Thermodynamics of materials

26. Chemical Potentials of Solutions III

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Lever Rule

- Suppose that we have N moles of a binary solution with overall composition $(x^{\circ}_{\mathsf{A}}, x^{\circ}_{\mathsf{B}})$.
- A homogeneous solution separates into two solutions, a solution with N^{α} moles and composition $(x^{\alpha}_{\mathsf{A}}, x^{\alpha}_{\mathsf{B}})$, and the other with N^{β} moles and composition $(x^{\beta}_{\mathsf{A}}, x^{\beta}_{\mathsf{B}})$.
- By mass conservation,

$$N_{\mathsf{A}} = x^{\circ}_{\mathsf{A}} N = x^{\alpha}_{\mathsf{A}} N^{\alpha} + x^{\beta}_{\mathsf{A}} N^{\beta}$$

$$N_{\mathsf{B}} = x^{\circ}_{\mathsf{B}} N = x^{\alpha}_{\mathsf{B}} N^{\alpha} + x^{\beta}_{\mathsf{B}} N^{\beta}$$

- Define the fractions of α and β phases in the two-phase mixture as

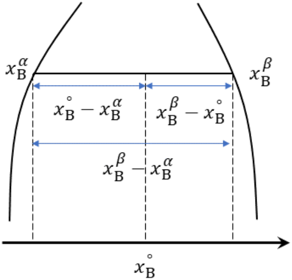
$$\varphi^{\alpha} = \frac{N^{\alpha}}{N} \qquad \varphi^{\beta} = \frac{N^{\beta}}{N}$$

- Therefore, we have

$$x_{\mathrm{A}}^{\circ} = x_{\mathrm{A}}^{\alpha}\varphi^{\alpha} + x_{\mathrm{A}}^{\beta}\varphi^{\beta} \qquad x_{\mathrm{B}}^{\circ} = x_{\mathrm{B}}^{\alpha}\varphi^{\alpha} + x_{\mathrm{B}}^{\beta}\varphi^{\beta}$$

it can be rewritten by

$$\varphi^{\alpha} = \frac{x_{\mathrm{B}}^{\beta} - x_{\mathrm{B}}^{\circ}}{x_{\mathrm{B}}^{\beta} - x_{\mathrm{B}}^{\alpha}} \qquad \varphi^{\beta} = \frac{x_{\mathrm{B}}^{\circ} - x_{\mathrm{B}}^{\alpha}}{x_{\mathrm{B}}^{\beta} - x_{\mathrm{B}}^{\alpha}}$$



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Chemical Potential Change of Solution Formation from Pure Components

- The chemical potential change for the formation of a homogeneous solution from pure components at the same temperature is given by

$$\Delta\mu(x_{\mathsf{A}_1}, x_{\mathsf{A}_2}, \cdots, x_{\mathsf{A}_n}) = \mu(x_{\mathsf{A}_1}, x_{\mathsf{A}_2}, \cdots, x_{\mathsf{A}_n}) - \sum_{i=1}^{n} x_{\mathsf{A}_i}\mu^{\circ}_{\mathsf{A}_i}$$

and

$$\Delta\mu_i = RT\ln a_i \qquad \Delta\mu = RT\sum_{i=1}^{n} x_i \ln a_i$$

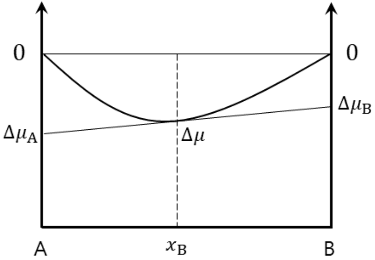
Chemical Potential Change of Solution Formation from Pure Components

- For binary A-B system,

$$x_\mathsf{A}\mathsf{A} + x_\mathsf{B}\mathsf{B} \rightarrow x_\mathsf{A}\mathsf{A}x_\mathsf{B}\mathsf{B}$$

then

$$\Delta\mu = x_\mathsf{A}\Delta\mu_\mathsf{A} + x_\mathsf{B}\Delta\mu_\mathsf{B}$$



Chemical Potential Change of Solution Formation from Pure Components

- The relation can be rewritten by

$$\Delta\mu = x_{\mathsf{A}}\Delta\mu_{\mathsf{A}} + x_{\mathsf{B}}\Delta\mu_{\mathsf{B}} = \Delta\mu_{\mathsf{A}} + x_{\mathsf{B}}\left(\Delta\mu_{\mathsf{B}} - \Delta\mu_{\mathsf{A}}\right) = \Delta\mu_{\mathsf{A}} + x_{\mathsf{B}}\frac{\partial\Delta\mu}{\partial x_{\mathsf{B}}}$$

therefore,

$$\Delta\mu_{\mathsf{A}} = \Delta\mu - x_{\mathsf{B}}\frac{\partial\Delta\mu}{\partial x_{\mathsf{B}}}$$

Consistently,

$$\Delta\mu_{\mathsf{B}} = \Delta\mu - x_{\mathsf{A}}\frac{\partial\Delta\mu}{\partial x_{\mathsf{A}}}$$

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Chemical Potential Change for Adding Pure Components into a Solution

- Consider a process of adding a small quantity of pure A into a large amount of solution with composition, x_{B}°, the chemical potential change of element A is

$$\Delta\mu_{\mathsf{A}} = \mu_{\mathsf{A}}\left(x_{\mathsf{B}}^{\circ}\right) - \mu_{\mathsf{A}}^{\circ} = RT\ln a_{\mathsf{A}}$$

