CM 3230  Thermodynamics, Fall 2016
Lecture 27

1. Fugacity in Liquid Phase (continued)

For an ideal liquid solution,

\[ \tilde{f}_{A}^{\text{liq}} = x_A f_{A}^{\text{liq}} \]

For a nonideal liquid solution,

\[ \tilde{f}_{A}^{\text{liq}} = \frac{\gamma_A}{\mathcal{H}_A} x_A f_{A}^{\text{liq}} \]

But it appears that when \( x_A \) small, a different line might be easier to fit experimental data.

(at small mole fraction): \( \tilde{f}_{A}^{\text{liq}} \approx x_A \mathcal{H}_A \)

This line is called “Henry’s law” which can be obtained for highly diluted solutions of component \( A \), where \( \mathcal{H}_A \) is called the “Henry’s law constant”. Thus, if these values of \( \mathcal{H}_A \) are available already, an alternative treatment for the fugacity of \( A \) in the mixture becomes

\[ \tilde{f}_{A}^{\text{liq}} = \left( \gamma_A^{\mathcal{H}_A} \right)^{-1} x_A \mathcal{H}_A \]

where \( \gamma_A^{\mathcal{H}_A} \) is known as the Henry’s law activity coefficient.
Q: How does \( \gamma_A^\infty \) relate to \( \gamma_A \)?

A: We first need to relate these two at the region near infinite dilution.

At infinite dilution, \( \gamma_A = \gamma_A^\infty \), or

\[
\hat{f}_A^\text{liq} = (\gamma_A^\infty)(x_A^\text{liq})
\]

Compare with,

\[
\gamma_A^\infty \hat{f}_A^\text{liq} = \mathcal{H}_A
\]

From which,

\[
\hat{f}_A^\text{liq} = (\gamma_A^\mathcal{H})x_A^\text{liq} = x_A\gamma_A^\mathcal{H} x_A^\text{liq}
\]

Comparing with

\[
\hat{f}_A^\text{liq} = x_A \gamma_A f_A^\text{liq}
\]

We obtain the desired relationship:

\[
\gamma_A = \gamma_A^\mathcal{H} \gamma_A^\infty \rightarrow \gamma_A^\mathcal{H} = \gamma_A/\gamma_A^\infty
\]

(Also, at pure \( A \), with \( \gamma_A = 1 \), we get \( \gamma_A^\mathcal{H} = 1/\gamma_A^\infty \)).

2. Temperature and Pressure Dependence of \( g^E \) and \( \gamma_i \)

First, using \( G^E \) in place of \( G \),

\[
dG^E = V^EdP - S^EdT + \sum_{i=1}^{N} G_i^Edn_i
\]

Then,

\[
\left( \frac{\partial G^E}{\partial P} \right)_{T,n_i} = \frac{V^E}{V^E} \text{dividing by } n_{\text{total}} \left( \frac{\partial g^E}{\partial P} \right)_{T,n_i} = v^E = \Delta_{\text{mix}}v
\]

\[
\left( \frac{\partial G^E}{\partial T} \right)_{T,n_i} = -\frac{S^E}{S^E} \text{dividing by } n_{\text{total}} \left( \frac{\partial g^E}{\partial T} \right)_{T,n_i} = -s^E
\]

Or,

\[
\left( \frac{\partial (g^E/T)}{\partial T} \right)_{T,n_i} = \frac{1}{T} \left( \frac{\partial g^E}{\partial T} \right) - \frac{1}{T^2} g^E = -\frac{(Ts^E + g^E)}{T^2} = -\frac{h^E}{T^2} = -\Delta_{\text{mix}}h/T^2
\]
**Q:** What about the activity coefficients (instead of $g^E$)?

**A:** First, we note (with $\mu_i^{\text{ideal soln}} = g_i$)

$$\bar{G}^E_i = RT \ln (\gamma_i) = \mu_i - \mu_i^{\text{ideal soln}} = \mu_i - g_i$$

Then, taking partial derivative with respect to $P$ (at constant $T$ and composition),

$$RT \left( \frac{\partial \ln (\gamma_i)}{\partial P} \right)_{T,n_i} = \left( \frac{\partial \mu_i}{\partial P} \right)_{T,n_i} - \left( \frac{\partial g_i}{\partial P} \right)_{T,n_i} = V_i - v_i$$

or

$$\left( \frac{\partial \ln (\gamma_i)}{\partial P} \right)_{T,n_i} = \frac{V_i - v_i}{RT}$$

If instead, taking partial derivative with respect to $T$ (at constant $P$ and composition),

$$\ln (\gamma_i) = \frac{\mu_i - g_i}{RT}$$

$$\left( \frac{\partial \ln (\gamma_i)}{\partial T} \right)_{T,n_i} = \frac{1}{RT} \left( \left( \frac{\partial \mu_i}{\partial T} \right)_{P,n_i} - \left( \frac{\partial g_i}{\partial T} \right)_{P,n_i} \right) - \frac{1}{RT^2} (\mu_i - g_i)$$

$$= - \frac{1}{RT^2} ([T\bar{S}_i + \bar{G}_i] - [T\bar{s}_i + g_i]) = - \left( \frac{\bar{H}_i - h_i}{RT^2} \right)$$

In summary,

$$\left( \frac{\partial g^E}{\partial P} \right)_{T,n_i} = \Delta_{\text{mix}} v$$

$$\left( \frac{\partial (g^E/T)}{\partial T} \right)_{T,n_i} = - \frac{\Delta_{\text{mix}} h}{T^2}$$

$$\left( \frac{\partial \ln (\gamma_i)}{\partial P} \right)_{T,n_i} = \frac{V_i - v_i}{RT}$$

$$\left( \frac{\partial \ln (\gamma_i)}{\partial T} \right)_{T,n_i} = - \left( \frac{\bar{H}_i - h_i}{RT^2} \right)$$

- See Example 7.13 to see how to find Margules parameter at another temperature (assuming $\Delta_{\text{mix}} h$ is not a function of temperature).
- Also, read page 447 to distinguish between two extreme cases: “Regular solution” and “Athermal solution”