

Exercice 1:  $f_{exp} = 2,698$ ,  $a = 4,049 \text{ \AA}^3$ ,  $M_{Al} = 26,98 \text{ g/mol}$

$$f_{th} = \frac{n \cdot M}{V a^3} = \frac{4(26,98)}{6,023 \times 10^{23} (4,049 \times 10^8)^3} = 2,699 \text{ g/cm}^3$$

On remarque que  $f_{exp} < f_{th} \Rightarrow$  la densité d'Al diminue  $\Rightarrow$  augmentation de volume  $\Rightarrow$  création des lacunes.

$$\frac{f_{th}}{f_{exp}} = \frac{V(\text{volume final})}{V(\text{volume initial})} = 1,00037 \Rightarrow V = \sqrt[3]{(1,00037)} = \sqrt[3]{1 + \frac{37}{10^5}}$$

Exercice 2:  
 $T_1 = 500^\circ\text{C} \rightarrow C_1 = \frac{1}{10^{10}}$ ,  $k_B = 1,38 \times 10^{-23} \text{ J.K}^{-1}$ ,  $1 \text{ eV} = 1,6022 \times 10^{-19} \text{ J}$

$T_2 = 600^\circ\text{C} \rightarrow C_2 = \frac{1}{10^9} = \frac{10}{10^{10}}$

$$a) C_f = \exp \frac{\Delta S}{k_B T} = \exp \frac{(\Delta H_f - T \Delta S_f)}{k_B T} = \exp \frac{\Delta S_f}{k_B} \cdot \exp \frac{-\Delta H_f}{k_B T}$$

$$\Rightarrow \log C_f = \log \exp \frac{\Delta S_f}{k_B} + \log \exp \frac{-\Delta H_f}{k_B T} \Rightarrow \log C_f = K - \frac{\Delta H_f}{k_B T}$$

C'est une fonction de la forme  $y = A - Bx$  où:  $B = \frac{-\Delta H_f}{k_B}$  et  $n = \frac{1}{T}$

$$\Rightarrow B = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\log C_2 - \log C_1}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{\log \frac{C_2}{C_1}}{\frac{T_1 - T_2}{T_1 T_2}} = \frac{-\Delta H_f}{k_B}$$

$$\Rightarrow -\Delta H_f = 1,38 \times 10^{-23} \left[ \frac{(873 \times 773) \log \left( \frac{10}{10^{10}} \right)}{773 - 873} \right] \Rightarrow \Delta H_f = 2,14 \times 10^{-19} \text{ J} = 1,33 \text{ eV}$$

\*  $\exp \frac{\Delta S}{k_B}$  ?

Il faut trouver la valeur de  $\frac{\Delta S}{k_B}$  ? pour trouver  $C_f$  à  $700^\circ\text{C}$ .

on prend:  $T_1 = 773 \text{ K}$ ,  $C_1 = 10^{10}$

$$\text{on a: } C_1 = \exp \frac{\Delta S}{k_B} \cdot \exp \frac{-\Delta H_f}{k_B T} \Rightarrow \log C_1 = \frac{\Delta S}{k_B} - \frac{\Delta H_f}{k_B T}$$

$$\Rightarrow \frac{\Delta S}{k_B} = \log 10^{10} + \frac{2,14 \times 10^{-19}}{1,38 \times 10^{-23} \times 773} \Rightarrow \frac{\Delta S}{k_B} = -2,9678$$

$$\Rightarrow \exp \frac{\Delta S}{k_B} = 0,05$$

b)  $T = 700^\circ\text{C} = 973 \text{ K} \Rightarrow C_3 = ?$

$$C_3 = \exp \frac{\Delta S}{k_B} \cdot \exp \frac{-\Delta H_f}{k_B T} = 0,05 \cdot \exp \left( \frac{2,14 \times 10^{-19}}{1,38 \times 10^{-23} \cdot 973} \right)$$

$$C_3 = \frac{60 \times 10^{-10}}{10^{10}} = \frac{60}{10^{20}}$$

\* la même chose pour  $T = 800^\circ\text{C} \rightarrow C_4 = ?$

### Exercice 03

$$T_1 = 800^\circ\text{C} \Rightarrow c_1 = 1/10^0$$

$$T_2 = 900^\circ\text{C} \Rightarrow c_2 = 1/10^3$$

a)  $\Delta H_f = ?$

$$\text{on a: } c_f = \exp \frac{-\Delta G_f}{k_B T} = \exp \frac{\Delta S}{k_B} \cdot \exp \frac{-\Delta H_f}{k_B T}$$

$$\Rightarrow -\Delta H_f = k_B \cdot \frac{\log c_2/c_1}{\frac{1}{T_1} - \frac{1}{T_2}} = -3,99 \times 10^{-19} \text{ J} \Rightarrow \Delta H_f = 3,99 \times 10^{-19} \text{ J}$$

