Thermodynamics of materials

28. Chemical Potentials of Solutions V

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November 5, 2024

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Electrochemical Potentials of Components in a Solution

- The electrochemcial potential of B, $\mu_{\mathrm{B}}^{\phi}(r)$, in the presence of an electric potential $\phi(r)$ is given by

$$\mu_{\mathrm{B}}^{\phi}(r) = \mu_{\mathrm{B}}^{\circ}(r) + RT \ln x_{\mathrm{B}}(r) + z_{\mathrm{B}} \mathcal{F} \phi(r)$$

  where $x_{\mathrm{B}}(r)$ is the composition of B in the presence of the electric potential, z_{B} is the valence of charged species B, and $\mathcal{F}$ is Faraday's constant.

- At equilibrium,

$$\mu_{\mathrm{B}}^{\phi}(r) = \mu_{\mathrm{B}}^{\mathrm{b}}$$

  Therefore,

$$RT \ln \left(\frac{x_{\mathrm{B}}(r)}{x_{\mathrm{B}}^{\circ}} \right) = -z_{\mathrm{B}} \mathcal{F} \phi(r)$$

  or

$$\frac{x_{\mathrm{B}}(r)}{x_{\mathrm{B}}^{\circ}} = \exp \left(- \frac{z_{\mathrm{B}} \mathcal{F} \phi(r)}{RT} \right)$$

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Particle Size Dependence of Solubility

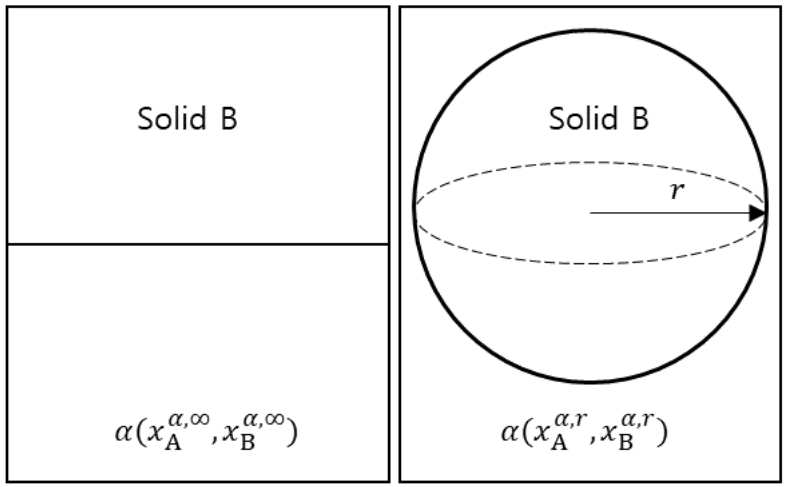
- For a pure solid B in the form with flat boundary ($r = \infty$) in the α phase matrix, when it is under the equilibrium,

$$\mu_{\mathrm{B}}^{\alpha,\infty} = \mu_{\mathrm{B}}^{\circ}$$

$$\mu_{\mathrm{B}}^{\alpha,\infty} = \mu_{\mathrm{B}}^{\circ} + RT \ln \gamma_{\mathrm{B}}^{\alpha,\infty} + RT \ln x_{\mathrm{B}}^{\alpha,\infty} = \mu_{\mathrm{B}}^{\circ}$$

therefore,

$$\ln \gamma_{\mathrm{B}}^{\alpha,\infty} + \ln x_{\mathrm{B}}^{\alpha,\infty} = 0 \rightarrow \gamma_{\mathrm{B}}^{\alpha,\infty} = \frac{1}{x_{\mathrm{B}}^{\alpha,\infty}}$$



Particle Size Dependence of Solubility

- For a pure solid B in the form with radius r under equilibrium,

$$\mu_{\mathrm{B}}^{r} = \mu_{\mathrm{B}}^{\circ} + \frac{2\gamma_{B\alpha} v_m}{r} = \mu_{\mathrm{B}}^{\circ} + RT \ln \gamma_{\mathrm{B}}^{\alpha,r} + RT \ln x_{\mathrm{B}}^{\alpha,r}$$

  then

$$RT \ln \gamma_{\mathrm{B}}^{\alpha,r} + RT \ln x_{\mathrm{B}}^{\alpha,r} = \frac{2\gamma_{B\alpha} v_m}{r}$$

