CM 3230 Thermodynamics, Fall 2016

Lecture 23

1. Two Phase (α-phase & β-phase) / Multicomponent \((i = 1, \ldots, N)\) / No Reaction

Equilibrium Conditions:

a. Thermal criteria: \(T^\alpha = T^\beta\)
b. Mechanical criteria: \(P^\alpha = P^\beta\)
c. Chemical criteria: (to be developed now)

- First recall that in the path from non-equilibrium, 
\[ dG_{sys} \leq 0 \]

At equilibrium, 
\[ dG_{sys} = dG^\alpha + dG^\beta = 0 \]

Based on natural dependency 
\[ G = G(T, P, n_1, \ldots, n_N), \]

\[ dG^\alpha = -S^\alpha dT + V^\alpha dP + \sum_{i=1}^{N} \left( \frac{\partial G}{\partial n_i} \right)^\alpha_{T,P,n_{j\neq i}} d n_i^\alpha \]
\[ dG^\beta = -S^\beta dT + V^\beta dP + \sum_{i=1}^{N} \left( \frac{\partial G}{\partial n_i} \right)^\beta_{T,P,n_{j\neq i}} d n_i^\beta \]

Now define,
\[ \mu_i^\alpha = \left( \frac{\partial G}{\partial n_i} \right)^\alpha_{T,P,n_{j\neq i}} = \text{chemical potential of component } i \text{ in the } \alpha\text{-phase} \]
\[ \mu_i^\beta = \left( \frac{\partial G}{\partial n_i} \right)^\beta_{T,P,n_{j\neq i}} = \text{chemical potential of component } i \text{ in the } \beta\text{-phase} \]

Since at equilibrium, \(dT = 0\) and \(dP = 0\)

\[ dG_{sys} = \sum_{i=1}^{N} \mu_i^\alpha d n_i^\alpha + \sum_{i=1}^{N} \mu_i^\beta d n_i^\beta = 0 \]

Assuming no reaction, \(n_i^\alpha + n_i^\beta = \text{constant, thus} \]
\[ d n_i^\alpha = -d n_i^\beta \]
This means any molar decrease of $i$ in the $\beta$-phase is the molar increase of $i$ in the $\alpha$-phase (and vice versa).

$$dG_{sys} = \sum_{i=1}^{N} \left( \mu_i^\alpha - \mu_i^\beta \right) d n_i^\alpha = 0$$

If $\mu_i^\alpha \neq \mu_i^\beta$ for some $i$, then some adjustments will have to occur among the other components to satisfy the equilibrium condition. However, the movement of the components from one phase to the other will stop (i.e. true equilibrium is achieved) when

$$\mu_i^\alpha = \mu_i^\beta \quad \text{for} \quad i = 1, \cdots, N$$

This is the chemical criteria for non-reactive multiphase equilibrium.

2. Extension to $\pi$ phases: $\alpha_1, \alpha_2, \cdots, \alpha_\pi$

Equilibrium criteria becomes

$$T^{\alpha_1} = T^{\alpha_2} = \cdots = T^{\alpha_\pi}$$

$$p^{\alpha_1} = p^{\alpha_2} = \cdots = p^{\alpha_\pi}$$

$$\mu_1^{\alpha_1} = \mu_1^{\alpha_2} = \cdots = \mu_1^{\alpha_\pi}$$

$$\vdots$$

$$\mu_N^{\alpha_1} = \mu_N^{\alpha_2} = \cdots = \mu_N^{\alpha_\pi}$$
Gibbs Phase Rule for Non-reactive Systems

Objective: Determine how many degrees of freedom are available to specify a system in equilibrium.

- Number of free variables in the criteria in a phase: \(T, P, x_1, \ldots, x_N \rightarrow (N + 1)\) variables because
  \[
  \sum_{i=1}^{N} x_i = 1
  \]
  For \(\pi\) number of phases, number of free variables becomes: \(\pi(N + 1)\)

- Number of equations from the set of equilibrium criteria:
  \[
  (\pi - 1) \text{number of equations relating } T^\alpha_j
  \]
  \[
  (\pi - 1) \text{ number of equations relating } P^\alpha_j
  \]
  \[
  (\pi - 1) \text{ number of equations relating } \mu_1^\alpha_j
  \]
  \[
  \vdots
  \]
  \[
  (\pi - 1) \text{ number of equations relating } \mu_N^\alpha_j
  \]
  ⇒ Total of \((\pi - 1)(N + 2)\) equations that needs to be satisfied

- Degree of freedom = number of variables – number of equations
  \[
  dof = \pi(N + 1) - (\pi - 1)(N + 2)
  \]
  \[
  = \pi[(N + 1) - (N + 2)] + (N + 2)
  \]
  \[
  = N - \pi + 2
  \]

Example: Vapor-Liquid equilibrium of a binary mixture
  \(\pi = 2\) (vapor and liquid phases)
  \(N = 2\) (substance A and B)
  \(dof = 2 - 2 + 2 = 2\)

Possible specifications:
  a) \(x_A, y_B\)
  b) \(T, P\)
  c) \(P, y_A\)
  d) \(T, x_B\)
  ... etc.

Note: since the other properties are related to \(T, P, x_i \ (i = 1, \ldots, N)\), it is also possible to specify: \((h^\alpha, v^\beta), (g^\alpha, T)\), etc.
3. Temperature and Pressure Dependence of $\mu_i$

Recall first

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i}dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i}dP + \sum_{i=1}^{N} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i}dn_i$$

Also,

$$dG = -SDT + VdP + \sum_{i=1}^{N} \mu_i dn_i$$

Using the property of second order partial derivatives,

$$\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i} = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i}$$

Or

$$\frac{\partial}{\partial n_i} (-S)_{T,P,n_j \neq i} = \frac{\partial}{\partial T} (\mu_i)_{T,P,n_i}$$

Thus,

$$\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i} = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i}$$

Again, using the property of second order partial derivatives,

$$\frac{\partial}{\partial n_i} (V)_{T,P,n_j \neq i} = \frac{\partial}{\partial P} (\mu_i)_{T,P,n_i}$$

Thus,

$$\frac{\partial}{\partial P} \mu_i = \bar{V}_i$$

However, this may not be convenient because partial molar entropy is not as easy to measure directly as partial molar enthalpy (via heat capacities) or partial molar volume.

→ we want an alternative approach, instead look for $\mu_i/T$.

$$\frac{\partial}{\partial T} \left(\frac{\mu_i}{T}\right) = \frac{1}{T} \frac{\partial}{\partial T} \mu_i - \frac{\mu_i}{T^2} = -\frac{\tilde{S}_i T - \tilde{G}_i}{T^2} = -\frac{\tilde{H}_i}{T^2}$$

Again, using the property of second order partial derivatives,

$$\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i} = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i}$$

Thus,

$$\frac{\partial}{\partial P} \mu_i = \bar{V}_i$$