$$\text{on a: } 1 \text{ cal} = 4,18 \text{ J} \Rightarrow \Delta H_f = \frac{3,99 \times 10^{-19}}{4,18} = 9,56 \times 10^{-20} \text{ cal}$$

$$\text{pour 1 mole} \Rightarrow \Delta H_{f, \text{mole}} = \Delta H_f \cdot N_A = 5,76 \cdot 10^4 \text{ cal/mole}$$

b) pour changer  $T_3$  il faut trouver  $\frac{\Delta S}{k_B}$

$$\text{pour } T_1 = 800^\circ\text{C} = 1073 \text{ K}, c_1 = 1/10^0$$

$$\log c_1 = \frac{\Delta S}{k_B} - \frac{\Delta H_f}{k_B T_1} \Rightarrow \frac{\Delta S}{k_B} = \log 10^0 + \frac{3,99 \times 10^{-19}}{1,38 \times 10^{-23} (1073)}$$

$$\Rightarrow \frac{\Delta S}{k_B} = 3,90$$

$$\text{Alors: pour } c_3 = 1/10^8 \rightarrow T_3$$

$$\log c_3 = \frac{\Delta S}{k_B} - \frac{\Delta H_f}{k_B T_3} \Rightarrow T_3 = \frac{\Delta H_f / k_B}{\frac{\Delta S}{k_B} - \log c_3} \Rightarrow T_3 = 1294 \text{ K} = 1021^\circ\text{C}$$

### Exercice 04

$$T_1 = 600^\circ\text{C} \rightarrow c_1$$

$$T_2 = 300^\circ\text{C} \rightarrow c_2$$

$$c_2 - c_1 = 1 \text{ atome/cm}^3$$

$$c_f = \frac{n_f}{V}, N = ?$$

$$\text{on a: } \rho = \frac{\text{masse d'un mole}}{\text{volume d'un mole}} \Rightarrow \rho = \frac{M}{V} \Rightarrow V = \frac{M}{\rho} = 10,25 \text{ cm}^3$$

$$10,27 \text{ cm}^3 \rightarrow N_A$$

$$1 \text{ cm}^3 \rightarrow N$$

$$\Rightarrow N = 5,86 \times 10^{22} \text{ atome/cm}^3$$

$$c = \frac{1}{5,86 \times 10^{22}} \approx c_2 - c_1 = 1,7 \times 10^{-23}$$

$$\text{d'autre part: } c_f = \exp \frac{-\Delta G_f}{k_B T} \Rightarrow -\frac{\Delta H}{k_B} = \frac{\log c_2/c_1}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$\Rightarrow \log \frac{c_2}{c_1} = -\frac{\Delta H}{k_B} \left( \frac{T_1 - T_2}{T_2 T_1} \right) = 7,64 \Rightarrow \frac{c_2}{c_1} = 2079$$

$$\text{Donc: } C_2 - C_1 = 1,7 \times 10^{-23} \Rightarrow C_2 = 1,7 \times 10^{-23} + C_1$$

$$\frac{C_2}{C_1} = \frac{1,7 \times 10^{-23} + C_1}{C_1} = \frac{1,7 \times 10^{-23}}{C_1} + 1 = 2079$$

$$\Rightarrow C_1 = \frac{1,7 \times 10^{-23}}{2078} = 8,18 \times 10^{-27} \text{ et } C_2 = 170 \times 10^{-23}$$

$$C_1 = \frac{n_1}{N} \Rightarrow n_1 = C_1 \cdot N = 8,18 \times 10^{-27} \times 5,86 \times 10^{22} \Rightarrow$$

$$n_{P_1} (600^\circ) = 4,79 \times 10^{-4} \text{ atome/cm}^3$$

$$n_{P_2} (300^\circ) = C_2 \cdot N = 9,96 \times 10^{-1} \text{ atome/cm}^3$$

b) Il faut trouver la valeur de  $\frac{\Delta S}{k_B}$  ?

$$\text{Donc: } C_1 = \exp \frac{\Delta S}{k_B} \cdot \exp \frac{-\Delta H_f}{k_B T_1} \Rightarrow \left( \frac{C_1}{k_B} \right) = \frac{\exp C_1}{\exp \left( \frac{\Delta H_f}{k_B T_1} \right)}$$

$$\Rightarrow \exp \frac{\Delta S}{k_B} = 1,8 \times 10^{-20}$$

$$\Rightarrow C_{P_2} = 1,8 \times 10^{-20} \cdot \exp \left( \frac{1,7 \times 10^{-19}}{1,38 \times 10^{-23} \cdot 1233} \right)$$

$$C_{P_2} = \dots$$