Thermodynamics of materials

29. Chemical Phase Equilibria and Phase Diagrams

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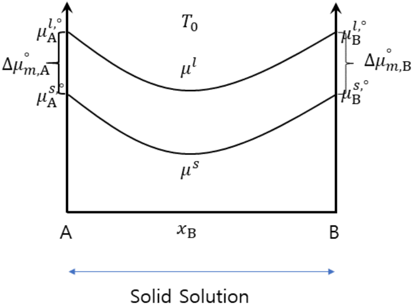
Equilibrium State from Chemical Potentials vs Composition

- For a single phase solid solution, the schematic chemical potential curve is given as belows:

$$\mu^\circ(x_\mathrm{B}) = x_\mathrm{A}\mu_\mathrm{A}^{s,\circ} + x_\mathrm{B}\mu_\mathrm{B}^{s,\circ}$$

At melting temperature

$$\Delta\mu_{m,\mathrm{A}}^\circ = \mu_\mathrm{A}^{l,\circ} - \mu_\mathrm{A}^{s,\circ} \qquad \Delta\mu_{m,\mathrm{B}}^\circ = \mu_\mathrm{B}^{l,\circ} - \mu_\mathrm{B}^{s,\circ}$$



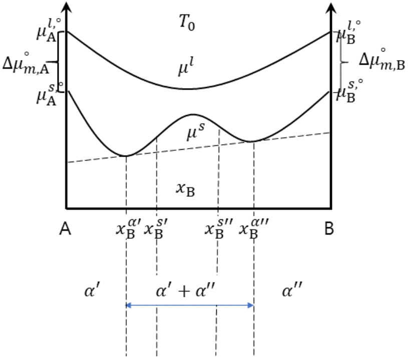
Equilibrium State from Chemical Potentials vs Composition

- Throughout the whole composition range at T_0, the homogeneous solid solution (ss) phase is the stable equilibrium state, and the liquid phase is not stable.
- In addition, the chemical potential curve of the solid has a positive curvature,

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

which implies that the homogeneous solid solution (ss) state is intrinsically stable through the whole composition range, and any two-phase mixture has a higher chemical potential than a homogeneous solution.

- The chemical potential curve of solid solution α shows a double-well shape with both positive and negative curvature regions as a function of composition:



Equilibrium State from Chemical Potentials vs Composition

- In previous slide,

$$\left(\frac{\partial^2 \mu^s}{\partial x_{\mathsf{B}}^2}\right)_{T,p} > 0 \qquad 0 < x_{\mathsf{B}} < x_{\mathsf{B}}^{s'} \qquad x_{\mathsf{B}}^{s''} < x_{\mathsf{B}} < 1$$

$$\left(\frac{\partial^2 \mu^s}{\partial x_{\mathsf{B}}^2}\right)_{T,p} < 0 \qquad x_{\mathsf{B}}^{s'} < x_{\mathsf{B}} < x_{\mathsf{B}}^{s''}$$

- When

$$x_{\mathsf{B}}^{\alpha'} < x_{\mathsf{B}} < x_{\mathsf{B}}^{s'} \qquad x_{\mathsf{B}}^{s''} < x_{\mathsf{B}} < x_{\mathsf{B}}^{\alpha''}$$

the solid solution is metastable.

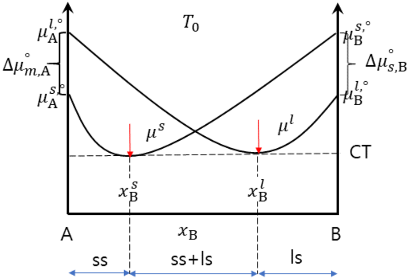
Equilibrium State from Chemical Potentials vs Composition

- When liquid-solid are under the equilibrium within certain region

$$x_{\mathrm{B}}^s < x_{\mathrm{B}} < x_{\mathrm{B}}^l$$

and solid and liquid are equilibrium phases

$$x_{\mathrm{B}} < x_{\mathrm{B}}^s(\text{solid}) \qquad x_{\mathrm{B}} > x_{\mathrm{B}}^l(\text{liquid})$$



Equilibrium State from Chemical Potentials vs Composition

- The composition is within region (between red arrows)

$$x_{\mathsf{B}}^{s} < x_{\mathsf{B}} < x_{\mathsf{B}}^{l}$$

we have

$$\mu_{\mathsf{A}}^{s}(x_{\mathsf{B}}^{s}) = \mu_{\mathsf{A}}^{l}(x_{\mathsf{B}}^{l})$$

which is left y-intersect,

$$\mu_{\mathsf{B}}^{s}(x_{\mathsf{B}}^{s}) = \mu_{\mathsf{B}}^{l}(x_{\mathsf{B}}^{l})$$

which is right y-intersect.

