**Notes on**

# Gibbs Energy Change in Phase Separation

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# 1 Binary System

Assume a homogeneous alloy system $A$-$B$ has an overall composition of $x^\circ$ with a Gibbs free energy of $G(x^\circ)$. After a phase transition, the system has decomposed into two parts: one with a composition of $x^+$ and molar fraction of $f^+$, the other with $x^-$ and $f^-$. The two parts have Gibbs free energies of $G(x^+)$ and $G(x^-)$, respectively. The total Gibbs free energy of the system becomes $f^+G(x^+) + f^-G(x^-)$ and the Gibbs free energy change is

$$\delta G = f^+G(x^+) + f^-G(x^-) - G(x^\circ) \tag{1}$$

where

$$f^+ + f^- = 1 \tag{2}$$

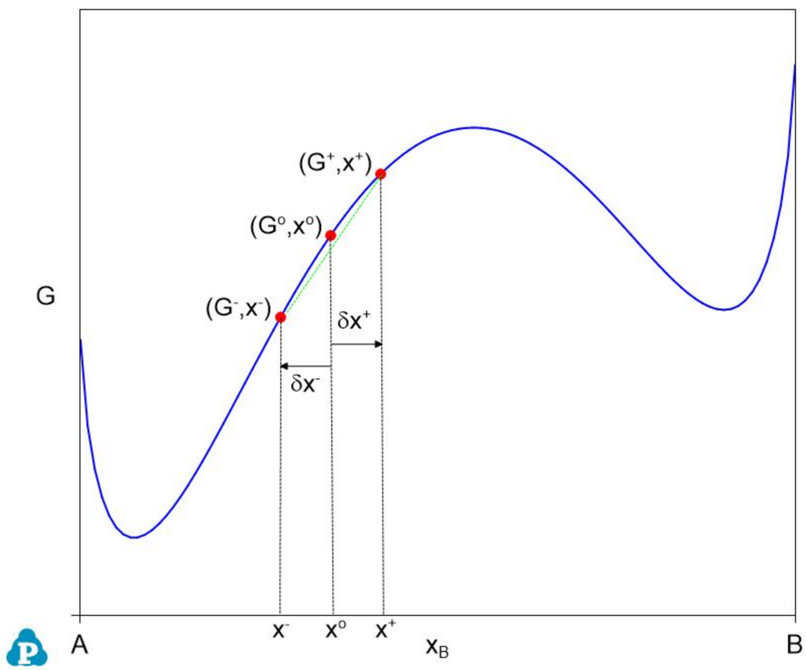


Figure 1: Gibbs free energy vs. x

With consideration of mass conservation, we have the following relationship (lever rule),

$$f^+x^+ + f^-x^- = x^\circ \tag{3}$$

Let's define $\delta x^+$ and $\delta x^+$ as

$$\delta x^+ = x^+ - x^\circ \tag{4}$$

$$\delta x^- = x^- - x^\circ \tag{5}$$

then we have

$$f^+\delta x^+ + f^-\delta x^- = 0 \tag{6}$$

or express $\delta x^-$ in terms of $\delta x^+$,

$$\delta x^- = -\frac{f^+}{f^-}\delta x^+ \tag{7}$$

Gibbs free energy can be expanded in a Taylor series at $x^\circ$ as

$$G(x^\circ + \delta x) = G(x^\circ) + \delta x\frac{dG}{dx} + \frac{1}{2}(\delta x)^2\frac{d^2G}{dx^2} + O((\delta x)^3) \tag{8}$$

where $\frac{dG}{dx}$ and $\frac{d^2G}{dx^2}$ are the derivatives at $x^\circ$. Substitution of Eq.(8) to Eq.(1) gives

$$\begin{aligned}\delta G =& f^+\left[G(x^\circ) + \delta x^+\frac{dG}{dx} + \frac{1}{2}(\delta x^+)^2\frac{d^2G}{dx^2} + O(|\delta x^+|^3)\right]\\ &+ f^-\left[G(x^\circ) + \delta x^-\frac{dG}{dx} + \frac{1}{2}(\delta x^-)^2\frac{d^2G}{dx^2} + O(|\delta x^-|^3)\right]\\ &- G(x^\circ)\end{aligned} \tag{9}$$

$$\begin{aligned}\delta G =&(f^+ + f^- - 1)G(x^\circ) + (f^+\delta x^+ + f^-\delta x^-)\frac{dG}{dx}\\ &+ \frac{1}{2}\left[f^+(\delta x^+)^2 + f^-(\delta x^-)^2\right]\frac{d^2G}{dx^2} + O(f^+|\delta x^+|^3 + f^-|\delta x^-|^3)\end{aligned} \tag{10}$$

