**Solution des exercices supplémentaires**

**Sol. Exercice 01 :**

Rappel :

| $\frac{R_i}{R}$ | Site : O | Site : T |
|---|---|---|
| * C.C | 0,154 | 0,29 |
| C.F.C | 0,414 | 0,226 |
| nbr de sites dans C.C | 6 | 12 |
| nbr de site dans C.F.C | 4 | 8 . |

$B \longrightarrow O$

$A \longrightarrow T$ .

$\frac{R_A}{R} = 0,29$

$\frac{R_B}{R} = 0,154$ .

$V_{tot} = a^3$

$$V_{occupé} = 2 \times \frac{4}{3}\pi R^3 + 12 \times \frac{4}{3}\pi R_A^3 + 6 \times \frac{4}{3}\pi R_B^3$$

$$= \frac{8}{3}\pi R^3 + 16\pi R_A^3 + 8\pi R_B^3$$

$$= \frac{8}{3}\pi R^3 + 16\pi (0,29)^3 R^3 + 8\pi (0,154)^3 R^3$$

$$= 9,69 R^3$$

où $R_{cc} = \frac{a\sqrt{3}}{4} \Rightarrow V_{occupé} = 9,69 \frac{a^3(\sqrt{3})^3}{4^3} = 0,79\, a^3$

$\boxed{\%\ \text{site vacants} = 100 - 79 = 21\%}$ .

**Sol. Exercice 02 :**

$$C.F.C \begin{cases} \rightarrow Oct\ (4) \\ \rightarrow Tet\ (8) \end{cases}$$

$$1/ : \frac{R_i}{R} = \frac{R_H}{R_A} = \frac{0{,}03}{0{,}133} = 0{,}226$$

$$\left( \frac{R_H}{R_A} < \frac{R_i}{R} \Big|_{\theta\ cfc} \right)$$

on sait que s'il y a une déplacement $\Rightarrow$ changent de $\tau$.

$\tau$ = la compacité = $\dfrac{\text{volume occupé par les atomes}}{\text{volume de la maille}}$.

$$\tau_{oct} = \frac{4\left(\frac{4}{3}\pi R_A^3\right) + 4\left(\frac{4}{3}\pi R_H^3\right)}{a_A^3}$$

4 sites oct

$$R_A = \frac{a\sqrt{2}}{4} \Rightarrow a_A = \frac{4R_A}{\sqrt{2}}.$$

$$\boxed{\tau_{oct} = 0{,}748 = 74{,}8\ \%}$$

$$\tau_{tet} = \frac{4\left(\frac{4}{3}\pi R_A^3\right) + 8\left(\frac{4}{3}\pi R_H^3\right)}{a_A^3}$$

$$\tau_{tet} = 0{,}756 \Rightarrow \tau = 75{,}6\ \% \simeq 75{,}5\ \%$$

donc les sites préférés sont les sites <u>Tet</u>.

2/ <u>La composition chimique</u>

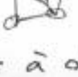
Les atomes de H préfèrent les sites tet. (8 sites) $\Rightarrow$ donc on a 4 atomes de A et 8 H $\Rightarrow$ le composé : $4\,\underbrace{(AH_2)}_{1\ \text{mole}}$.

3/ $\frac{a\sqrt{3}}{4}$ voisinage

$$H \begin{cases} \rightarrow 4A \rightarrow \frac{a\sqrt{3}}{4} \\ \rightarrow 6H \rightarrow \frac{a}{2} \end{cases} \rightarrow \text{le voisinage (premier) de H et 4A à distance } \frac{a\sqrt{3}}{4}.$$

$H \rightarrow C.S$

$A \rightarrow C.F.C$



$x^2 = \left(\frac{1}{4}a\right)^2 \times 3$

**Sol. Exercice 03 :**

$a_\gamma = 0,3624$ mm

1/ La densité :

a/ Fe, C, Mn occupent les sites de $Fe_\gamma$ ⇒ tous les atomes en substitution.