- It means that within two phase region, the concentration of solid and liquid are fixed, respectively. For example, when

$$\mu_{\mathsf{B}}^{s}(x_{\mathsf{B}}^{s}) = \mu_{\mathsf{B}}^{l}(x_{\mathsf{B}}^{l})$$

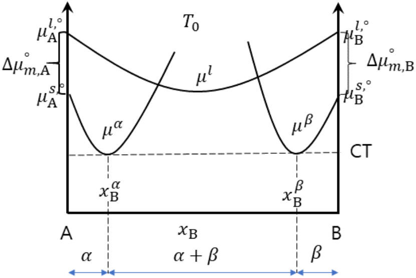
the solid phase concentration is always x_{B}^{s} and that of liquid is x_{B}^{l}, on the other hand the phase fraction of liquid increases as x_{B} increases.

Equilibrium State from Chemical Potentials vs Composition

- When α phase-β phase are under the equilibrium within certain region

$$x_{\mathrm{B}}^{\alpha} < x_{\mathrm{B}} < x_{\mathrm{B}}^{\beta}$$

and liquid is not an equilibrium phase at temperature $T = T_0$. We expect that when temperature increases, the system will achieve eutectic equilibrium, which will be discussed later.



Equilibrium State from Chemical Potentials vs Composition

- When α phase and liquid coexist

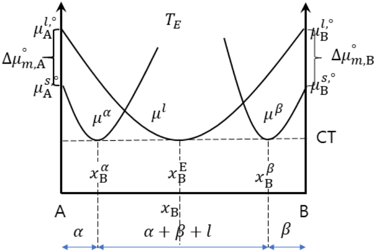
$$x_B^\alpha < x_B < x_B^E$$

α phase, liquid, β phase coexist

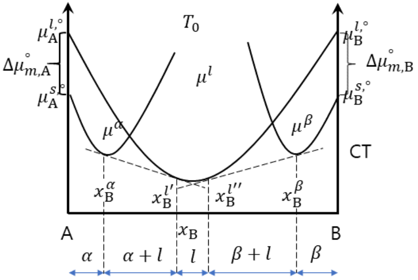
$$x_B = x_B^E$$

β phase and liquid phase coexist

$$x_\alpha^E < x_B < x_B^\beta$$



- When the temperature is higher than eutectic temperature T_E,



Equilibrium State from Chemical Potentials vs Composition

- When α phase and liquid phase $\left(x_{\mathrm{B}}^{l'}\right)$ coexist

  $$x_{\mathrm{B}}^{\alpha} < x_{\mathrm{B}} < x_{\mathrm{B}}^{l'}$$

  then liquid region occurs, and the concentration of liquid increases as x_{B} increases.

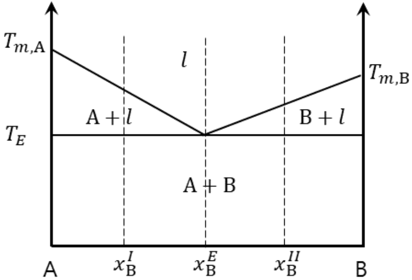
  $$x_{\mathrm{B}}^{l'} < x_{\mathrm{B}} < x_{\mathrm{B}}^{l''}$$

  when x_{B} increases more, liquid phase $\left(x_{\mathrm{B}}^{l''}\right)$ and β phase $\left(x_{\mathrm{B}}^{\beta}\right)$ coexist.

  $$x_{\mathrm{B}}^{l''} < x_{\mathrm{B}} < x_{\mathrm{B}}^{\beta}$$

Equilibrium State from Chemical Potentials vs Composition

- When mutual solubility of A and B of solid phase is negligible, the typical phase diagram is shown as belows:



Equilibrium State from Chemical Potentials vs Composition

- At $x_{\mathsf{B}} = x_{\mathsf{B}}^{I}$, as temperature increases,

$$\mathsf{A} + \mathsf{B} \rightarrow \mathsf{A} + l\left(x_{\mathsf{B}}^{E}\right) \rightarrow \mathsf{A} + l\left(x_{\mathsf{B}}^{I}\right) \rightarrow l\left(x_{\mathsf{B}}^{I}\right)$$

- At $x_{\mathsf{B}} = x_{\mathsf{B}}^{E}$, as temperature increases,

$$\mathsf{A} + \mathsf{B} \rightarrow \mathsf{A} + \mathsf{B} + l\left(x_{\mathsf{B}}^{E}\right) \rightarrow l\left(x_{\mathsf{B}}^{E}\right)$$