- With assumption

$$\gamma_{\mathrm{B}}^{\alpha,r} = \gamma_{\mathrm{B}}^{\alpha,\infty} = \frac{1}{x_{\mathrm{B}}^{\alpha,\infty}}$$

  then

$$\frac{x_{\mathrm{B}}^{\alpha,r}}{x_{\mathrm{B}}^{\alpha,\infty}} = \exp\left(\frac{2\gamma_{B\alpha} v_m}{rRT}\right)$$

  which expresses the composition of B in the solution α outside a pure solid B particle with radius r relative to the composition of B in the solution next to a flat particle solution interface.

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Interfacial Segregation

- At A-B system, when the B atoms in the bulk region and grain boundary are under the equilibrium,

$$\mu_{\mathrm{B}}^{\mathrm{gb}} = \mu_{\mathrm{B}}^{\mathrm{b}}$$

the equilibrium concentration at bulk is x_{B}° and that at grain boundary is $x_{\mathrm{B}}^{\mathrm{gb}}$, then

$$E_{\mathrm{B}}^{\mathrm{gb},\circ} + k_{\mathrm{B}}T \ln x_{\mathrm{B}}^{\mathrm{gb}} = E_{\mathrm{B}}^{\mathrm{b},\circ} + k_{\mathrm{B}}T \ln x_{\mathrm{B}}^{\circ}$$

where $E^{\mathrm{b},\circ}$ is the formation energy per atom B at bulk of A and $E_{\mathrm{B}}^{\mathrm{gb},\circ}$ is the formation energy per atom at a grain boundary of A.

- Then we have

$$x_{\mathrm{B}}^{\mathrm{gb}} = x_{\mathrm{B}}^{\circ} \exp\left(- \frac{E_{\mathrm{B}}^{\mathrm{gb},\circ} - E_{\mathrm{B}}^{\mathrm{b},\circ}}{k_{\mathrm{B}}T} \right) = x_{\mathrm{B}}^{\circ} \exp\left(- \frac{\Delta E_{\mathrm{B}}^{\mathrm{gb}}}{k_{\mathrm{B}}T} \right)$$

where $\Delta E_{\mathrm{B}}^{\mathrm{gb}}$ is the segregation energy of atom B.

Interfacial Segregation

- If we include the vibrational contributions and contributions from the formation volume difference of B atoms at the grain boundary and in the bulk, then $\Delta E_{\mathrm{B}}^{\mathrm{gb}}$ can be replaced by $\Delta \mu_{\mathrm{B}}^{\mathrm{gb},\circ}$, the standard chemical potential differnece between B atoms at the grain boundary and in the bulk,

$$x_{\mathrm{B}}^{\mathrm{gb}} = x_{\mathrm{B}}^{\circ} \exp\left(- \frac{\mu_{\mathrm{B}}^{\mathrm{gb},\circ} - \mu_{\mathrm{B}}^{\mathrm{b},\circ}}{k_{\mathrm{B}} T} \right) = x_{\mathrm{B}}^{\circ} \exp\left(- \frac{\Delta \mu_{\mathrm{B}}^{\mathrm{gb},\circ}}{k_{\mathrm{B}} T} \right)$$

Interfacial Segregation

- Consider the case involving vacancy segregation to a grain boundary in a single-component solid A. When a vacancy $V_{\mathrm{A}}^{\mathrm{b}}$ moves from inside the bulk of a grain to become a vacancy $V_{\mathrm{A}}^{\mathrm{gb}}$ at a grain boundary.
- An atom A originally at the grain boundary $\mathrm{A}_{\mathrm{A}}^{\mathrm{gb}}$ moves to inside the bulk of the grain to become $\mathrm{A}_{\mathrm{A}}^{\mathrm{b}}$. This process can be expressed as a reaction:

$$\mathrm{A}_{\mathrm{A}}^{\mathrm{gb}} + V_{\mathrm{A}}^{\mathrm{b}} \longleftrightarrow \mathrm{A}_{\mathrm{A}}^{\mathrm{b}} + V_{\mathrm{A}}^{\mathrm{gb}}$$

