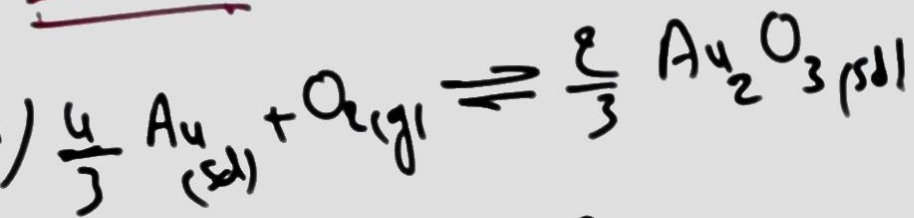


Ex 102



$$F = r - k - v + i - q$$

$$F = 3 - 1 - 0 + 2 - 3 = 1$$

$$2) \Delta_f H^\circ(\text{Au}_2\text{O}_3)_{s,1} = ?$$

$$\Delta_f H^\circ = \frac{2}{3} \Delta_f H^\circ(\text{Au}_2\text{O}_3)_{s,1} - \left(\frac{4}{3} \Delta_f H^\circ(\text{Au})_{s,1} + \Delta_f H^\circ(\text{O}_2)_{g,1} \right)$$

$$\Delta_f H^\circ(\text{Au}_2\text{O}_3)_{s,1} = \frac{3}{2} \Delta_r H^\circ(298)$$

$$\Delta_r G^\circ(298) = \Delta_r H^\circ(298) - 298 \Delta_r S^\circ(298)$$

$$\Delta_r H^\circ(298) = \Delta_r G^\circ(298) + 298 \Delta_r S^\circ(298)$$

$$= \left(\frac{2}{3} \mu^\circ_{\text{Au}_2\text{O}_3} - \mu^\circ_{\text{O}_2} - \frac{4}{3} \mu^\circ_{\text{Au}} \right) + 298 \left(\frac{2}{3} S^\circ_{\text{Au}_2\text{O}_3} - \left(\frac{4}{3} S^\circ_{\text{Au}} + S^\circ_{\text{O}_2} \right) \right)$$

$$\Delta_r G^\circ(298) = \sum \nu_i \mu^\circ_{i(298)} - \sum \nu_k \mu^\circ_{k(298)}$$

$$\Delta_r S^\circ(298) = \sum \nu_i S^\circ_{i(298)} - \sum \nu_k S^\circ_{k(298)}$$

$$\Delta_r H^\circ(298) = \frac{2}{3} (163,3) + 298 (-185,16) \cdot 10^{-3}$$

$$\Delta_r H^\circ(298) = 53,168 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\text{Au}_2\text{O}_3) = \frac{3}{2} \Delta_r H^\circ(298)$$

$$\Delta_f H^\circ(\text{Au}_2\text{O}_3) = 80,53 \text{ kJ mol}^{-1}$$

Ex 102

II - 2)
 $D_{C,E} H_m(Au)$: indépendante de T
 $Au \rightleftharpoons \frac{P^c}{T} Au_{(g)}$

φ : sol/lig
 $N_{(l,T)}^{*,g} = N_{(l,T)}^{*,\varphi}$

$H_m^{*,g} - TS_m^{*,g} = H_m^{*,\varphi} - TS_m^{*,\varphi}$
 $D_{\varphi \rightarrow g} \int_m^x = \frac{D_{\varphi \rightarrow g} H_m^*}{T}$ ①

$dN^{*,g} = dN^{*,\varphi}$
 $(N_m^{*,g} dP - S_m^{*,g} dT) = (N_m^{*,\varphi} dP - S_m^{*,\varphi} dT)$

$(N_m^{*,g} - V_m^{*,\varphi}) dP = (S_m^{*,g} - S_m^{*,\varphi}) dT$
 $\frac{dP}{dT} = \frac{D_{\varphi \rightarrow g} \int_m^x}{D_{\varphi \rightarrow g} V_m^*}$ ②

① $\cup$ ②
 $\frac{dP}{dT} = \frac{D_{\varphi \rightarrow g} H_m^*}{T D_{\varphi \rightarrow g} V_m^*}$

$D_{\varphi \rightarrow g} V_m^* = V_m^{*,g} - V_m^{*,\varphi}$
 $\approx V_m^{*,g} = \frac{RT}{P}$

$\frac{dP}{dT} = \frac{D_{\varphi \rightarrow g} H_m^*}{RT^2} \cdot P$

$\int_{P^0}^{P^c} \frac{dP}{P} = \int_{T_{\varphi \rightarrow g}}^T \frac{D_{\varphi \rightarrow g} H_m^*}{RT^2} \cdot dT$
 $L_m \frac{P^c}{P^0} = \frac{D_{\varphi \rightarrow g} H_m^*}{RT_{\varphi \rightarrow g}} - \frac{D_{\varphi \rightarrow g} H_m^*}{RT}$