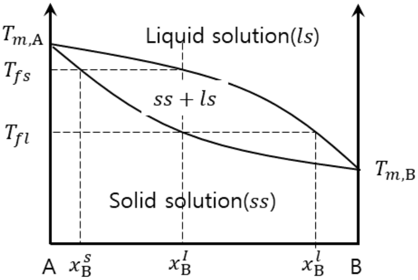
- At $x_{\mathsf{B}} = x_{\mathsf{B}}^{II}$, as temperature increases,

$$\mathsf{A} + \mathsf{B} \rightarrow \mathsf{B} + l\left(x_{\mathsf{B}}^{E}\right) \rightarrow \mathsf{B} + l\left(x_{\mathsf{B}}^{II}\right) \rightarrow l\left(x_{\mathsf{B}}^{II}\right)$$

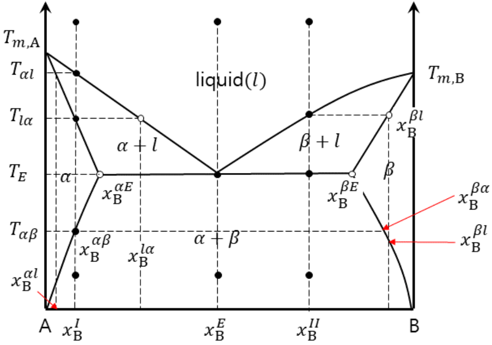
Equilibrium State from Chemical Potentials vs Composition

- Both the liquid and solid states exhibit homogeneous solutions in which A and B are completely mutually soluble.
- Upon heating of a A-B solid solution from low temperature, the evolution sequence of equilibrium states at x_B^I is

$$ss(x_\mathrm{B}^I) \rightarrow ss(x_\mathrm{B}^I) + ls(x_\mathrm{B}^l) \rightarrow ss(x_\mathrm{B}^s) + ls(x_\mathrm{B}^l) \rightarrow ls(x_\mathrm{B}^I)$$

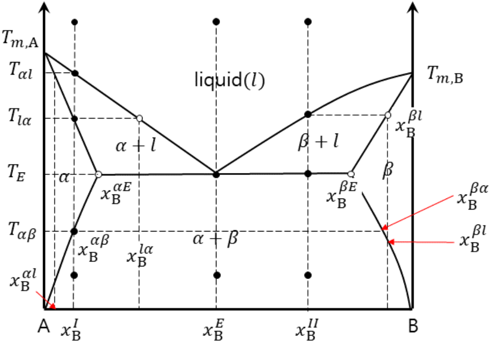


- The eutectic diagram with limited solubility between two solids. When A-B mutual solubility is not negligible, for example at $T = T_{\alpha\beta}$, the solubility of B in A is x_{B}^{I}.



Equilibrium State from Chemical Potentials vs Composition

- The eutectic diagram with limited solubility between two solids. When A-B mutual solubility is not negligible, for example at $T = T_{\alpha\beta}$, the solubility of B in A is x_{B}^{I}.



Equilibrium State from Chemical Potentials vs Composition

- At x_{B}^{I}, temperature is $T_{\alpha\beta}$ and increases very slowly, the equilibrium states are

$$\alpha + \beta \to \alpha\left(x_{\mathsf{B}}^{I}\right) + \beta\left(x_{\mathsf{B}}^{\beta\alpha}\right) \to \alpha\left(x_{\mathsf{B}}^{I}\right) \to \alpha\left(x_{\mathsf{B}}^{I}\right) + l\left(x_{\mathsf{B}}^{l\alpha}\right)$$
$$\to \alpha\left(x_{\mathsf{B}}^{\alpha l}\right) + l\left(x_{\mathsf{B}}^{I}\right) \to l\left(x_{\mathsf{B}}^{I}\right)$$

- At x_{B}^{E}, when temperature is below then T_{E} and increases very slowly, the equilibrium states are

$$\alpha + \beta \to \alpha\left(x_{\mathsf{B}}^{\alpha E}\right) + \beta\left(x_{\mathsf{B}}^{\beta E}\right) \to l\left(x_{\mathsf{B}}^{\alpha E}\right)$$

- At x_{B}^{II}, temperature is $T_{\alpha\beta}$ and increases very slowly, the equilibrium states are

$$\alpha + \beta \to \alpha\left(x_{\mathsf{B}}^{\alpha E}\right) + \beta\left(x_{\mathsf{B}}^{\beta E}\right) \to l\left(x_{\mathsf{B}}^{E}\right) + \beta\left(x_{\mathsf{B}}^{\beta E}\right)$$
$$\to l\left(x_{\mathsf{B}}^{II}\right) + \beta\left(x_{\mathsf{B}}^{\beta l}\right) \to l\left(x_{\mathsf{B}}^{II}\right)$$