$$\rho = \frac{\text{masse des atomes dans la maille}}{\text{Volume de la maille}}$$

$$= \frac{n_A m_A + n_B m_B + n_C m_C}{V}$$

on a : $n_A = n f_A$ $\qquad f_A = \frac{n_A}{\sum n_i}$ fraction atomique

$n_B = n f_B$

$n_C = n f_C$

$$\rho = \frac{n f_A \frac{M_A}{N} + n f_B \frac{M_B}{N} + n f_C \frac{M_C}{N}}{V}$$

$$\rho = \frac{n}{N V}\left[ f_A M_A + f_B M_B + f_C M_C \right]$$

$V = a^3$

$n = 4$ ( C.F.C austénite ).

fraction atomique $\qquad f_{Fe} = \dfrac{\frac{86,56}{55,85}}{\left(\frac{86,56}{55,85} + \frac{12,10}{54,93} + \frac{1,34}{12}\right)} = 0,82 \simeq 82\%$

$f_{Mn} = 12\%$

$f_C = 6\%$

$$\rho = \frac{4}{6,023 \cdot 10^{23} (0,3624 \cdot 10^{-7})^3} \left[ 82 \times 55,85 + 12 \times 54,93 + 6 \times 12 \right]$$

$\rho = 7,41 \ g/cm^3 \Rightarrow \boxed{d = 7,41}$

b/ les atomes C occupent les sites interstitiels, $M_n$ occupe les sites substitutionnels : $\rho = \frac{m}{V} \rightarrow ? \rightarrow V_{int}$

$f_{Fe} + f_{Mn} = 82\% + 12\% = 94\%$ des atomes qui sont participés au volume.

$$\left.\begin{array}{l} 100 \longrightarrow V = a_\gamma^3 \\ 94 \longrightarrow V_{int} ? \end{array}\right\} V_{int} = \frac{94 \times a^3}{100} = \underbrace{0{,}94\, a_\gamma^3}_{V}$$

$$\rho_{int} = \frac{m\,(f_{A\to B} M_{A\to B})}{\mathcal{N}\, V_{int}} = \frac{m\,(f_{A\to B} M_{A\to B})}{\mathcal{N}\; 0{,}94\, V} = \frac{\rho_{sub}}{0{,}94}$$

$$\rho_{int} = 7{,}88 \ \frac{g}{cm^3} \Rightarrow \boxed{d = 7{,}88}$$

**Sol. Exercice 04 :**

1. Calcule du nombre moyen des liaisons

$$\bar{N}_{AA} = m_A P_A^{\alpha} Z \cdot P_A^{\beta} = m_A P_A^{\alpha} \cdot Z \cdot P_A^{\beta} = m_A X_A \cdot Z \cdot X_A .$$

$$= m_A Z \cdot X_A^2 .$$

$$\bar{N}_{BB} = m_B Z \cdot X_B^2 .$$

$$\bar{N}_{AB} = m_A^{\alpha} \cdot Z P_B^{\beta} + m_A^{\beta} Z \cdot (1 - P_A^{\gamma})$$

$$= m_A^{\alpha} \cdot Z \cdot X_B + m_A^{\beta} \cdot Z X_B$$

$$= m_A P_A^{\alpha} \cdot Z \cdot X_B + m_A P_A^{\beta} \cdot Z \cdot X_B .$$

$$= m_A Z \cdot X_B \left( \underbrace{P_A^{\alpha} + P_A^{\beta}}_{2X_A} \right)$$

$$= 2 m_A Z \cdot X_A X_B .$$

**2.**

$\Delta G_m = \Delta H_m - T\,\Delta S_m$

$$\Delta H_m = H_{sol} - H_1^0$$

$$H_1^0 = X_A H_A^0 + X_B H_B^0$$

$$H_{sol} = \bar{N}_{AA} H_{AA} + \bar{N}_{BB} H_{BB} + \bar{N}_{AB} H_{AB} .$$

$$\bar{N}_{AA} = \frac{N}{2} Z \cdot X_A^2$$

$$\bar{N}_{BB} = \frac{N}{2} Z \cdot X_B^2$$

$$\bar{N}_{AB} = N \cdot Z \cdot X_A X_B .$$

$$H_{sol} = \frac{NZ}{2} \left[ X_A^2 H_{AA} + X_B^2 H_{BB} + 2 X_A X_B H_{AB} \right] .$$

$$= \frac{NZ}{2} \left[ (1 - X_B) X_A H_{AA} + (1 - X_A) X_B H_{BB} + 2 X_A X_B H_{AB} \right] .$$

