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1/ Corps pur

Potential chimique: Enthalpie libre molaire  $G^{*,i}$

$$\mu_i^{*,i}(P,T) = G_i^{*,i}(P,T) = \frac{G^{*,i}}{n}$$

Rq: pour un mélange:

$$\mu_i(P,T) = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

$$dG^{*,i} = V^{*,i} dP - S^{*,i} dT$$

$$dG^{*,i} = d\mu^{*,i} = V^{*,i} dP - S^{*,i} dT$$

$$3) d\mu^{*,i} = V_m^{*,i} dP - S_m^{*,i} dT$$

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

Corps pur en phase condensée:  $\varphi: (cd)$

$V_m^{*,cd}$  indépendant de P

$$\int_{P^0}^P d\mu^{*,i,cd} = \int_{P^0}^P V_m^{*,i,cd} dP$$

$$\mu_{i,cd}^{*,i}(P^0,T)$$

$$\mu_{i,cd}^{*,i}(P,T) = \mu_{i,cd}^{*,i}(T) + V_m^{*,i,cd} (P - P^0)$$

$$4) \mu_{i,g}^{*,i}(P,T) = \mu_{i,g}^{*,i}(T) + RT \ln \frac{P}{P^0}$$

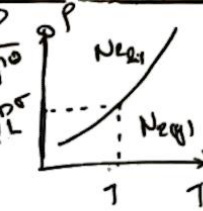
5) a)  $N_{e,i} \rightleftharpoons N_{e,g}$   
Condition d'équilibre:

$$\mu_{N_e,i}^{*,i} = \mu_{N_e,g}^{*,i}$$

$$\mu_{N_e,i}^{*,i}(T) + V_m^{*,i,g} (P_L - P^0) = \mu_{N_e,i}^{*,i}(T) + RT \ln \frac{P_L}{P^0}$$

$$\mu_{N_e,i}^{*,i}(T) = \mu_{N_e,i}^{*,i}(T) + RT \ln \frac{P_L}{P^0}$$

$$\ln \frac{P_L}{P^0} = \left( \frac{\mu_{N_e,i}^{*,i}(T) - \mu_{N_e,i}^{*,i}(T)}{RT} \right)$$



Potential chimique

$$\mu_{i,g}^{*,i}(P,T) = H_m^{*,i} - TS_m^{*,i}$$

$$d\mu_{i,g}^{*,i} = V_m^{*,i} dP - S_m^{*,i} dT$$

$$\mu_{i,g}^{*,i}(P^0,T) = \mu_{i,g}^{*,i}(T)$$

$$\mu_{i,cd}^{*,i}(P,T) = \mu_{i,cd}^{*,i}(T) + V_m^{*,i,cd} (P - P^0)$$

$$\mu_{i,cd}^{*,i}(P,T) \approx \mu_{i,cd}^{*,i}(T)$$

$$\mu_{i,g}^{*,i}(P,T) = \mu_{i,g}^{*,i}(T) + RT \ln \frac{P}{P^0}$$

$$Rq: \frac{P_L}{P^0} = \exp \left( \frac{\mu_{i,cd}^{*,i}(T) - \mu_{i,g}^{*,i}(T)}{RT} \right)$$

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5) c) Relation de Gibbs-Helmholtz

$$\left( \frac{d\left(\frac{G}{T}\right)}{dT} \right)_P = - \frac{H}{T^2}$$

Rq

$$\Delta_r G_m^\circ = -RT \ln K_m^\circ$$

$$\left( \frac{d\left(\frac{\Delta_r G_m^\circ}{T}\right)}{dT} \right)_P = - \frac{\Delta_r H_m^\circ}{T^2}$$

$$\left( \frac{d \ln K_m^\circ}{dT} \right) = \frac{\Delta_r H_m^\circ}{RT^2}$$

Loi de Van't Hoff

$$\left( \frac{d\left(\frac{G_m^{i,4}}{T}\right)}{dT} \right)_P = - \frac{H_m^{i,4}}{T^2}$$

$$\left( \frac{d\left(\frac{p^{i,4}}{T}\right)}{dT} \right)_P = - \frac{H_m^{i,4}}{T^2}$$

$$\left( \frac{d\left(\frac{p^{o,i,4}}{T}\right)}{dT} \right)_P = - \frac{H_m^{o,i,4}}{T^2}$$

