Series lectures of phase-field model

01. Quick Review of Thermodynamics

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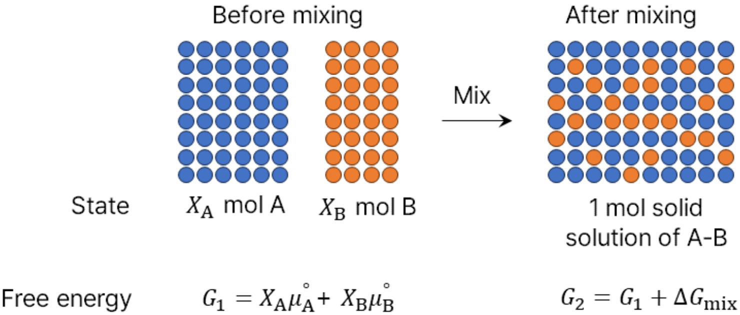
Quick review for solution thermodynamics



Before mixing

After mixing

Mix

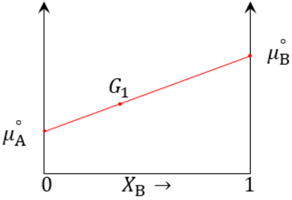
State: X_{A} mol A, X_{B} mol B; 1 mol solid solution of A-B

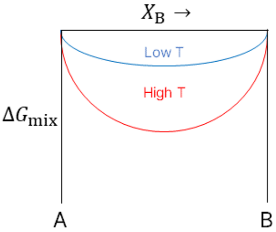
Free energy:

$$G_1 = X_{\mathrm{A}}\overset{\circ}{\mu}_{\mathrm{A}} + X_{\mathrm{B}}\overset{\circ}{\mu}_{\mathrm{B}}$$

$$G_2 = G_1 + \Delta G_{\mathrm{mix}}$$

Ideal solution





The integral molar Gibbs free energy of ideal solution is

$$G_m^{\text{id}} = X_{\text{A}}\mu_{\text{A}}^\circ + X_{\text{B}}\mu_{\text{B}}^\circ + RT\left[X_{\text{A}}\ln X_{\text{A}} + X_{\text{B}}\ln X_{\text{B}}\right]$$

Extend to Regular solution

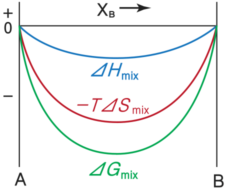
	Ideal	Regular
ΔH_{mix}	0	$\Omega X_{\mathsf{A}} X_{\mathsf{B}}$
ΔS_{mix}	$-R\big[X_{\mathsf{A}} \ln X_{\mathsf{A}} + X_{\mathsf{B}} \ln X_{\mathsf{B}}\big]$	$-R\big[X_{\mathsf{A}} \ln X_{\mathsf{A}} + X_{\mathsf{B}} \ln X_{\mathsf{B}}\big]$
ΔG_{mix}	$RT\big[X_{\mathsf{A}} \ln X_{\mathsf{A}} + X_{\mathsf{B}} \ln X_{\mathsf{B}}\big]$	$\Omega X_{\mathsf{A}} X_{\mathsf{B}} + RT\big[X_{\mathsf{A}} \ln X_{\mathsf{A}} + X_{\mathsf{B}} \ln X$
ΔV_{mix}	0	0

Table: Comparsion between Ideal and Regular solution

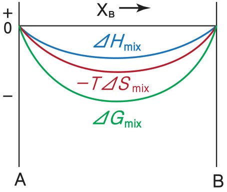
The integral molar Gibbs free energy of regular solution is

$$G_m^{\mathsf{reg}} = X_{\mathsf{A}} \mu_{\mathsf{A}}^{\circ} + X_{\mathsf{B}} \mu_{\mathsf{B}}^{\circ} + RT\big[X_{\mathsf{A}} \ln X_{\mathsf{A}} + X_{\mathsf{B}} \ln X_{\mathsf{B}}\big] + \Omega X_{\mathsf{A}} X_{\mathsf{B}}$$

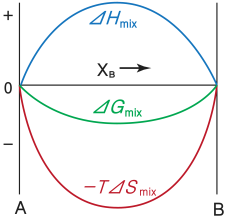
Behavior of regular solution



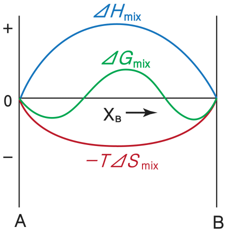
(a) $\Omega < 0$, high T



(b) $\Omega < 0$, low T



(c) $\Omega > 0$, high T



(d) $\Omega > 0$, low T

2nd law of thermodynamics in the Materials science

- The system evolves to minimize the Gibbs energy of the system.
- Equilibrium means that chemical potential of every species in every phase is same under constant T and p.