φ : (sol): $Au_{(s)} \xrightleftharpoons[T]{P_{s,l}} Au_{(l)}$
Sublimation
 $L_m \frac{P^c}{P^0} = \frac{D_{sub} H_m^*}{RT_{sub}^0} - \frac{D_{sub} H_m^*}{RT}$
 $= A - \frac{B}{T}$

φ : (g): $Au_{(g)} \xrightleftharpoons[T]{P_{g,l}} Au_{(l)}$
Separation
 $L_m \frac{P^c}{P^0} = \frac{D_{\varphi \rightarrow g} H_m^*}{RT_{\varphi \rightarrow g}} - \frac{D_{\varphi \rightarrow g} H_m^*}{RT}$
 $= C - \frac{D}{T}$

φ : (s): $Au_{(s)} \xrightleftharpoons[T]{P_{s,l}} Au_{(l)}$
équilibre de sublimation
 $T = 1200 K: L_m \frac{P^c}{P^0} = A - \frac{B}{1200} = -9,09$

$T = 1100 K: L_m \frac{P^c}{P^0} = A - \frac{B}{1100} = -2,73$
 $B = \frac{9,09 - 2,73}{\frac{1}{1100} - \frac{1}{1200}} = 40600 (K)$

donc $A = -9,09 + \frac{40600}{1200} = 24,67$

donc $L_m \frac{P^c}{P^0} = 24,67 - \frac{40600}{T}$

$$\underline{C = 12,43}$$

II - 2)
b) équation de vaporisation

$$\ln \frac{p^c}{p^0} = C - \frac{D}{T}$$

$$T = 1200, \quad \ln \frac{p^c}{p^0} = -20,02 = C - \frac{D}{1200}$$

$$T = 1100, \quad \ln \frac{p^c}{p^0} = -13,13 = C - \frac{D}{1100}$$

$$D = \frac{20,02 - 13,13}{\frac{1}{1200} - \frac{1}{1100}}$$

$$D = 38940 \text{ (K)}$$

$$C = -20,02 + \frac{38940}{1200} = 12,43$$

$$\ln \frac{p^c}{p^0} = 12,43 - \frac{38940}{T}$$

II-3) a)

$$T = T_{\text{sub}} \text{ pour } p^c = p^0$$

$$\ln 24,67 - \frac{40500}{T_{\text{sub}}} = 0$$

$$T_{\text{sub}} = \frac{40500}{24,67} = 1641,67 \text{ K}$$

$$T = T_{\text{vap}} \text{ pour } p^c = p^0$$

$$12,43 - \frac{38940}{T_{\text{vap}}} = 0$$

$$T_{\text{vap}} = \frac{38940}{12,43} = 3132,7 \text{ K}$$

3) b) déterminer $\Delta_{\text{sub}} H_m^*(\text{Au})$ et $\Delta_{\text{fus}} H_m^*(\text{Au})$

$$\begin{aligned} \text{Au}_{\text{sol}} &\rightleftharpoons \text{Au}_{\text{vap}} \\ \ln \frac{p_{\text{sol}}^c}{p^0} &= \frac{\Delta_{\text{sub}} H_m^*}{R T_{\text{sub}}^0} - \frac{\Delta_{\text{sub}} H_m^*}{R T} \\ &= 24,67 - \frac{40500}{T} \end{aligned}$$

$$\text{Par identification} \quad \frac{\Delta_{\text{sub}} H_m^*}{R} = 40500$$

$$\begin{aligned} \Delta_{\text{sub}} H_m^* &= R(40500) \\ &= 8,314(40500) \\ &= 336,717 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Au}_l &\rightleftharpoons \text{Au}_{\text{vap}} \\ \ln \frac{p^c}{p^0} &= \frac{\Delta_{\text{vap}} H_m^*}{R T_{\text{vap}}^0} - \frac{\Delta_{\text{vap}} H_m^*}{R T} \\ &= 12,43 - \frac{38940}{T} \end{aligned}$$

$$\text{Par identification: } \frac{\Delta_{\text{vap}} H_m^*}{R} = 38940$$

$$\Delta_{\text{vap}} H_m^* = R(38940) = 323,74 \text{ kJ mol}^{-1}$$

Au peut être Au_{sol} , Au_l ou Au_{g} en équilibre
3 phase (Au_{sol} , Au_l et Au_{g})

$$\text{donc } \Delta_{\text{sub}} H_m^* = \Delta_{\text{fus}} H_m^* + \Delta_{\text{vap}} H_m^*$$

$$\begin{aligned} \Delta_{\text{fus}} H_m^*(\text{Au}) &= \Delta_{\text{sub}} H_m^*(\text{Au}) - \Delta_{\text{vap}} H_m^*(\text{Au}) \\ &= 336,717 - 323,74 \\ &= 12,977 \text{ kJ mol}^{-1} \end{aligned}$$

