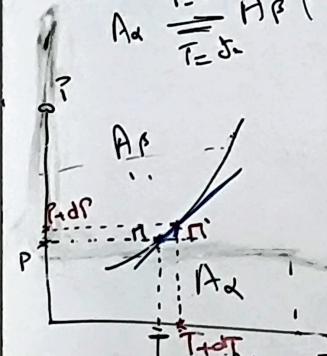


II - Relação de Clapeyron

$$A_\alpha \xrightleftharpoons[T=\bar{T}]{P=\bar{P}} A_\beta \quad (n=1)$$



$\pi(P,T)$: para equilíbrio

$$\Delta G = 0$$

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

$$\mu_i^{*,\beta}(P,T) - \mu_i^{*,\alpha}(P,T) = 0$$

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

$$H_m^{*,\beta} - TS_m^{*,\beta} = H_m^{*,\alpha} - TS_m^{*,\alpha}$$

$$(H_m^{*,\beta} - H_m^{*,\alpha}) = T(S_m^{*,\beta} - S_m^{*,\alpha})$$

$$\Delta_{\alpha \rightarrow \beta} H_m^* = T \Delta_{\alpha \rightarrow \beta} S_m^*$$

$$\Delta_{\alpha \rightarrow \beta} S_m^* = \frac{\Delta_{\alpha \rightarrow \beta} H_m^*}{T} \quad (1')$$

point π

$$\mu_i^{*,\beta}(P,T) + d\mu_i^{*,\beta} = \mu_i^{*,\alpha}(P,T) + d\mu_i^{*,\alpha}$$

$$d\mu_A^{*,\beta} = d\mu_A^{*,\alpha} \quad (2)$$

$$(V_m^{*,\beta} dP - S_m^{*,\beta} dT) = (V_m^{*,\alpha} dP - S_m^{*,\alpha} dT)$$

$$(V_m^{*,\beta} - V_m^{*,\alpha}) dP = (S_m^{*,\beta} - S_m^{*,\alpha}) dT$$

$$\Delta_{\alpha \rightarrow \beta} V_m^* dP = \Delta_{\alpha \rightarrow \beta} S_m^* dT$$

$$\left(\frac{dP}{dT} \right)_{\alpha \rightarrow \beta} = \frac{\Delta_{\alpha \rightarrow \beta} S_m^*}{\Delta_{\alpha \rightarrow \beta} V_m^*} \quad (2')$$

(1) e (2')

$$\left(\frac{dP}{dT} \right)_{\alpha \rightarrow \beta} = \frac{\Delta_{\alpha \rightarrow \beta} H_m^*}{T \Delta_{\alpha \rightarrow \beta} V_m^*}$$

Relação de Clapeyron.

$$\mu_i^{*,\varphi}(P,T) = H_m^{*,\varphi} - TS_m^{*,\varphi}$$

$$d\mu_i^{*,\varphi} = V_m^{*,\varphi} dP - S_m^{*,\varphi} dT$$

$$\left(\frac{\partial \mu_i^{*,\varphi}}{\partial P} \right)_T = V_m^{*,\varphi}$$

$$\left(\frac{\partial \mu_i^{*,\varphi}}{\partial T} \right)_P = -S_m^{*,\varphi}$$

Relação de Clapeyron

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

$$d\mu_A^{*,\beta} = d\mu_A^{*,\alpha} \quad (2)$$

III - Construction du diagramme.

uneine (P,T)
 A suppo. $D_{c.e} H_m^*$ indépendante de T
 c.e. : changement d'état physique
 1) Equilibre de sublimation
 $A_{sd} \xrightleftharpoons{T} A_{(g)} \quad (n=1)$

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

$$\Delta_{\text{sub}} V_m^* = V_m^{*,g} - V_m^{*,l} \approx V_m^{*,g} = \frac{RT}{P}$$

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

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

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

$$\ln \frac{P_{sd}^c}{P_0} = \frac{\Delta_{\text{sub}} H_m^*}{RT_{\text{sub}}} - \frac{\Delta_{\text{sub}} H_m^*}{RT}$$

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

$$\ln \frac{P_{sd}^c}{P_0} = A - \frac{B}{T} ; B(K)$$

$$\log \frac{P_{sd}^c}{P_0} = \frac{\Delta_{\text{sub}} H_m^*}{2,3 RT_{\text{sub}}} - \frac{\Delta_{\text{sub}} H_m^*}{2,3 R} \cdot \frac{1}{T}$$

$$\log \frac{P_{sd}^c}{P_0} = a - \frac{b}{T}$$

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

$$P_{\text{sat}} P_{sd}^c = P_0$$

$$\text{à } T = T_{\text{sub}}$$

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

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

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

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

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

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

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

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

Pour établir la relation de Clausius-Clapeyron

$$\mu_{x,B} = \mu_{x,A} \quad (1)$$

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

III - Construction du diagramme.