Because of Eqs.(2) and (6), the first two terms on the right-hand side of the previous equation become zero. Then, replacing $\delta x^-$ by Eq.(7) yields

$$\delta G =\frac{1}{2}\frac{f^+}{f^-}(\delta x^+)^2\frac{d^2G}{dx^2} + O(|\delta x^+|^3) \tag{11}$$

Define a quantity $k$ as

$$k = \frac{f^+}{f^-}(\delta x^+)^2 \tag{12}$$

and let $\delta x = |\delta x^+|$, Eq. (11) becomes

$$\delta G =\frac{1}{2}k\frac{d^2G}{dx^2} + O(\delta x^3) \tag{13}$$

Since both $f^+$ and $f^-$ are positive, $k$ must be positive, too. Therefore, the Gibbs free energy change in this separation is proportional to the second derivative of the Gibbs free energy of the original system.

# 2 Ternary System

The molar fractions of components in a ternary alloy system $A$-$B$-$C$ are $(x_1, x_2, x_3)$ and its Gibbs free energy is $G(x_1, x_2)$ if $(x_1, x_2)$ are chosen as the independent variables.

Consider an alloy system with a composition of $(x_1^\circ, x_2^\circ)$ and Gibbs free energy of $G(x_1^\circ, x_2^\circ)$. Assume it decomposes into two parts. One has a composition of $(x_1^+, x_2^+)$, Gibbs free energy of $G(x_1^+, x_2^+)$ and phase fraction of $f^+$, and another with $(x_1^-, x_2^-)$, $G(x_1^-, x_2^-)$ and $f^-$. The Gibbs free energy change of this decomposition is given by

$$\delta G = f^+ G(x_1^+, x_2^+) + f^- G(x_1^-, x_2^-) - G(x_1^\circ, x_2^\circ) \tag{14}$$

where

$$f^+ + f^- = 1 \tag{15}$$

$$f^+ x_j^+ + f^- x_j^- = x_j^\circ \qquad (j = 1, 2) \tag{16}$$

Define $\delta x_j^+$ and $\delta x_j^+$ as

$$\delta x_j^+ = x_j^+ - x_j^\circ \qquad (j = 1, 2) \tag{17}$$

$$\delta x_j^- = x_j^- - x_j^\circ \qquad (j = 1, 2) \tag{18}$$

Substituting $x_j^+$ from Eq.(17) and $x_j^-$ from Eq.(18) into from Eq.(16) yields

$$f^+ \delta x_j^+ + f^- \delta x_j^- = 0 \qquad (j = 1, 2) \tag{19}$$

Use Taylor series to expand $G(x_1^+, x_2^+)$ and $G(x_1^-, x_2^-)$,

$$G(x_1^+, x_2^+) = G(x_1^\circ, x_2^\circ) + \delta x_1^+ \frac{\partial G}{\partial x_1} + \delta x_2^+ \frac{\partial G}{\partial x_2} \tag{20}$$

$$+ \frac{1}{2}\left[(\delta x_1^+)^2 \frac{\partial^2 G}{\partial x_1^2} + 2\delta x_1^+ \delta x_2^+ \frac{\partial^2 G}{\partial x_1 \partial x_2} + (\delta x_2^+)^2 \frac{\partial^2 G}{\partial x_2^2}\right] + O((\delta x)^3) \tag{21}$$

$$G(x_1^-, x_2^-) = G(x_1^\circ, x_2^\circ) + \delta x_1^- \frac{\partial G}{\partial x_1} + \delta x_2^+ \frac{\partial G}{\partial x_2} \tag{22}$$

$$+ \frac{1}{2}\left[(\delta x_1^-)^2 \frac{\partial^2 G}{\partial x_1^2} + 2\delta x_1^- \delta x_2^- \frac{\partial^2 G}{\partial x_1 \partial x_2} + (\delta x_2^-)^2 \frac{\partial^2 G}{\partial x_2^2}\right] + O((\delta x)^3) \tag{23}$$

where $\delta x = \max(|\delta x_1^+|, |\delta x_2^+|, |\delta x_1^-|, |\delta x_2^-|)$. Substitution of Eqs.(21) and (23) into Eq.(14) gives