- At equilibrium,

$$\mu_{\mathrm{A}_{\mathrm{A}}^{\mathrm{gb}}} + \mu_{V_{\mathrm{A}}^{\mathrm{b}}} = \mu_{\mathrm{A}_{\mathrm{A}}^{\mathrm{b}}} + \mu_{V_{\mathrm{A}}^{\mathrm{gb}}}$$

Interfacial Segregation

- Introducing formation energy, we have

$$E_{\mathrm{A}_{\mathrm{A}}^{\mathrm{gb}}} + k_{\mathrm{B}}T\ln x_{\mathrm{A}}^{\mathrm{gb}} + E_{V_{\mathrm{A}}^{\mathrm{b}}} + k_{\mathrm{B}}T\ln x_{V}^{\mathrm{b}}$$
$$= E_{\mathrm{A}_{\mathrm{A}}^{\mathrm{b}}} + k_{\mathrm{B}}T\ln x_{\mathrm{A}}^{\mathrm{b}} + E_{V_{\mathrm{A}}^{\mathrm{gb}}} + k_{\mathrm{B}}T\ln x_{V}^{\mathrm{gb}}$$

  where x_A^{gb} is the fraction of grain boundary sites occupied by A atoms.

- Then we have

$$k_{\mathrm{B}}T\ln\frac{x_V^{\mathrm{gb}}x_{\mathrm{A}}^{\mathrm{b}}}{x_V^{\mathrm{b}}x_{\mathrm{A}}^{\mathrm{gb}}} = -\left[\left(E_{\mathrm{A}_{\mathrm{A}}^{\mathrm{b}}} + E_{V_{\mathrm{A}}^{\mathrm{gb}}}\right) - \left(E_{\mathrm{A}_{\mathrm{A}}^{\mathrm{gb}}} + E_{V_{\mathrm{A}}^{\mathrm{b}}}\right)\right] = -\Delta E_{\mathrm{gb}}$$

  or

$$\frac{x_V^{\mathrm{gb}}x_{\mathrm{A}}^{\mathrm{b}}}{x_V^{\mathrm{b}}x_{\mathrm{A}}^{\mathrm{gb}}} = \exp\left(-\frac{\Delta E_{\mathrm{gb}}}{k_{\mathrm{B}}T}\right)$$

Interfacial Segregation

- Therefore,

$$\frac{x_V^{\mathsf{gb}}}{1-x_V^{\mathsf{gb}}} = \frac{x_V^{\mathsf{b}}}{1-x_V^{\mathsf{b}}} \exp\left(-\frac{\Delta E_{\mathsf{gb}}}{k_{\mathsf{B}}T}\right)$$

  For the case

$$1-x_V^{\mathsf{gb}} \simeq 1 \qquad 1-x_V^{\mathsf{b}} \simeq 1$$

  we have

$$x_V^{\mathsf{gb}} = x_V^{\mathsf{b}} \exp\left(-\frac{\Delta E_{\mathsf{gb}}}{k_{\mathsf{B}}T}\right)$$

- If we include the vibrational contribution and consider the effect of formation volumes, we can replace ΔE_{gb} with $\Delta G^{\circ}_{\mathsf{gb}}$, the standard segregation free energy.

Interfacial Segregation

- For a A-B binary solution,

$$\mathrm{A}^{\mathrm{gb}} + \mathrm{B}^{\mathrm{b}} \longleftrightarrow \mathrm{A}^{\mathrm{b}} + \mathrm{B}^{\mathrm{gb}}$$

- At equilibrium, we have

$$\mu_{\mathrm{A}}^{\mathrm{gb}} + \mu_{\mathrm{B}}^{\mathrm{b}} = \mu_{\mathrm{A}}^{\mathrm{b}} + \mu_{\mathrm{B}}^{\mathrm{gb}}$$

  which can be rewritten as

$$\mu_{\mathrm{B}}^{\mathrm{b}} - \mu_{\mathrm{A}}^{\mathrm{b}} = \mu_{\mathrm{B}}^{\mathrm{gb}} - \mu_{\mathrm{A}}^{\mathrm{gb}}$$

- The bulk solid solution phase as

$$\mu^{\mathrm{b}} = x_{\mathrm{A}}^{\mathrm{b}}\mu_{\mathrm{A}}^{\mathrm{b}} + x_{\mathrm{B}}^{\mathrm{b}}\mu_{\mathrm{B}}^{\mathrm{b}}$$

