Thermodynamics of materials

24. Chemical Potentials of Solutions I

Kunok Chang
kunok.chang@khu.ac.kr

Kyung Hee University

October 31, 2024

Table of Contents

Table of Contents

Representation of Chemical Composition

- The composition is

$$N_1, N_2, \cdots, N_i, \cdots, N_n$$

for each component $1, 2, 3, \cdots, n$ then the mole fraction x_i is

$$x_i = \frac{N_i}{\sum_{i=1}^{n} N_i} = \frac{N_i}{N}$$

where N is the total number of moles of an n-component materials. Subsequently,

$$\sum_{i=1}^{n} x_i = 1 \qquad \sum_{i=1}^{n} dx_i = 0$$

Representation of Chemical Composition

- The concentration c_i is

$$c_i = \frac{N_i}{V}$$

where V is the total volume of the solution and we have

$$x_i = \frac{c_i}{c}$$

Table of Contents

Multicomponent Solution

- The fundamental equation is

$$dU = TdS - pdV + \mu_1 dN_1 + \mu_2 dN_2 + \cdots \mu_n dN_n$$

the chemical potential is

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}$$

- In other way,

$$dG = -SdT + Vdp + \mu_1 dN_1 + \mu_2 dN_2 + \cdots \mu_n dN_n$$

the chemical potential is

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}}$$

Table of Contents

Multicomponent Solution

- Since

$$G = U - TS + pV = \mu N = \mu_1 N_1 + \mu_2 N_2 + \cdots \mu_n N_n$$

the chemical potential of a homogeneous multicomponent system is

$$\mu = \frac{G}{N} = g = u - Ts + pv = \mu_1 x_1 + \mu_2 x_2 + \cdots + \mu_n x_n$$

and

$$d\mu = -sdT + vdp + \mu_1 dx_1 + \mu_2 dx_2 + \cdots + \mu_n dx_n$$

- The chemical potential of each individual component is

$$d\mu_i = -s_i dT + v_i dp$$

where s_i and v_i are the molar entropy and volume of component i.

Table of Contents

Chemical Potential of a Mixture of Pure Components

- The chemical potential of a mixture of pure components is

$$\mu^\circ(T, p, x_i) = x_1\mu_1^\circ(T, p) + x_2\mu_2^\circ(T, p) + \cdots + x_n\mu_n^\circ(T, p)$$

  where $\mu_i^\circ(T, p)$ is the chemical potential of pure component i.
- For example, for a binary mixture of pure A and pure B, chemical potential of mixture is

$$\mu^\circ(T, p, x_\mathsf{B}) = x_\mathsf{A}\mu_\mathsf{A}^\circ(T, p) + x_\mathsf{B}\mu_\mathsf{B}^\circ(T, p)$$

Table of Contents

Chemical Potential of a Multicomponent Solution

- At given pressure, the chemical potential μ_i of a component i in a solution is expressed by

$$\mu_i(T, x_i) = \mu_i^\circ(T) + RT \ln a_i(T, x_i)$$

where a_i is the activity of component i.

- The activity can be decomposed into

$$a_i = x_i \gamma_i$$

where γ_i is the activity coefficient. For ideal solution $\gamma_i = 1$, which means that an activity is a mole fraction.

Table of Contents

Chemical Potential of a Multicomponent Solution

- For homogeneous binary solution and their components are A and B,

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

where

$$\mu_{\mathsf{A}} = \mu^{\circ}_{\mathsf{A}}(T) + RT\ln a_{\mathsf{A}}$$

$$\mu_{\mathsf{B}} = \mu^{\circ}_{\mathsf{B}}(T) + RT\ln a_{\mathsf{B}}$$

- The chemical potential of a solution is

$$\mu(T, x_i) = \sum_{i=1}^{n} x_i\mu_i(T, x_i)$$

it is

$$\mu(T, x_i) = \sum_{i=1}^{n} x_i\mu^{\circ}_i(T) + RT\sum_{i=1}^{n} x_i\ln a_i(T, x_i)$$