Integral molar quantity and Partial molar quantity

For binary solution, the chemical potential defined by the J/atom is

$$\mu_\mathsf{A} = \left(\frac{\partial G}{\partial n_\mathsf{A}}\right)_{n_\mathsf{B}} \qquad \mu_\mathsf{B} = \left(\frac{\partial G}{\partial n_\mathsf{B}}\right)_{n_\mathsf{A}}$$

where n_A and n_B are numbers of A and B atoms.

$$\begin{aligned}\mu_\mathsf{A} &= \left(\frac{\partial G}{\partial n_\mathsf{A}}\right)_{n_\mathsf{B}} = \left(\frac{\partial\left(nG_m\right)}{\partial n_\mathsf{A}}\right)_{n_\mathsf{B}} \\ &= G_m + n\cdot\left(\frac{\partial G_m}{\partial X_\mathsf{A}}\right)_{X_\mathsf{B}}\left(\frac{\partial X_\mathsf{A}}{\partial n_\mathsf{A}}\right)_{n_\mathsf{B}} + n\cdot\left(\frac{\partial G_m}{\partial X_\mathsf{B}}\right)_{X_\mathsf{A}}\left(\frac{\partial X_\mathsf{B}}{\partial n_\mathsf{A}}\right)_{n_\mathsf{B}}\end{aligned} \tag{1}$$

where

$$n = n_\mathsf{A} + n_\mathsf{B}$$

$$X_\mathsf{A} = \frac{n_\mathsf{A}}{n} \qquad X_\mathsf{B} = \frac{n_\mathsf{B}}{n}$$

Since

$$\left(\frac{\partial X_\mathsf{A}}{\partial n_\mathsf{A}}\right)_{n_\mathsf{B}} = \frac{1}{n} - \frac{n_\mathsf{A}}{n^2} = \frac{n - n_\mathsf{A}}{n^2} = \frac{1 - X_\mathsf{A}}{n} = \frac{X_\mathsf{B}}{n}$$

$$\left(\frac{\partial X_\mathsf{B}}{\partial n_\mathsf{A}}\right)_{n_\mathsf{B}} = -\frac{n_\mathsf{B}}{n^2} = -\frac{X_\mathsf{B}}{n}$$

Put it back to Eq. 1,

$$\mu_\mathsf{A} = G_m + X_\mathsf{B}\left[\left(\frac{\partial G_m}{\partial X_\mathsf{A}}\right)_{X_\mathsf{B}} - \left(\frac{\partial G_m}{\partial X_\mathsf{B}}\right)_{X_\mathsf{A}}\right]$$

Consistently,

$$\mu_\mathsf{B} = G_m + X_\mathsf{A}\left[\left(\frac{\partial G_m}{\partial X_\mathsf{B}}\right)_{X_\mathsf{A}} - \left(\frac{\partial G_m}{\partial X_\mathsf{A}}\right)_{X_\mathsf{B}}\right]$$

Then we can introduce the diffusion potential $\mu_\mathsf{A} - \mu_\mathsf{B}$ by

$$\mu_\mathsf{A} - \mu_\mathsf{B} = \left(\frac{\partial G_m}{\partial X_\mathsf{A}}\right)_{X_\mathsf{B}} - \left(\frac{\partial G_m}{\partial X_\mathsf{B}}\right)_{X_\mathsf{A}}$$

The total derivative is

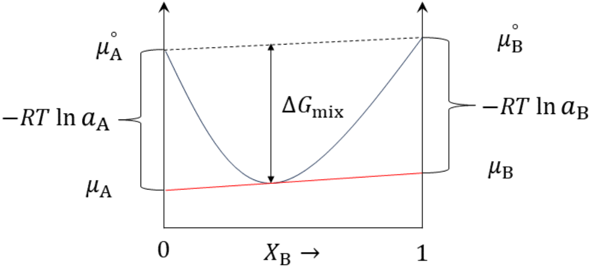
$$\frac{dG_m}{dX_{\mathsf{A}}} = \left(\frac{\partial G_m}{\partial X_{\mathsf{A}}}\right)_{X_{\mathsf{B}}} \frac{\partial X_{\mathsf{A}}}{\partial X_{\mathsf{A}}} + \left(\frac{\partial G_m}{\partial X_{\mathsf{B}}}\right)_{X_{\mathsf{A}}} \frac{\partial X_{\mathsf{B}}}{\partial X_{\mathsf{A}}} = \left(\frac{\partial G_m}{\partial X_{\mathsf{A}}}\right)_{X_{\mathsf{B}}} - \left(\frac{\partial G_m}{\partial X_{\mathsf{B}}}\right)_{X_{\mathsf{A}}}$$

Consistently,

$$\frac{dG_m}{dX_{\mathsf{B}}} = \left(\frac{\partial G_m}{\partial X_{\mathsf{B}}}\right)_{X_{\mathsf{A}}} - \left(\frac{\partial G_m}{\partial X_{\mathsf{A}}}\right)_{X_{\mathsf{B}}} \tag{2}$$

therefore,

$$\mu_{\mathsf{B}} = G_m - X_{\mathsf{A}} \frac{dG_m}{dX_{\mathsf{A}}} \qquad \mu_{\mathsf{A}} = G_m - X_{\mathsf{B}} \frac{dG_m}{dX_{\mathsf{B}}} \tag{3}$$