- The differential form is

$$d\mu^{\mathrm{b}} = \mu_{\mathrm{A}}^{\mathrm{b}} dx_{\mathrm{A}}^{\mathrm{b}} + \mu_{\mathrm{B}}^{\mathrm{b}} dx_{\mathrm{B}}^{\mathrm{b}} = \left(\mu_{\mathrm{B}}^{\mathrm{b}} - \mu_{\mathrm{A}}^{\mathrm{b}}\right) dx_{\mathrm{B}}^{\mathrm{b}}$$

Interfacial Segregation

- Therefore, the slope of the tangent line to the chemical potential of the bulk solid solution at composition at $x_{\mathrm{B}}^{\mathrm{b}}$ is given by

$$\left(\frac{\partial \mu^{\mathrm{b}}}{\partial x_{\mathrm{B}}^{\mathrm{b}}}\right)_{x_{\mathrm{B}}^{\mathrm{b}}} = \mu_{\mathrm{B}}^{\mathrm{b}}\left(x_{\mathrm{B}}^{\mathrm{b}}\right) - \mu_{\mathrm{A}}^{\mathrm{b}}\left(x_{\mathrm{B}}^{\mathrm{b}}\right)$$

  at grain boundary,

$$\left(\frac{\partial \mu^{\mathrm{gb}}}{\partial x_{\mathrm{B}}^{\mathrm{gb}}}\right)_{x_{\mathrm{B}}^{\mathrm{gb}}} = \mu_{\mathrm{B}}^{\mathrm{gb}}\left(x_{\mathrm{B}}^{\mathrm{gb}}\right) - \mu_{\mathrm{A}}^{\mathrm{gb}}\left(x_{\mathrm{B}}^{\mathrm{gb}}\right)$$

- At equilibrium,

$$\left(\frac{\partial \mu^{\mathrm{b}}}{\partial x_{\mathrm{B}}^{\mathrm{b}}}\right)_{x_{\mathrm{B}}^{\mathrm{b}}} = \mu_{\mathrm{B}}^{\mathrm{b}}\left(x_{\mathrm{B}}^{\mathrm{b}}\right) - \mu_{\mathrm{A}}^{\mathrm{b}}\left(x_{\mathrm{B}}^{\mathrm{b}}\right) = \left(\frac{\partial \mu^{\mathrm{gb}}}{\partial x_{\mathrm{B}}^{\mathrm{gb}}}\right)_{x_{\mathrm{B}}^{\mathrm{gb}}} = \mu_{\mathrm{B}}^{\mathrm{gb}}\left(x_{\mathrm{B}}^{\mathrm{gb}}\right) - \mu_{\mathrm{A}}^{\mathrm{gb}}\left(x_{\mathrm{B}}^{\mathrm{gb}}\right)$$

Interfacial Segregation

- The chemical potentials of A and B at the bulk and grain boundary are

$$\mu_{\mathrm{A}}^{\mathrm{gb}} = \mu_{\mathrm{A}}^{\mathrm{gb},\circ} + k_{\mathrm{B}}T \ln a_{\mathrm{A}}^{\mathrm{gb}}$$

$$\mu_{\mathrm{A}}^{\mathrm{b}} = \mu_{\mathrm{A}}^{\mathrm{b},\circ} + k_{\mathrm{B}}T \ln a_{\mathrm{A}}^{\mathrm{b}}$$

$$\mu_{\mathrm{B}}^{\mathrm{gb}} = \mu_{\mathrm{B}}^{\mathrm{gb},\circ} + k_{\mathrm{B}}T \ln a_{\mathrm{B}}^{\mathrm{gb}}$$

$$\mu_{\mathrm{B}}^{\mathrm{b}} = \mu_{\mathrm{B}}^{\mathrm{b},\circ} + k_{\mathrm{B}}T \ln a_{\mathrm{B}}^{\mathrm{b}}$$