uneine (P,T)
 A supposons $D_{c.e.} H_m^*$ indépendante de T
 c.e. : changement d'état physique
 1) Equilibre de sublimation
 $A_{sd} \xrightleftharpoons{T} A(g) \quad (n=1)$

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

$$\Delta_{\text{sub}} V_m^* = V_m^{*,g} - V_m^{*,l} \approx V_m^{*,g} = \frac{RT}{P}$$

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

$$\int_{P_0}^{P_{sd}} \frac{dP}{P} = \int_{T_0}^T \frac{\Delta_{\text{sub}} H_m^*}{RT^2} dT$$

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

$$\ln \frac{P_{sd}^s}{P_0} = \frac{\Delta_{\text{sub}} H_m^*}{RT_{\text{sub}}^0} - \frac{\Delta_{\text{sub}} H_m^*}{RT}$$

$\ln P_{sd}^s = f\left(\frac{1}{T}\right)$: fonction affine
 ($D_{c.e.} H_m^*$: indépendante de T)

$$\ln \frac{P_{sd}^s}{P_0} = A - \frac{B}{T} ; B(K)$$

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

$$\log \frac{P_{sd}^s}{P_0} = a - \frac{b}{T}$$

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

Pour $P_{sd}^s = P_0$
 on a $T = T_{\text{sub}}$

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

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

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

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

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

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

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

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

Pour établir la relation de Clapeyron

$$N_{A(P,T)}^{*,B} = N_{A(P,T)}^{*,A} \quad (1)$$

$$dN^{*,B} = dN^{*,A} \quad (2)$$

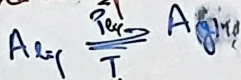
III - Construction du diagramme.

uneine (P,T)

à supposer $\Delta_c H_m^*$ indépendante de T

ϵ : changement d'état physique

1) Equilibre de vaporisation



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

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

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

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

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

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

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

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

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

$$\text{car } P_L^G = P^0 \text{ au } T = T_{eq}^0$$

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

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

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

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

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

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

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

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

Pour établir la relation de Clapeyron

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

$$d\mu_{A(P,T)}^{x,B} = d\mu_{A(P,T)}^{x,A} \quad (2)$$

Série n°4

Ex n°1

5) Carbone diamant: (d)

$$d_{C-C} = 154 \text{ pm}$$

$$Z(C) = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 \times 1$$

$$Z(C) = 8 : \text{nb d'atomes de C par maille}$$

$$\rho_{(d)} = \frac{Z \cdot M_C}{N_A \cdot a^3}$$

$$= \frac{8 \cdot M_C}{N_A \cdot a^3}$$

$$d_{C-C} = \frac{a\sqrt{3}}{4}$$

$$a = \frac{4}{\sqrt{3}} (d_{C-C})$$

$$\rho_{(d)} = \frac{Z \cdot M_C}{N_A \left(\frac{4}{\sqrt{3}}\right)^3 (d_{C-C})^3}$$

AN.

$$\rho_{(d)} = \frac{8 \times 12}{6,02 \times 10^{23} \left(\frac{4}{\sqrt{3}}\right)^3 (154 \times 10^{-10})^3}$$

$$\rho_{(d)} = 3,56 \text{ g.cm}^{-3}$$

$$1 \text{ pm} = 10^{-12} \text{ m} = 10^{-10} \text{ cm}$$

$$1 \text{ nm} = 10^{-9} \text{ m} = 10^{-7} \text{ cm}$$

6) C (graphite)

d_1 : distance entre les atomes de C du même feuillet.

$$d_1 = d_{C-C} = \frac{a\sqrt{3}}{3} = \frac{a}{\sqrt{3}}$$

d_2 : distance entre les feuillets (A et B): $d_2 = \frac{c}{2}$

densité du C (gr): d

$$d = \frac{\rho_{(gr)}}{\rho_{eau}}$$

$$\rho_{(gr)} = d_{(gr)} \cdot \rho_{eau}$$

$$\rho_{(gr)} = \frac{Z \cdot M_C}{N_A \cdot a^2 \cdot c \cdot \frac{\sqrt{3}}{2}}$$

$$\rho_{(gr)} = \frac{4 \cdot M_C}{N_A (d_1 \sqrt{3})^2 (d_2) \frac{\sqrt{3}}{2}}$$

$$\rho_{(gr)} = \frac{4 \cdot M_C}{3\sqrt{3} N_A d_1^2 \cdot d_2} = d_{(gr)} \cdot \rho_{eau}$$

$$d_2 = \frac{4 \cdot M_C}{3\sqrt{3} N_A d_1^2 d_{(gr)} \rho_{eau}}$$

$$d_2 = \frac{4 \times 12}{3\sqrt{3} (6,02 \times 10^{23}) (0,142 \times 10^{-7})^2 \times 2,3 \times 1} = 3,33 \text{ Å}$$