$$\begin{aligned}\delta G =& (f^+ + f^- - 1) G(x_1^\circ, x_2^\circ) + (f^+ \delta x_1^+ + f^- \delta x_1^-) \frac{\partial G}{\partial x_1} + (f^+ \delta x_2^+ + f^- \delta x_2^-) \frac{\partial G}{\partial x_2} \\ &+ \frac{1}{2}\Big\{ \left[f^+ (\delta x_1^+)^2 + f^- (\delta x_1^-)^2\right] \frac{\partial^2 G}{\partial x_1^2} + 2\left[f^+ \delta x_1^+ \delta x_2^+ + f^- \delta x_1^- \delta x_2^-\right] \frac{\partial^2 G}{\partial x_1 \partial x_2} \\ &+ \left[f^+ (\delta x_2^+)^2 + f^- (\delta x_2^-)^2\right] \frac{\partial^2 G}{\partial x_2^2} \Big\} + O((\delta x)^3)\end{aligned} \tag{24}$$

The first two terms on the right-hand side in the previous equation are zeros according to Eqs.(15) and (19). Substituting $x_j^-$ from Eq.(19) into Eq.(24) gives

$$\delta G = \frac{1}{2}\frac{f^+}{f^-}\left\{(\delta x_1^+)^2 \frac{\partial^2 G}{\partial x_1^2} + 2\delta x_1^+ \delta x_2^+ \frac{\partial^2 G}{\partial x_1 \partial x_2} + (\delta x_2^+)^2 \frac{\partial^2 G}{\partial x_2^2}\right\} + O((\delta x)^3) \tag{25}$$

which can be written in the matrix form as

$$\delta G = \frac{1}{2}\frac{f^+}{f^-}\begin{pmatrix} \delta x_1^+ & \delta x_2^+ \end{pmatrix}\begin{pmatrix} \dfrac{\partial^2 G}{\partial x_1^2} & \dfrac{\partial^2 G}{\partial x_1 \partial x_2} \\ \dfrac{\partial^2 G}{\partial x_2 \partial x_1} & \dfrac{\partial^2 G}{\partial x_2^2} \end{pmatrix}\begin{pmatrix} \delta x_1^+ \\ \delta x_2^+ \end{pmatrix} + O((\delta x)^3) \tag{26}$$

If the Hessian matrix is positive definite, $\delta G > 0$. If the Hessian matrix is negative definite, $\delta G < 0$. In other cases, the sign of $\delta G$ depends on the Hessian of Gibbs free energy and the the direction of the decomposition, i.e., the vector $\delta \boldsymbol{X}^+ = (\delta x_1^+, \delta x_2^+)$.

# 3 Multi-Component System

The composition of a system in an $n$-component system is expressed as a vector $\boldsymbol{X} = (x_1, x_2, \cdots, x_{n-1})^T$.

Consider an alloy system with a composition of $\boldsymbol{X}^\circ$ and Gibbs free energy of $G(\boldsymbol{X}^\circ)$. Assume it decomposes into two parts with compositions of $\boldsymbol{X}^+$ and $\boldsymbol{X}^-$, phase fractions of $f^+$ and $f^-$, and Gibbs free energies of $G(\boldsymbol{X}^+)$ and $G(\boldsymbol{X}^-)$. The Gibbs free energy change of this decomposition is given by

$$\delta G = f^+ G(\boldsymbol{X}^+) + f^- G(\boldsymbol{X}^-) - G(\boldsymbol{X}^\circ) \tag{27}$$