- By consistent treatment as before,

$$k_{\mathrm{B}}T \ln \frac{a_{\mathrm{B}}^{\mathrm{gb}} a_{\mathrm{A}}^{\mathrm{b}}}{a_{\mathrm{B}}^{\mathrm{b}} a_{\mathrm{A}}^{\mathrm{gb}}} = -\left[\left(\mu_{\mathrm{A}}^{\mathrm{b},\circ} + \mu_{\mathrm{B}}^{\mathrm{gb},\circ} \right) - \left(\mu_{\mathrm{A}}^{\mathrm{gb},\circ} + \mu_{\mathrm{B}}^{\mathrm{b},\circ} \right) \right] = -\Delta G_{\mathrm{gb}}^{\circ}$$

or

$$\frac{a_{\mathrm{B}}^{\mathrm{gb}}}{a_{\mathrm{A}}^{\mathrm{gb}}} = \frac{a_{\mathrm{A}}^{\mathrm{b}}}{a_{\mathrm{B}}^{\mathrm{b}}} \exp\left(-\frac{\Delta G_{\mathrm{gb}}^{\circ}}{k_{\mathrm{B}}T} \right)$$

Interfacial Segregation

- Proceed to

$$\frac{x_{\mathrm{B}}^{\mathrm{gb}}\gamma_{\mathrm{B}}^{\mathrm{gb}}}{x_{\mathrm{A}}^{\mathrm{gb}}\gamma_{\mathrm{A}}^{\mathrm{gb}}} = \frac{x_{\mathrm{B}}^{\mathrm{b}}\gamma_{\mathrm{B}}^{\mathrm{b}}}{x_{\mathrm{A}}^{\mathrm{b}}\gamma_{\mathrm{A}}^{\mathrm{b}}} \exp\left(-\frac{\Delta G_{\mathrm{gb}}^{\circ}}{k_{\mathrm{B}}T}\right)$$

  then

$$\frac{x_{\mathrm{B}}^{\mathrm{gb}}\gamma_{\mathrm{B}}^{\mathrm{gb}}}{(1-x_{\mathrm{B}}^{\mathrm{gb}})\gamma_{\mathrm{A}}^{\mathrm{gb}}} = \frac{x_{\mathrm{B}}^{\mathrm{b}}\gamma_{\mathrm{B}}^{\mathrm{b}}}{(1-x_{\mathrm{B}}^{\mathrm{b}})\gamma_{\mathrm{A}}^{\mathrm{b}}} \exp\left(-\frac{\Delta G_{\mathrm{gb}}^{\circ}}{k_{\mathrm{B}}T}\right)$$

- When A-B follows regular solution model,

$$k_{\mathrm{B}}T\ln\gamma_{\mathrm{A}}^{\mathrm{b}} = \alpha^{\mathrm{b}}\left(x_{\mathrm{B}}^{\mathrm{b}}\right)^2 \qquad k_{\mathrm{B}}T\ln\gamma_{\mathrm{B}}^{\mathrm{b}} = \alpha^{\mathrm{b}}\left(x_{\mathrm{A}}^{\mathrm{b}}\right)^2$$

$$k_{\mathrm{B}}T\ln\gamma_{\mathrm{A}}^{\mathrm{gb}} = \alpha^{\mathrm{gb}}\left(x_{\mathrm{B}}^{\mathrm{gb}}\right)^2 \qquad k_{\mathrm{B}}T\ln\gamma_{\mathrm{B}}^{\mathrm{gb}} = \alpha^{\mathrm{gb}}\left(x_{\mathrm{A}}^{\mathrm{gb}}\right)^2$$

Interfacial Segregation

- Then we have

$$\frac{x_{\mathrm{B}}^{\mathrm{gb}}}{\left(1-x_{\mathrm{B}}^{\mathrm{gb}}\right)} \exp\left[\frac{\alpha^{\mathrm{gb}}\left(1-2x_{\mathrm{B}}^{\mathrm{gb}}\right)}{k_{\mathrm{B}}T}\right]$$
$$= \frac{x_{\mathrm{B}}^{\mathrm{b}}}{\left(1-x_{\mathrm{B}}^{\mathrm{b}}\right)} \exp\left[\frac{\alpha^{\mathrm{b}}\left(1-2x_{\mathrm{B}}^{\mathrm{b}}\right)}{k_{\mathrm{B}}T} - \frac{\Delta G_{\mathrm{gb}}^{\circ}}{k_{\mathrm{B}}T}\right]$$