Table of Contents

Obtaining Chemical Potentials of Components from Chemical Potential of Solution

- The chemical potential of the solution is at given temperature and pressure is

$$\mu = \sum_{i=1}^{n} \mu_i x_i \rightarrow d\mu = \sum_{i=1}^{n} \mu_i dx_i$$

- Since $\sum_{i=1}^{n} x_i = 1$,

$$x_i = 1 - \sum_{j=1, j \neq i}^{n} x_j$$

therefore,

$$\mu = \mu_i + \sum_{j=1, j \neq i}^{n} x_j (\mu_j - \mu_i)$$

Obtaining Chemical Potentials of Components from Chemical Potential of Solution

- We have

$$\sum_{i=1}^{n} dx_i = 0 \qquad dx_i = -\sum_{j=1, j\neq i}^{n} dx_j$$

then we have

$$\left(\frac{\partial \mu}{\partial x_j}\right)_{j\neq i} = \mu_j - \mu_i$$

Obtaining Chemical Potentials of Components from Chemical Potential of Solution

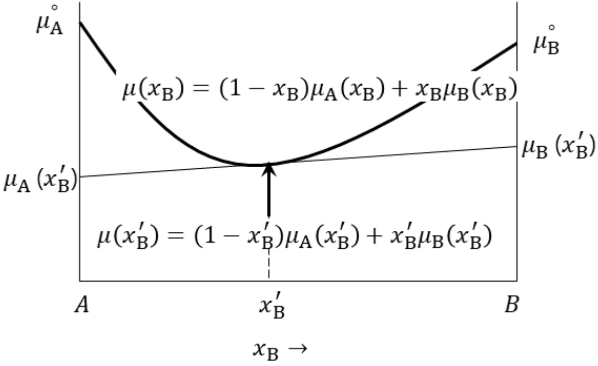
- Therefore,

$$\mu = \mu_i + \sum_{j=1, j\neq i}^{n} x_j(\mu_j - \mu_i) = \mu_i + \sum_{j=1, j\neq i}^{n} x_j \frac{\partial \mu}{\partial x_j}$$

then

$$\mu_i = \mu - \sum_{j=1, j\neq i}^{n} x_j \frac{\partial \mu}{\partial x_j}$$

Obtaining Chemical Potentials of Components from Chemical Potential of Solution



Obtaining Chemical Potentials of Components from Chemical Potential of Solution

- For binary solution, the chemical potential of the solution is

$$\begin{aligned}\mu(x_\mathsf{B}) &= x_\mathsf{A}\mu_\mathsf{A}(x_\mathsf{B}) + x_\mathsf{B}\mu_\mathsf{B}(x_\mathsf{B}) = (1-x_\mathsf{B})\mu_\mathsf{A}(x_\mathsf{B}) + x_\mathsf{B}\mu_\mathsf{B}(x_\mathsf{B}) \\ &= \mu_\mathsf{A}(x_\mathsf{B}) + x_\mathsf{B}\big(\mu_\mathsf{B}(x_\mathsf{B}) - \mu_\mathsf{A}(x_\mathsf{B})\big)\end{aligned}$$

then

$$d\mu(x_\mathsf{B}) = \mu_\mathsf{A}(x_\mathsf{B})dx_\mathsf{A} + \mu_\mathsf{B}(x_\mathsf{B})dx_\mathsf{B} = \big(\mu_\mathsf{B}(x_\mathsf{B}) - \mu_\mathsf{A}(x_\mathsf{B})\big)dx_\mathsf{B}$$

- At $x_\mathsf{B} = x'_\mathsf{B}$,

$$\mu_\mathsf{A}(x'_\mathsf{B}) = \mu(x'_\mathsf{B}) - x'_\mathsf{B}\big(\mu_\mathsf{A}(x'_\mathsf{B}) - \mu_\mathsf{B}(x'_\mathsf{B})\big) = \mu(x'_\mathsf{B}) - x'_\mathsf{B}\left.\frac{\partial\mu(x_\mathsf{B})}{\partial x_\mathsf{B}}\right|_{x'_\mathsf{B}}$$

- At $x_\mathsf{A} = x'_\mathsf{A}$,

$$\mu_\mathsf{B}(x'_\mathsf{A}) = \mu(x'_\mathsf{A}) - x'_\mathsf{A}\big(\mu_\mathsf{B}(x'_\mathsf{A}) - \mu_\mathsf{A}(x'_\mathsf{A})\big) = \mu(x'_\mathsf{A}) - x'_\mathsf{A}\left.\frac{\partial\mu(x_\mathsf{A})}{\partial x_\mathsf{A}}\right|_{x'_\mathsf{A}}$$

Table of Contents

Gibbs-Duhem Equation for Multicomponent Systems

- The differential form of Gibbs free energy is

$$dG = -SdT + Vdp + \mu_1 dN_1 + \mu_2 dN_2 + \cdots + \mu_n dN_n$$

Since

$$G = -ST + Vp + \mu_1 N_1 + \mu_2 N_2 + \cdots + \mu_n N_n$$

therefore, we reach the Gibbs-Duhem equation for multicomponent system,

$$-TdS + pdV + N_1 d\mu_1 + N_2 d\mu_2 + \cdots + N_n d\mu_n = 0$$

- At a given S and V, for a binary solution,

$$N_1 d\mu_1 + N_2 d\mu_2 = 0$$

divide into N,

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

- When the chemical potential is given by activity, we have

$$x_1 d\ln a_1 + x_2 d\ln a_2 = 0$$

$$x_1 d\ln \gamma_1 + x_2 d\ln \gamma_2 = 0$$

with fact that

$$x_1 d\ln x_1 + x_2 d\ln x_2 = 0$$