$$= \frac{NZ}{2} \left[ H_{AA} - X_A X_B H_{AA} + X_B H_{BB} - X_A X_B H_{BB} + 2 X_A X_B H_{AB} \right] .$$

$$= \frac{NZ}{2} X_A X_B \left[ 2 H_{AB} - (H_{AA} + H_{BB}) \right] + \frac{NZ}{2} \left[ X_A H_{AA} + X_B H_{BB} \right] .$$

$$ol = \lambda X_A X_B + \frac{NZ}{2} \left[ X_A H_{AA} + X_B H_{BB} \right]$$

$$\Delta H_m = H_{sol} - H_1^\circ$$

$$= \frac{NZ}{2}\left[X_A^2 H_{AA} + X_B^2 H_{BB} + 2X_AX_B H_{AB}\right] - \frac{NZ}{2}\left[X_A H_{AA} + X_B H_{BB}\right]$$

$$= \frac{NZ}{2}\left[(X_A^2 - X_A) H_{AA} + (X_B^2 - H_B) H_{BB} + 2X_AX_B H_{AB}\right]$$

$$= \frac{NZ}{2}\left[X_A(X_A - 1) H_{AA} + X_B(X_B - 1) H_{BB} + 2X_AX_B H_{AB}\right)$$

$$= \frac{NZ}{2}\left[-X_AX_B H_{AA} - X_B X_A H_{BB} + 2X_AX_B H_{AB}\right]$$

$$= \frac{NZ}{2} X_AX_B\left[-H_{AA} - H_{BB} + 2H_{AB}\right]$$

$$= \frac{NZ}{2} X_AX_B\left[2H_{AB} - (H_{AA} + H_{BB})\right] = \lambda X_AX_B.$$

$$\boxed{\Delta H_m = \lambda X_AX_B}$$

$\Delta S_m = \Delta S_m^{id}$ et comme $\Delta H_m^{id} = 0$

donc : $\Delta G_m^{id} = -T\Delta S_m^{id}$

$$\Delta S_m^{id} = -\frac{\Delta G_m^{id}}{T}.$$

$$\Delta G_m^{id} = G_{sol}^{id} - G_1^\circ$$

$$= X_A\bar{G}_A + X_B\bar{G}_B - G_1^\circ$$

$$= X_A\big[\underbrace{\mu_A^\circ}_{G_A^{\circ\prime\prime}} + RT\ln a_A\big] + X_B\big[\underbrace{\mu_B^\circ}_{G_B^{\circ\prime\prime}} + RT\ln X_B\big]$$

idéale : $X_A = a_A$, $X_B = a_B$

donc : $\Delta G_m^{id} = RT\left[X_A\ln X_A + X_B\ln X_B\right].$

$$\Delta S_m = \Delta S_m^{id} = -\frac{\Delta G_m^{id}}{T}$$

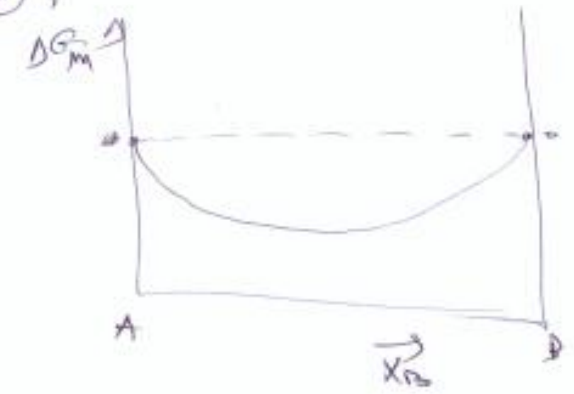
$$\Delta S_m = -R\left[X_A\ln X_A + X_B\ln X_B\right].$$

$$\boxed{\Delta S_m = -N k_B\left[X_A\ln X_A + X_B\ln X_B\right]}$$

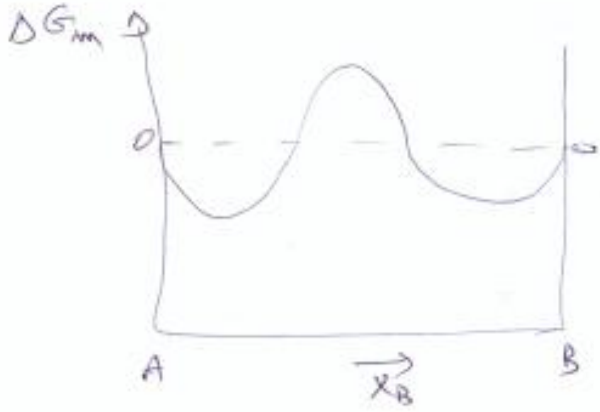
$$\Delta G_m = \Delta H_m - T\Delta S_m .$$

$$\boxed{\Delta G_m = \lambda x_A x_B + RT\,(x_A \ln x_A + x_B \ln x_B)}$$

3 :




← alliage monophasé.

