Thermodynamics of materials

25. Chemical Potentials of Solutions II

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Stability of a Solution and Thermodynamic Factor

- At given T and p, we have

$$\Delta S^{\text{ir}} = \delta^2 S = -\frac{\sum_{i=1}^{n} d\mu_i dN_i}{T} < 0$$

proceed to

$$\Delta G = -T\Delta S^{\text{ir}} = \sum_{i=1}^{n} d\mu_i dN_i > 0$$

- The perturbations $d\mu_i$ is

$$d\mu_i = \sum_{j=1}^{n} \left(\frac{\partial \mu_i}{\partial N_j}\right) dN_j$$

then

$$\Delta G = \sum_{i=1}^{n}\sum_{j=1}^{n} \left(\frac{\partial \mu_i}{\partial N_j}\right) dN_i dN_j = \sum_{i=1}^{n}\sum_{j=1}^{n} \left(\frac{\partial^2 G}{\partial N_i \partial N_j}\right) dN_i dN_j$$

Stability of a Solution and Thermodynamic Factor

- For thermodynamically stable solution,

$$\Delta G = \sum_{i=1}^{n}\sum_{j=1}^{n}\left(\frac{\partial^2 G}{\partial N_i \partial N_j}\right) dN_i dN_j > 0$$

- For A-B binary solution, stability conditions of a homogeneous solution is

$$\left(\frac{\partial^2 G}{\partial N_\mathsf{A}^2}\right)_{T,p,N_\mathsf{B}} = \left(\frac{\partial \mu_\mathsf{A}}{\partial N_\mathsf{A}}\right)_{T,p,N_\mathsf{B}} > 0$$

$$\left(\frac{\partial^2 G}{\partial N_\mathsf{B}^2}\right)_{T,p,N_\mathsf{A}} = \left(\frac{\partial \mu_\mathsf{B}}{\partial N_\mathsf{B}}\right)_{T,p,N_\mathsf{A}} > 0$$

$$\begin{vmatrix} \frac{\partial^2 G}{\partial N_\mathsf{A}^2} & \frac{\partial^2 G}{\partial N_\mathsf{A}\partial N_\mathsf{B}} \\ \frac{\partial^2 G}{\partial N_\mathsf{A}\partial N_\mathsf{B}} & \frac{\partial^2 G}{\partial N_\mathsf{B}^2} \end{vmatrix} = \begin{vmatrix} \frac{\partial \mu_\mathsf{A}}{\partial N_\mathsf{A}} & \frac{\partial \mu_\mathsf{B}}{\partial N_\mathsf{A}} \\ \frac{\partial \mu_\mathsf{A}}{\partial N_\mathsf{B}} & \frac{\partial \mu_\mathsf{B}}{\partial N_\mathsf{B}} \end{vmatrix} > 0$$

Stability of a Solution and Thermodynamic Factor

- If the total number of moles N is fixed,

$$\Delta G = -T\Delta S^{\mathsf{ir}} = d\mu_{\mathsf{A}} dN_{\mathsf{A}} + d\mu_{\mathsf{B}} dN_{\mathsf{B}} = d(\mu_{\mathsf{B}} - \mu_{\mathsf{A}}) dN_{\mathsf{B}} > 0$$

- For $N = 1\,\mathrm{mol}$,

$$\Delta \mu = d\mu_{\mathsf{A}} dx_{\mathsf{A}} + d\mu_{\mathsf{B}} dx_{\mathsf{B}} = d(\mu_{\mathsf{B}} - \mu_{\mathsf{A}}) dx_{\mathsf{B}} > 0$$

since

$$\left(\frac{\partial \mu}{\partial x_{\mathsf{B}}}\right)_{T,p} = \mu_{\mathsf{B}} - \mu_{\mathsf{A}}$$

therefore,

$$\Delta \mu = d\mu_{\mathsf{A}} dx_{\mathsf{A}} + d\mu_{\mathsf{B}} dx_{\mathsf{B}} = \left(\frac{\partial \mu}{\partial x_{\mathsf{B}}}\right)_{T,p} dx_{\mathsf{B}} > 0$$

$$\Delta \mu = d\mu_{\mathsf{A}} dx_{\mathsf{A}} + d\mu_{\mathsf{B}} dx_{\mathsf{B}} = d\left(\frac{\partial^2 \mu}{\partial x_{\mathsf{B}}^2}\right)_{T,p} (dx_{\mathsf{B}})^2 > 0$$

Stability of a Solution and Thermodynamic Factor

- For a binary solution,

$$\left(\frac{\partial^2 \mu}{\partial x_{\mathsf{B}}^2}\right)_{T,p} > 0 \qquad \left(\frac{\partial^2 \mu}{\partial x_{\mathsf{A}}^2}\right)_{T,p} > 0$$