$$5) d) \ln \frac{p_L^{i,r}}{p^o} = \frac{(p^{o,L} - p^{o,g})}{RT}$$

$$\frac{d\left(\ln \frac{p_L^{i,r}}{p^o}\right)}{dT} = \frac{1}{R} \left( \frac{d\left(\frac{p^{o,L}}{T}\right)}{dT} - \frac{d\left(\frac{p^{o,g}}{T}\right)}{dT} \right)$$

$$\left( \frac{d\left(\ln \frac{p_L^{i,r}}{p^o}\right)}{dT} \right) = \frac{1}{R} \left( - \frac{H_m^{o,L}}{T^2} + \frac{H_m^{o,g}}{T^2} \right)$$

$$\left( \frac{d\left(\ln \frac{p_L^{i,r}}{p^o}\right)}{dT} \right) = \frac{(H_m^{o,g} - H_m^{o,L})}{RT^2} = \frac{\Delta_{vap} H_m^\circ}{RT^2}$$

$$5) e) \int_{\ln \frac{p^o}{p^o}}^{\ln \frac{p_L^{i,r}}{p^o}} d\left(\ln \frac{p_L^{i,r}}{p^o}\right) = \int_{T_{vap}^o}^T \frac{\Delta_{vap} H_m^\circ}{RT^2} dT$$

$$\ln \frac{p_L^{i,r}}{p^o} = \frac{\Delta_{vap} H_m^\circ}{RT_{vap}^o} - \frac{\Delta_{vap} H_m^\circ}{RT} = A - \frac{B}{T}$$

5) b)

Par identification

$$A = \frac{\Delta_{vap} H_m^\circ}{RT_{vap}^o} = \frac{5,6 \cdot 10^3}{8,314 / 77,34}$$

$$B = \frac{\Delta_{vap} H_m^\circ}{R} = \frac{5,6 \cdot 10^3}{8,314}$$

$$B = 673,56 \text{ (K)}$$

$$\ln \frac{p_L^{i,r}}{p^o} = 8,71 - \frac{673,56}{T}$$

$NP-2015$   $P^0 = 10^5 \text{ Pa}$   
 $P. 37$   $P^0 = 10^5 \text{ Pa}$   
 $Ag_{(s)} \rightleftharpoons Ag_{(l)}$   
 $T(K) : P^0$   
 $\ln \frac{P}{P^0} = \frac{12,87 - \frac{3,19 \cdot 10^4}{T}}$

$T = 962^\circ \text{C} = 1235 \text{ K}$   
 $P_L(T=1235 \text{ K}) = 10^5 \text{ Pa} \left( \frac{12,87 - \frac{3,19 \cdot 10^4}{1235}}{12,87 - \frac{3,19 \cdot 10^4}{1235}} \right)$   
 $P_L(T=1235 \text{ K}) = 0,235 \text{ Pa}$

$1) \text{ point sublimation}$   
 $T_{\text{sub}} (1 - P_{\text{sub}} \approx P^0) = T_{\text{sub}}^0$   
 $= 12,87 - \frac{3,19 \cdot 10^4}{T_{\text{sub}}} = 0$

$T_{\text{sub}}^0 = \frac{3,19 \cdot 10^4}{12,87}$

$T_{\text{sub}} = 248,6 \text{ (K)}$



$\mu_{Ag}^{s,g} = \mu_{Ag}^{l,g}$

$H_m^{s,g} - TS_m^{s,g} = H_m^{l,g} - TS_m^{l,g}$   
 $(H_m^{s,g} - H_m^{l,g}) = T(S_m^{s,g} - S_m^{l,g})$

$\Delta_{\text{sub}} S_m = \frac{\Delta_{\text{sub}} H_m^0}{T}$

$d\mu^{s,g} = d\mu^{l,g}$   
 $V_m^{s,g} dP - S_m^{s,g} dT = V_m^{l,g} dP - S_m^{l,g} dT$   
 $(V_m^{s,g} - V_m^{l,g}) dP = (S_m^{s,g} - S_m^{l,g}) dT$   
 $\left( \frac{dP}{dT} \right)_{\text{sub}} = \frac{\Delta_{\text{sub}} S_m}{\Delta_{\text{sub}} V_m}$

$\frac{dP}{dT} = \frac{\Delta_{\text{sub}} H_m^0}{T \Delta_{\text{sub}} V_m}$

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

$\frac{dP}{dT} = \frac{\Delta_{\text{sub}} H_m^0}{RT^2}$

$\int_{P^0}^P \frac{dP}{P} = \int_{T_{\text{sub}}^0}^T \frac{\Delta_{\text{sub}} H_m^0}{RT^2} dT$