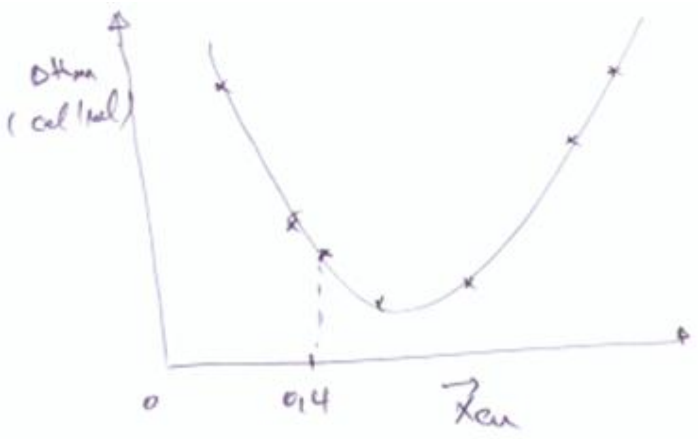



alliage donne une zone de démixtion.

4 : $\dfrac{d\Delta G_m}{dx} = 0$ → représente une partie de diagramme de phase. (courbe de solubilité des deux élément).

$\dfrac{d^2\Delta G_m}{dx^2} = 0$ ⇒ la courbe spinodale.

**Sol. Exercice 05 :**




Pour $X_{Cu} = 0,4$ :

la tangente en $X_{Cu} = 0,4$ donne : $\Delta H_{Cu} = -1940$ cal/mol

$\Delta H_{Au} = -580$ cal/mol.

$$\Delta G_m = \Delta H_m - T\Delta S_m .$$

$$\Delta H_m = X_{Cu}\,\Delta H_{Cu} + X_{Au}\,\Delta H_{Au} .$$

$$\boxed{\Delta H_m = -1124 \text{ cal/mol}}$$

$$\Delta S_m = -R\left(X_{Cu}\ln X_{Cu} + X_{Au}\ln X_{Au}\right).$$

$$\boxed{\Delta S_m = 1,3372 \text{ cal/K.mol}}$$

à 500°C → 773K

$$\boxed{\Delta G_m = -2157,7 \text{ cal/mol}}$$

$$\Delta G_m = X_{Cu}\,\Delta G_{Cu} + X_{Au}\,\Delta G_{Au}.$$

$$\Delta G_{Cu} = RT \ln a_{Cu} = \Delta H_{Cu} - T\Delta S_{Cu}.$$

$$\Delta G_{Au} = RT \ln a_{Au} = \Delta H_{Au} - T\Delta S_{Au}.$$

$$\Delta S_m = -R(X_{Cu}\ln X_{Cu} + X_{Au}\ln X_{Au})$$

$$\Delta S_m = X_{Cu}\,\Delta S_{Cu} + X_{Au}\,\Delta S_{Au}.$$

par comparaison

$$\Delta S_{Cu} = -R\ln X_{Cu} = 1,8206 \text{ cal/K.mol}$$

$$\Delta S_{Au} = -R\ln X_{Au} = 1,0150 \text{ cal/K.mol.}$$

$$\Rightarrow \Delta G_{Cu} = \Delta H_{Cu} - T\Delta S_{Cu} = -3347,324 \text{ cal/mol}$$

$$\Delta G_{Au} = -1364,595 \text{ cal/mol}.$$

donc on peut calculer l'activité de l'élément Cu et Au:

$$X_{Cu} = 0,4 \Rightarrow X_{Au} = 0,7.$$

$$\Delta G_{Cu} = RT \ln a_{Cu} \Rightarrow \boxed{\begin{array}{l} a_{Cu} = 0,113 \\ a_{Au} = 0,411. \end{array}}$$