- The second derivative of chemical potential of the solution is

$$\left(\frac{\partial^2 \mu}{\partial x_{\mathsf{B}}^2}\right)_{T,p} = \left(\frac{\partial(\mu_{\mathsf{B}} - \mu_{\mathsf{A}})}{\partial x_{\mathsf{B}}}\right)_{T,p} = \left(\frac{\partial \mu_{\mathsf{B}}}{\partial x_{\mathsf{B}}}\right)_{T,p} + \left(\frac{\partial \mu_{\mathsf{A}}}{\partial x_{\mathsf{A}}}\right)_{T,p}$$

- We express the chemical potentials of a component in terms of activity coefficient and composition,

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i + RT \ln x_i$$

Stability of a Solution and Thermodynamic Factor

- It follows that

$$\left(\frac{\partial \mu_{\mathsf{A}}}{\partial \ln x_{\mathsf{A}}}\right)_{T,p} = RT\left(1 + \frac{\partial \gamma_{\mathsf{A}}}{\partial \ln x_{\mathsf{A}}}\right) = RT\psi$$

$$\left(\frac{\partial \mu_{\mathsf{B}}}{\partial \ln x_{\mathsf{B}}}\right)_{T,p} = RT\left(1 + \frac{\partial \gamma_{\mathsf{B}}}{\partial \ln x_{\mathsf{B}}}\right) = RT\psi$$

proceed to

$$\left(\frac{\partial \mu_{\mathsf{A}}}{\partial x_{\mathsf{A}}}\right)_{T,p} = \frac{RT}{x_{\mathsf{A}}}\psi \qquad \left(\frac{\partial \mu_{\mathsf{B}}}{\partial x_{\mathsf{B}}}\right)_{T,p} = \frac{RT}{x_{\mathsf{B}}}\psi$$

- The second derivative of chemical potential is

$$\left(\frac{\partial^2 \mu}{\partial x_{\mathsf{B}}^2}\right)_{T,p} = \left(\frac{\partial \mu_{\mathsf{A}}}{\partial x_{\mathsf{A}}}\right)_{T,p} + \left(\frac{\partial \mu_{\mathsf{B}}}{\partial x_{\mathsf{B}}}\right)_{T,p} = \frac{RT}{x_{\mathsf{A}} x_{\mathsf{B}}}\psi$$

Stability of a Solution and Thermodynamic Factor

- Also we have

$$\psi = \left(1 + \frac{\partial \ln \gamma_{\mathsf{A}}}{\partial \ln x_{\mathsf{A}}}\right) = \left(1 + \frac{\partial \ln \gamma_{\mathsf{B}}}{\partial \ln x_{\mathsf{B}}}\right) = \frac{x_{\mathsf{A}} x_{\mathsf{B}}}{RT} \left(\frac{\partial^2 \mu}{\partial x_{\mathsf{B}}^2}\right)_{T,p}$$

is called the thermodynamic factor in chemical diffusion kinetics.

- For a stable solution,

$$\psi > 0$$

which implies that

$$\left(\frac{\partial \mu_{\mathsf{A}}}{\partial x_{\mathsf{A}}}\right)_{T,p} > 0 \qquad \left(\frac{\partial \mu_{\mathsf{B}}}{\partial x_{\mathsf{B}}}\right)_{T,p} > 0 \qquad \left(\frac{\partial^2 \mu}{\partial x_{\mathsf{B}}^2}\right)_{T,p} > 0$$

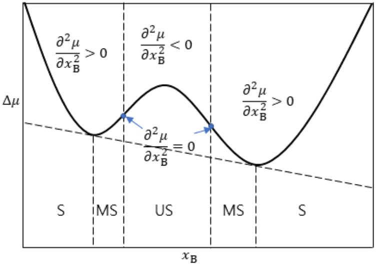
The thermodynamic stability limit is reached if

$$\left(\frac{\partial \mu_{\mathsf{A}}}{\partial x_{\mathsf{A}}}\right)_{T,p} = 0 \qquad \left(\frac{\partial \mu_{\mathsf{B}}}{\partial x_{\mathsf{B}}}\right)_{T,p} = 0 \qquad \left(\frac{\partial^2 \mu}{\partial x_{\mathsf{B}}^2}\right)_{T,p} = 0$$

- In a unstable region,

$$\psi < 0 \quad \left(\frac{\partial \mu_{\mathsf{A}}}{\partial x_{\mathsf{A}}}\right)_{T,p} < 0 \quad \left(\frac{\partial \mu_{\mathsf{B}}}{\partial x_{\mathsf{B}}}\right)_{T,p} < 0 \quad \left(\frac{\partial^2 \mu}{\partial x_{\mathsf{B}}^2}\right)_{T,p} < 0$$

Stability of a Solution and Thermodynamic Factor



- The conditions for stable(S), metastable(MS) and unstable(US) are schematically drawn.
- Finally, at a critical point, the critical temperature and composition at which two spinodal points merge into one, the chemical potential of component i satisfies the following conditions,

$$\left(\frac{\partial^2 \mu}{\partial x_{\mathrm{B}}^2}\right)_{T,p} = 0$$