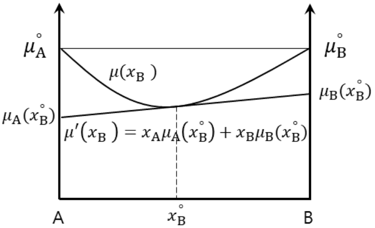
consistently,

$$\Delta\mu_{\mathsf{B}} = \mu_{\mathsf{B}}\left(x_{\mathsf{B}}^{\circ}\right) - \mu_{\mathsf{B}}^{\circ} = RT\ln a_{\mathsf{B}}$$

Chemical Potential Change for Adding Pure Components into a Solution

- The change of chemical potential ($\Delta\mu$) is

$$
\begin{aligned}
\mu'(x_{\mathrm{B}}) - \mu^{\circ}(x_{\mathrm{B}}) &= \left[x_{\mathrm{A}}\mu_{\mathrm{A}}(x_{\mathrm{B}}^{\circ}) + x_{\mathrm{B}}\mu_{\mathrm{B}}(x_{\mathrm{B}}^{\circ})\right] - \left[x_{\mathrm{A}}\mu_{\mathrm{A}}^{\circ} + x_{\mathrm{B}}\mu_{\mathrm{B}}^{\circ}\right] \\
&= x_{\mathrm{A}}\left[\mu_{\mathrm{A}}(x_{\mathrm{B}}^{\circ}) - \mu_{\mathrm{A}}^{\circ}\right] + x_{\mathrm{B}}\left[\mu_{\mathrm{B}}(x_{\mathrm{B}}^{\circ}) - \mu_{\mathrm{B}}^{\circ}\right] \\
&= RT\left[x_{\mathrm{A}} \ln a_{\mathrm{A}}(x_{\mathrm{B}}^{\circ}) + x_{\mathrm{B}} \ln a_{\mathrm{B}}(x_{\mathrm{B}}^{\circ})\right]
\end{aligned}
$$



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- The chemical potential of a small amount of solution with composition $x_1^p, x_2^p, \cdots, x_n^p$ in a large amount of solution with composition $x_1^m, x_2^m, \cdots, x_n^m$ is given by

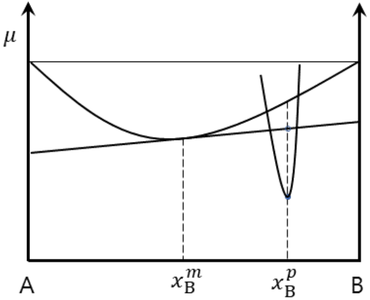
$$\mu'\left(x_j^p\right) = \sum_{i=1}^{n} x_i^p \mu_i\left(x_j^m\right)$$

for A-B binary solution,

$$\mu'\left(x_{\mathsf{A}}^p, x_{\mathsf{B}}^p\right) = x_{\mathsf{A}}^p \mu_{\mathsf{A}}\left(x_{\mathsf{A}}^m, x_{\mathsf{B}}^m\right) + x_{\mathsf{B}}^p \mu_{\mathsf{B}}\left(x_{\mathsf{A}}^m, x_{\mathsf{B}}^m\right)$$

Driving Force for Precipitation in a Solution

- For the homogeneous solution, the chemical potential at composition (x_A^p, x_B^p) is visualized by open circle and that of precipitate is represented by a solid circle. The difference between two values are driving force D for the precipitation process.



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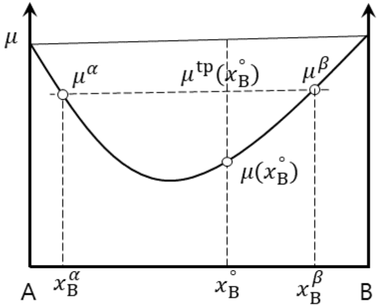
- The chemical potential of two-phase state is

$$\mu^{\mathsf{tp}}(x_{\mathsf{B}}^{\circ}) = \varphi^{\alpha}(x_{\mathsf{B}}^{\circ})\mu^{\alpha} + \varphi^{\beta}(x_{\mathsf{B}}^{\circ})\mu^{\beta}$$

which means that the solution is favorable comparing to the two-phase mixture (dotted line). In mathematical form,

$$\mu^{\mathsf{tp}}(x_{\mathsf{B}}^{\circ}) > \mu(x_{\mathsf{B}}^{\circ})$$

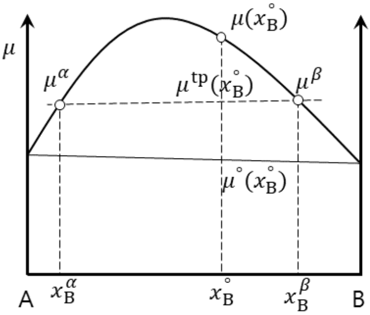


Chemical Potential of a Two-phase Mixture

- When the chemical potential-composition plot is given by below: it means that the solution is unfavorable comparing to the two-phase mixture (dotted line). In mathematical form,

$$\mu^{\mathsf{tp}}(x_{\mathsf{B}}^{\circ}) < \mu(x_{\mathsf{B}}^{\circ})$$

- The most stable state is two-phase mixture of pure A and B.



- If the plot is double-well shape, we have

$$\mu^{\mathsf{tp}}(x_{\mathsf{B}}^{\circ}) < \mu(x_{\mathsf{B}}^{\circ}) < \mu^{\circ}(x_{\mathsf{B}}^{\circ})$$

- The most stable state is two-phase mixture of state of x_{B}^{α} and x_{B}^{β}, represented by two green solid circles.