$\ln \frac{P}{P^0} = \frac{\Delta_{\text{sub}} H_m^0}{RT_{\text{sub}}^0} - \frac{\Delta_{\text{sub}} H_m^0}{RT}$

$\ln \frac{P}{P^0} = \frac{12,87 - \frac{3,19 \cdot 10^4}{T}}$

$\frac{\Delta_{\text{sub}} H_m^0}{R} = 3,19$

$\Delta_{\text{sub}} H_m^0 = R(3,19 \cdot 10^4)$

$\Delta_{\text{sub}} H_m^0 = \Delta_{\text{sub}} H_m^0$   
 $\Delta_{\text{sub}} H_m^0 = 26,21 \text{ kJ/mol}$

$\Delta_{\text{sub}} H_m^0 = 26,21 \text{ kJ/mol}$

$1) \text{ d) Argentum Triple}$   
 $T(T_{\text{tr}}, P_{\text{tr}})$   
 $(Ag_{(s)}, Ag_{(l)}, Ag_{(g)})$

$\Delta_{\text{sub}} H_m^0 = \Delta_{\text{sub}} H_m^0 + \Delta_{\text{sub}} H_m^0$

$\Delta_{\text{sub}} H_m^0 (Ag) = 11,3 + 26,21$

$\Delta_{\text{sub}} H_m^0 (Ag) = 27,51 \text{ kJ/mol}$

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2. nous L-V (Ag-Cu)

On suppose que la mélange  
liq. de (Ag-Cu) est idéal

Dans V=0 ; Dmix H=0

T<sub>A-B</sub> ≈ T<sub>A-A</sub> = T<sub>B-B</sub> ; a<sub>i</sub>(l<sub>g</sub>) = x<sub>i</sub>

(A) et (B) respectent le 1<sup>er</sup> de Raoult

P<sub>i</sub> = x<sub>i</sub> P<sub>i</sub><sup>c</sup>

b) B<sub>g</sub> ⇌ B<sub>liq</sub>

0 < x<sub>B</sub> < 1 (binaire - mélange)

P<sub>B</sub>(g) = P<sub>B</sub>

$\frac{P_{B,g}}{P_0} + RT \ln \frac{P_B}{P_0} = \frac{P_{B,g}}{P_0} + RT \ln x_B$

Mélange (4)

$\mu_i(P,T) = \mu_i^0(T) + RT \ln a_i$

x<sub>B</sub> = 1 : B<sub>g</sub> ⇌ B<sub>liq</sub>

$\mu_{B,g}(T) = \mu_{B,l}(T)$

$\mu_{B,g}(T) = \mu_{B,g}^0(T) + RT \ln \frac{P_{B,g}}{P_0}$

① et ②

$\mu_{B,g}(T) + RT \ln \frac{P_B}{P_0} = \mu_{B,g}^0(T) + RT \ln \frac{P_{B,g}}{P_0} + RT \ln x_B$

$RT \ln \frac{P_B}{P_0} = RT \ln x_B \frac{P_{B,g}}{P_0}$

$P_B = x_B P_{B,g}$

donc  $P_A = x_A P_{A,g} = (1 - x_B) P_{A,g}$

1) c)

Condition d'équilibre : P = f(x<sub>B</sub>)

Ensemble des p<sub>r</sub> de l'équilibre (l<sub>g</sub> + 1 bulle l<sub>g</sub>)

pression l<sub>g</sub> et (l<sub>g</sub> + v<sub>0</sub>)

P = P<sub>A</sub> + P<sub>B</sub> = x<sub>A</sub> P<sub>A,g</sub><sup>c</sup> + x<sub>B</sub> P<sub>B,g</sub><sup>c</sup>

P = (1 - x<sub>B</sub>) P<sub>A,g</sub><sup>c</sup> + x<sub>B</sub> P<sub>B,g</sub><sup>c</sup>

P = P<sub>A,g</sub><sup>c</sup> + x<sub>B</sub> (P<sub>B,g</sub><sup>c</sup> - P<sub>A,g</sub><sup>c</sup>)

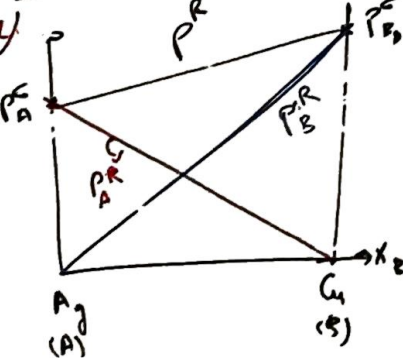
liq. = 0

Graphs showing pressure (P) vs composition (x<sub>B</sub>) for an ideal binary mixture. The left graph shows the total pressure P = P<sub>A</sub> + P<sub>B</sub> as a function of x<sub>B</sub>, with a curve starting at P<sub>A,g</sub><sup>c</sup> and ending at P<sub>B,g</sub><sup>c</sup>. The right graph shows the partial pressure of component B, P<sub>B</sub>, as a function of x<sub>B</sub>, which is a straight line from 0 to P<sub>B,g</sub><sup>c</sup>.

