapeur saturante de (sol)
 $(P_{\text{sat}}^G) = P_{\text{sat}}^* = P_{\text{sat}}$

$$\ln \frac{P_{\text{sat}}^G}{P_0} = \frac{A_{\text{sub}} H_m^*}{RT_{\text{sub}}^0} - \frac{D_{\text{sub}} H_m^*}{RT}$$

$\ln P_{\text{sat}}^G = f\left(\frac{1}{T}\right)$: fonction affine
 ($D_{c,e} H_m^*$: indépendante de T)

$$\ln \frac{P_{\text{sat}}^G}{P_0} = A - \frac{B}{T} ; B(K)$$

$$\log \frac{P_{\text{sat}}^G}{P_0} = \frac{D_{\text{sub}} H_m^*}{2,3 RT_{\text{sub}}^0} - \frac{D_{\text{sub}} H_m^*}{2,3 R} \cdot \frac{1}{T}$$

$$\log \frac{P_{\text{sat}}^G}{P_0} = a - \frac{b}{T}$$

$$\log x = \frac{\ln x}{\ln 10} = \frac{\ln x}{2,3}$$

$$\text{Pour } P_{\text{sat}}^G = P_0$$

$$\text{on a } T = T_{\text{sub}}^0$$

$$a - \frac{b}{T_{\text{sub}}^0} = 0$$

$$T_{\text{sub}}^0 = \frac{b}{a} = \frac{B}{A}$$

$$D_{\text{sub}} H_m^* > 0$$

$$D_{\text{vap}} H_m^* > 0$$

$$D_{\text{fus}} H_m^* > 0$$

$$D_{\text{sub}} S_m^* > 0$$

$$D_{\text{vap}} S_m^* > 0$$

$$D_{\text{fus}} S_m^* > 0$$

Pour établir la relation de Clapeyron

$$\mu^{x,B}_{A(P,T)} = \mu^{x,A}_{A(P,T)} \quad (1)$$

$$d\mu^{x,B} = d\mu^{x,A} \quad (2)$$

III - Construction du diagramme.

une (P,T)
 A suppr. D_c, E, H_m indépendante de T
 c.e. changement d'état physique
 1) Equilibre de vaporisation

$A_{liq} \xrightleftharpoons[T]{P_{eq}} A_{g}$

$$\left(\frac{dP}{dT} \right)_{eq} = \frac{\Delta_{vap} H_m^*}{T \Delta_{vap} V_m^*}; \Delta_{vap} V_m^* = V_m^{*g} - V_m^{*l}$$

$$\Delta_{vap} V_m^* = V_m^{*g} = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta_{vap} H_m^*}{RT^2} \cdot ?$$

$$\int_{P^0}^{P^G} \frac{dP}{P} = \int_{T_{eq}^0}^T \frac{\Delta_{vap} H_m^*}{RT^2} dT$$

$P_{liq}^G = P_L^G$: pression de saturation du liq

$$\ln \frac{P_L^G}{P^0} = \frac{\Delta_{vap} H_m^*}{RT_{eq}^0} - \frac{\Delta_{vap} H_m^*}{RT}$$

$$= C - \frac{D}{T}$$

$$\log \frac{P_L^G}{P^0} = \frac{\Delta_{vap} H_m^*}{2,3 RT_{eq}^0} - \frac{\Delta_{vap} H_m^*}{2,3 R} \cdot \frac{1}{T}$$

$$= c - \frac{d}{T}$$

pour $P_L^G = P^0$ on a $T = T_{eq}^0$

$$T_{eq}^0 = \frac{d}{c} = \frac{D}{C}$$

$$\int c = \frac{\Delta_{vap} H_m^*}{2,3 RT_{eq}^0}; d(K) = \frac{\Delta_{vap} H_m^*}{2,3 R}$$

$$\Delta_{sub} H_m^* > 0$$

$$\Delta_{vap} H_m^* > 0$$

$$\Delta_{fus} H_m^* > 0$$

$$\Delta_{sub} S_m^* > 0$$

$$\Delta_{vap} S_m^* > 0$$

$$\Delta_{fus} S_m^* > 0$$

Pour établir la relation de Clapeyron

$$\mu_{A(P,T)}^{*,g} = \mu_{A(P,T)}^{*,l} \quad (1)$$

$$d\mu_{A(P,T)}^{*,g} = d\mu_{A(P,T)}^{*,l} \quad (2)$$