From Eq.2, therefore, we can verify that the y intersect of tangential line is the chemical potential of two elements.

$$G_m(X_\mathsf{B} = 0) = G_m - X_\mathsf{B} \times \left(\frac{dG_m}{dX_\mathsf{B}} \right) = \mu_\mathsf{A}$$

Chemical potential of regular solution

For regular solution,

$$G_m = X_\mathsf{A}\mu_\mathsf{A}^\circ + X_\mathsf{B}\mu_\mathsf{B}^\circ + RT\Big[X_\mathsf{A}\ln X_\mathsf{A} + X_\mathsf{B}\ln X_\mathsf{B}\Big] + \Omega X_\mathsf{A}X_\mathsf{B}$$

From Eq. 3,

$$\begin{aligned}\mu_\mathsf{B} &= X_\mathsf{A}\mu_\mathsf{A}^\circ + X_\mathsf{B}\mu_\mathsf{B}^\circ + RT\Big[X_\mathsf{A}\ln X_\mathsf{A} + X_\mathsf{B}\ln X_\mathsf{B}\Big] + \Omega X_\mathsf{A}X_\mathsf{B} \\ &\quad - X_\mathsf{A}\Big[\mu_\mathsf{A}^\circ - \mu_\mathsf{B}^\circ + RT\Big[\ln X_\mathsf{A} - \ln X_\mathsf{B}\Big] + \Omega X_\mathsf{B} - \Omega X_\mathsf{A}\Big] \\ &= \mu_\mathsf{B}^\circ + RT\ln X_\mathsf{B} + \Omega X_\mathsf{A}^2\end{aligned}$$

Consistently,

$$\mu_\mathsf{A} = \mu_\mathsf{A}^\circ + \Omega\big(1 - X_\mathsf{A}\big)^2 + RT\ln X_\mathsf{A}$$

$$\mu_\mathsf{B} = \mu_\mathsf{B}^\circ + \Omega\big(1 - X_\mathsf{B}\big)^2 + RT\ln X_\mathsf{B}$$

Chemical equilibrium

For binary A-B system, when α-β phases are under equilibrium,

$$\mu_{\mathsf{A}}^{\alpha}(X_{\mathsf{A}}^{\alpha,e}) = \mu_{\mathsf{A}}^{\beta}(X_{\mathsf{A}}^{\beta,e}) \qquad \mu_{\mathsf{B}}^{\alpha}(X_{\mathsf{B}}^{\alpha,e}) = \mu_{\mathsf{B}}^{\beta}(X_{\mathsf{B}}^{\beta,e})$$

where e superscript denotes the equilibrium state. Using Eq. 3, the first equation can be re-written,

$$G_m^{\alpha}\left(X_{\mathsf{B}}^{\alpha,e}\right) - X_{\mathsf{B}}^{\alpha,e}\frac{dG_m^{\alpha}}{dX_{\mathsf{B}}}\bigg|_{X_{\mathsf{B}}^{\alpha,e}} = G_m^{\beta}\left(X_{\mathsf{B}}^{\beta,e}\right) - X_{\mathsf{B}}^{\beta,e}\frac{dG_m^{\beta}}{dX_{\mathsf{B}}}\bigg|_{X_{\mathsf{B}}^{\beta,e}}$$

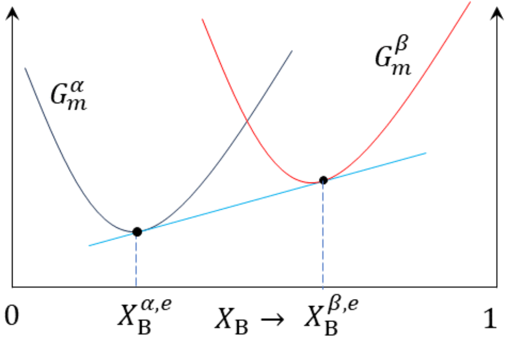
When

$$\frac{dG_m^{\alpha}}{dX_{\mathsf{B}}}\bigg|_{X_{\mathsf{B}}^{\alpha,e}} = \frac{dG_m^{\beta}}{dX_{\mathsf{B}}}\bigg|_{X_{\mathsf{B}}^{\beta,e}} = \frac{dG_m}{dX_{\mathsf{B}}}$$

Proceed to

$$\frac{dG_m}{dX_{\mathsf{B}}} = \frac{G_m^{\alpha}\left(X_{\mathsf{B}}^{\alpha,e}\right) - G_m^{\beta}\left(X_{\mathsf{B}}^{\beta,e}\right)}{X_{\mathsf{B}}^{\alpha,e} - X_{\mathsf{B}}^{\beta,e}}$$

The condition is named as the *common tangent condition*, which means the system is under the equilibrium, which can be visualized as below:



On the common tangent line, the chemical potentials of the A, B solutes are constant, therefore, the activities are constant within two-phase region.