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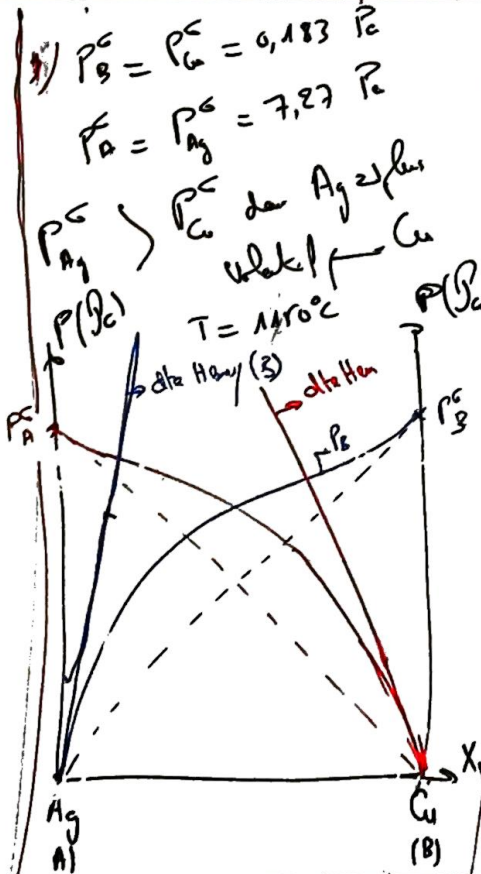
Système L-V (Ag-Cu)



$$P_B = X_B P_B^G$$

$$P_A = X_A P_A^G$$

$$= (1 - X_B) P_A^G$$



4)  $(P_i)_{\text{réel}} = f(X_i)$ : courbe  
le mélange L-f de (Ag-Cu) est réel  
Courbe  $(P_i)$  au dessus de la de Raoult  
 $(P_i)_{\text{réel}} > (P_i)_{\text{Raoult}}$   
 $\Rightarrow$  Ecart positif:  $\gamma_i > 1$  (excess H)  
 $\Rightarrow$  le mélange L-f de réel (Ag-Cu) est  
réel et avec absorption  
5)  $X_i \rightarrow 0$ : (i) est dilué: 80%  
à la loi d'Henry:  $P_i = k_i X_i$   
 $\Rightarrow$  la courbe  $(P_i)$ : f de la loi d'Henry  
de  $k_i$ : pente de la loi d'Henry (i)

$K_B^H = \frac{0,05 - 0}{0,1 - 0} = 0,45 \text{ Pa}$   
 $K_A^H$ : pente de la loi d'Henry (A)  
 $K_A^H = \frac{2 - 0}{0,2 - 0} = 20 \text{ Pa}$   
A) plus volatil que B  
 $P_A > P_B$   
 $K_A^H > K_B^H$   
le  $\Delta_{\text{mix}} H > 0$   
 $I_{A-B} < I_{A-A} \text{ et } I_{B-B}$   
 $a_i = \gamma_i X_i$   
 $K_i^H > P_i^G$

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6) une solution diluée en Ag

Ag : (A)  
Cu : (B)

$w_A \rightarrow 0$

Ag : soluté : obéit à la loi d'Henry

$$P_A = X_A K_A^H$$

$X_{Cu} \rightarrow 1$  : Cu : solvant  
Cu obéit à la loi de Raoult

$$P_{Cu} = X_{Cu} P_{Cu}^0$$

$$X_A = 1 - X_B = 0,99$$

$$X_A = \frac{w_A}{w_A + (1 - w_A) \cdot \frac{M_A}{M_B}}$$

$$X_A = 0,003 \rightarrow 0$$

6) A suit la loi d'Henry

$$X_A \rightarrow 0$$

donc B suit la loi de Raoult

$$P_B = X_B P_B^0 = 0,18$$

$$P_A = X_A K_A^H = 0,06$$

$$Y_B = \frac{P_B}{P} = \frac{P_B}{P_A + P_B} = \frac{0,18}{0,18 + 0,06} = 0,75$$

$$X_B = 0,75$$