Ex n° 2

IV) $T_{\text{fus}}(\text{Au})$ sous $P = 200 \text{ bar}$



Départ de relation de Clapeyron:

$$\left. \frac{dP}{dT} \right|_{\text{fus}} = \frac{\Delta_{\text{fus}} H_m^*}{T \Delta_{\text{fus}} V_m^*}$$

$$\Delta_{\text{fus}} V_m^* = V_{m, \text{liq}}^* - V_{m, \text{sol}}^*$$

$$= n_{\text{Au}} \left(\frac{1}{\rho_{\text{liq}}^*} - \frac{1}{\rho_{\text{sol}}^*} \right)$$

$$\Delta_{\text{fus}} V_m^* = 197 \left(\frac{1}{17,31} - \frac{1}{19,31} \right)$$

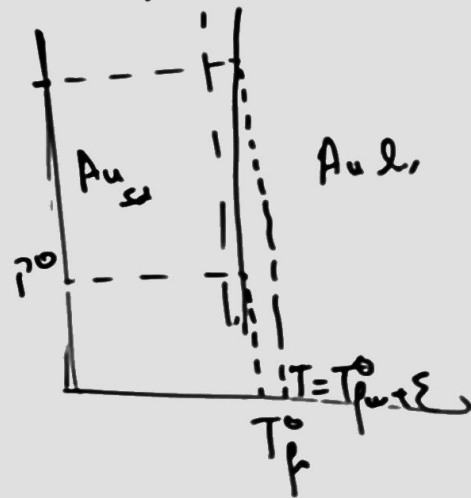
$$= 1,17 \text{ cm}^3 \text{ mol}^{-1}$$

$$\frac{dP}{dT} = \frac{\Delta_{\text{fus}} H_m^*}{T \Delta_{\text{fus}} V_m^*} \cdot \frac{1}{T} \quad \left| P = 200 \text{ bar} \right. \quad P^0$$

$$\int_{P^0}^P dP = \int_{T_{\text{fus}}^0}^T \frac{\Delta_{\text{fus}} H_m^*}{T \Delta_{\text{fus}} V_m^*} \cdot \frac{dT}{T} \quad \left| T_{\text{fus}} > T_{\text{fus}}^0 \right.$$

$$(P - P^0) = \frac{\Delta_{\text{fus}} H_m^*}{\Delta_{\text{fus}} V_m^*} \cdot \ln \frac{T}{T_{\text{fus}}^0}$$

$$\text{C.à d } T_{\text{fus}} = T_{\text{fus}}^0 + \varepsilon$$



$$T = T_{\text{fus}}^0 \exp \left[\frac{\Delta_{\text{fus}} V_m^*}{\Delta_{\text{fus}} H_m^*} (P - P^0) \right]$$

AN

$$T = 1337 \exp \left[\frac{1,17 \cdot 10^{-6}}{12,55 \cdot 10^{-3}} (200 - 1) \cdot 10^5 \right]$$

$$T_{\text{fus}}(P = 200 \text{ bar}) = 1339,5 \text{ K}$$

$$\frac{D_{fu} H_m^*}{D_{fu} V_m^*} \cdot \frac{1}{T} \bigg|_{P=200 \text{ bar}}^{p^0} \bigg|_{T_{fus}}^{T^0}$$

$$= \int_{T_{fus}}^{T^0} \frac{D_{fu} H_m^*}{D_{fu} V_m^*} \cdot \frac{dT}{T}$$

C.é d $T_{fus} = T_{fus}^0 + \varepsilon$

$$= \frac{D_{fu} H_m^*}{D_{fu} V_m^*} \cdot \ln \frac{T}{T_{fus}^0}$$

$$= T_{fus}^0 \exp \left[\frac{D_{fu} V_m^*}{D_{fu} H_m^*} (p - p^0) \right]$$

$$= 1337 \exp \left[\frac{1,17 \cdot 10^{-6}}{12,55 \cdot 10^{-3}} (200 - 1) \cdot 10^5 \right]$$

$$(p = 200 \text{ bar}) = 1339,5 \text{ K}$$