Carbone graphite

$$Z = 8 \times \frac{1}{8} + 1 \times 1 + 2 \times \frac{1}{2} + 4 \times \frac{1}{4}$$

$$Z = 4$$

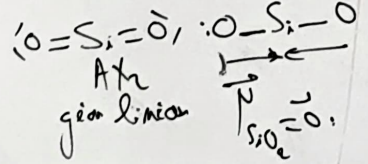
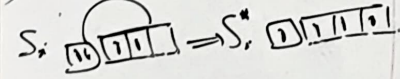
Série 104

Ex 102, 80: 1s² 2s² 2p⁴
 $\begin{array}{|c|c|c|c|} \hline 11 & 11 & 11 & 11 \\ \hline \end{array}$

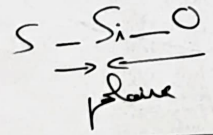
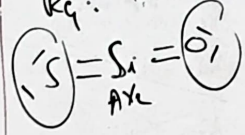
1/ Si: 1s² 2s² 2p⁶ 3s² 3p²
 couche de valence: 3s² 3p²

Si ∈ 3^{ème} ligne
 14^{ème} colonne de T.P

3/ SiO₂: Si } 2 O:

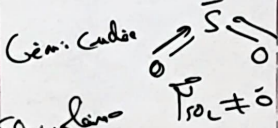
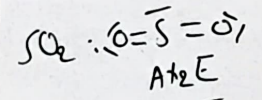


SiO₂: apolaire.
 Rq: SiO

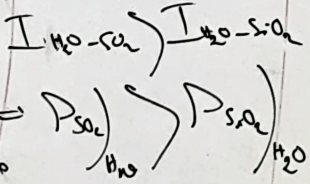


SiO₂ ; H₂O
 apolaire polaire

I_{H₂O-SiO₂}: D_e
 L₂: L.V.D.W très faible
 due à polarisabilité de
 SiO₂ de H₂O et très faible



SO₂: polaire
 I_{H₂O-SO₂} - ra
 pol - polaire
 $\left\{ \begin{array}{l} K_0 \\ D_0 \\ L \end{array} \right.$



5/ C: 2s² 2p²: 14^{ème} colon
 Si: 3s² 3p²: 14^{ème} colon

Si et C ∈ 2^{ème} colonne
 donc ont la même structure

Cristallographie:
 Diamant.

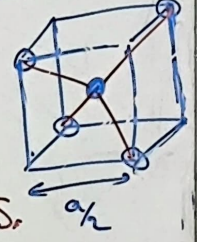
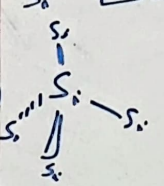
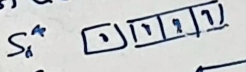
6/a/ Si: semi-métal
 structure diamant
 $\Rightarrow$ Cristal covalent

Si diamant:

- * non conducteur (liaison covalente simple: e⁻(s) fixer)
- * T_{fm} élevée car la liaison covalente est forte

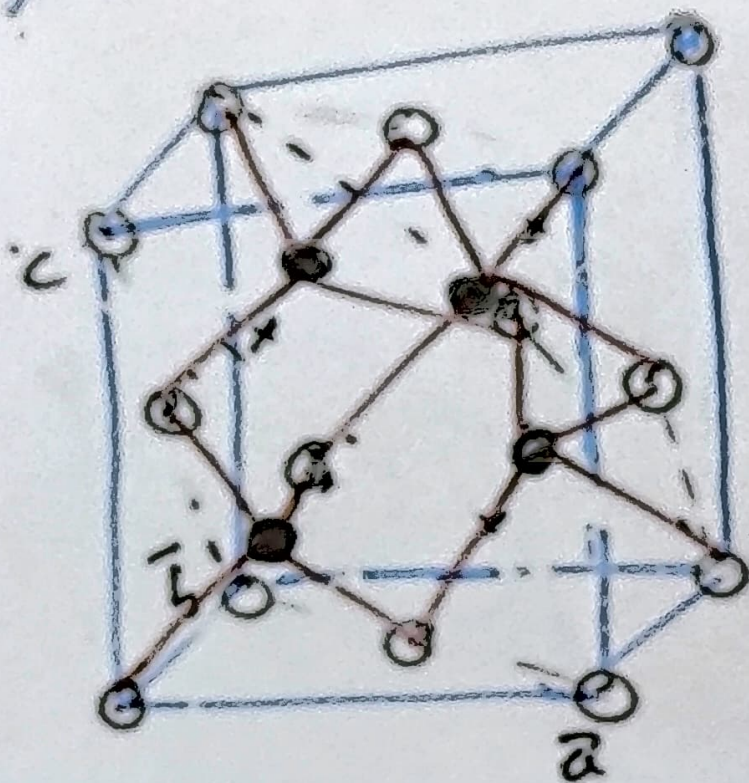
(Si) diamant: structure

tétraaédrique: AX₄
 chaque atome de (Si) central
 est lié à 4 autres voisins (Si)



Serie 04

6) b) S_2 : Struktur diamant



—: $S_1 - S_2$

$$d_{S_1-S_2} = \frac{a\sqrt{3}}{4} = 0.357a$$