with constraints of

$$f^+ + f^- = 1 \tag{28}$$

$$f^+ \boldsymbol{X}^+ + f^- \boldsymbol{X}^- = \boldsymbol{X}^\circ \tag{29}$$

Define $\delta \boldsymbol{X}^+$ and $\delta \boldsymbol{X}^+$ as

$$\delta \boldsymbol{X}^+ = \boldsymbol{X}^+ - \boldsymbol{X}^\circ \tag{30}$$

$$\delta \boldsymbol{X}^- = \boldsymbol{X}^- - \boldsymbol{X}^\circ \tag{31}$$

then

$$\boldsymbol{X}^+ = \boldsymbol{X}^\circ + \delta \boldsymbol{X}^+ \tag{32}$$

$$\boldsymbol{X}^- = \boldsymbol{X}^\circ + \delta \boldsymbol{X}^- \tag{33}$$

Substituting Eqs.(32) and (33) into from Eq.(29) gives

$$f^+ \delta \boldsymbol{X}^+ + f^- \delta \boldsymbol{X}^- = 0 \tag{34}$$

Use Taylor series to expand $G(\boldsymbol{X}^+)$ and $G(\boldsymbol{X}^-)$,

$$G(\boldsymbol{X}^+) = G(\boldsymbol{X}^\circ) + \nabla G^T \delta \boldsymbol{X}^+ + \frac{1}{2}(\delta \boldsymbol{X}^+)^T \boldsymbol{H} \delta \boldsymbol{X}^+ + O(\|\delta \boldsymbol{X}^+\|^3) \tag{35}$$

$$G(\boldsymbol{X}^-) = G(\boldsymbol{X}^\circ) + \nabla G^T \delta \boldsymbol{X}^- + \frac{1}{2}(\delta \boldsymbol{X}^-)^T \boldsymbol{H} \delta \boldsymbol{X}^- + O(\|\delta \boldsymbol{X}^-\|^3) \tag{36}$$

where $\boldsymbol{H}$ is the Hessian matrix of the Gibbs free energy $G$ defined as

$$\boldsymbol{H} = \begin{pmatrix} \frac{\partial^2 G}{\partial x_1^2} & \frac{\partial^2 G}{\partial x_1 \partial x_2} & \frac{\partial^2 G}{\partial x_1 \partial x_3} & \cdots & \frac{\partial^2 G}{\partial x_1 \partial x_{n\text{-}1}} \\ \frac{\partial^2 G}{\partial x_2 \partial x_1} & \frac{\partial^2 G}{\partial x_2^2} & \frac{\partial^2 G}{\partial x_2 \partial x_3} & \cdots & \frac{\partial^2 G}{\partial x_2 \partial x_{n\text{-}1}} \\ \frac{\partial^2 G}{\partial x_3 \partial x_1} & \frac{\partial^2 G}{\partial x_3 \partial x_2} & \frac{\partial^2 G}{\partial x_3^3} & \cdots & \frac{\partial^2 G}{\partial x_3 \partial x_{n\text{-}1}} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 G}{\partial x_{n\text{-}1} \partial x_1} & \frac{\partial^2 G}{\partial x_{n\text{-}1} \partial x_2} & \frac{\partial^2 G}{\partial x_{n\text{-}1} \partial x_3} & \cdots & \frac{\partial^2 G}{\partial x_{n\text{-}1}^2} \end{pmatrix} \tag{37}$$

Define

$$\|\delta \boldsymbol{X}\| = \max(\|\delta \boldsymbol{X}^+\|, \|\delta \boldsymbol{X}^-\|) \tag{38}$$

Substitution of Eqs.(35) and (36) into Eq.(27) gives

$$\begin{aligned} \delta G =& (f^+ + f^- - 1)G(\boldsymbol{X}^+) + \nabla G^T (f^+ \delta \boldsymbol{X}^+ + f^- \delta \boldsymbol{X}^-) \\ &+ \frac{1}{2}\Big\{ \left[ f^+ (\delta \boldsymbol{X}^+)^T \boldsymbol{H} \delta \boldsymbol{X}^+ + f^- (\delta \boldsymbol{X}^-)^T \boldsymbol{H} \delta \boldsymbol{X}^- \right] \Big\} + O((\|\delta \boldsymbol{X}\|)^3) \end{aligned} \tag{39}$$

The first two terms on the right-hand side in the previous equation are zeros according to Eqs.(28) and (34). Substituting $\delta \boldsymbol{X}^-$ from Eq.(34) into Eq.(39) gives

$$\delta G = \frac{1}{2} \frac{f^+}{f^-} (\delta \boldsymbol{X}^+)^T \boldsymbol{H} \delta \boldsymbol{X}^+ + O((\|\delta \boldsymbol{X}\|)^3) \tag{40}$$

If the Hessian matrix $\boldsymbol{H}$ is positive definite, $\delta G > 0$, the phase point is stable. If the Hessian matrix $\boldsymbol{H}$ is negative definite, $\delta G < 0$, the phase point is unstable. In other cases, the sign of $\delta G$ depends on the Hessian of Gibbs free energy $\boldsymbol{H}$ and the the direction of the decomposition, i.e., the vector $\delta \boldsymbol{X}^+$ or $\delta \boldsymbol{X}^-$.