CM 3230 Thermodynamics, Fall 2014

Lecture 28

Brief Review of Chapter 6 and 7

1. Partial molar properties (within a phase)

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} ; \overline{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}} ; \bar{S}_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \mu_i$$

- Identities:

$$v = \sum_{i=1}^{N} x_i \bar{V}_i \ ; \ h = \sum_{i=1}^{N} x_i \overline{H}_i \ ; \ g = \sum_{i=1}^{N} x_i \mu_i \text{ ; ... etc.}$$

- Gibbs-Duhem relationships:

$$0 = \sum_{i=1}^{N} x_i d\bar{V}_i \ ; 0 = \sum_{i=1}^{N} x_i d\overline{H}_i \ ; 0 = \sum_{i=1}^{N} x_i d\mu_i \text{ ; ... etc.}$$

- Property change of mixing:

$$\Delta_{mix} v = v - \sum_{i=1}^{N} x_i v_i = \sum_{i=1}^{N} x_i (\bar{V}_i - v_i)$$

$$\Delta_{mix} h = h - \sum_{i=1}^{N} x_i h_i = \sum_{i=1}^{N} x_i (\overline{H}_i - h_i)$$

$$\Delta_{mix} g = g - \sum_{i=1}^{N} x_i g_i = \sum_{i=1}^{N} x_i (\bar{G}_i - g_i)$$

; ... etc.

→ Special case: ideal solution

$$\Delta_{mix} v^{\text{ideal soln}} = 0$$

$$\Delta_{mix} h^{\text{ideal soln}} = 0$$

$$\Delta_{mix} s^{\text{ideal soln}} = -R \sum_{i=1}^{N} x_i \ln(x_i)$$

$$\Delta_{mix} g^{\text{ideal gas}} = RT \sum_{i=1}^{N} x_i \ln(x_i)$$

- Excess properties:

$$\begin{aligned} g^E &= \text{excess Gibbs energy} \\ &= \Delta_{mix} g - \Delta_{mix} g^{\text{ideal soln}} \\ &= \left(g - \sum_{i=1}^{N} x_i g_i \right) - RT \sum_{i=1}^{N} x_i \ln(x_i) \\ &= \sum_{i=1}^{N} x_i \, \bar{G}_i^E \end{aligned}$$

2. **Fugacity**

   a. **Definition:** property of a substance, having units of pressure, invented by G.N. Lewis, to allow calculations of changes in chemical potential that mimics (generalizes) calculations used for ideal gas behavior.

$$\mu_i^{\text{②}} - \mu_i^{\text{①}} = RT \ln\left(\frac{\hat{f}_i^{\text{②}}}{\hat{f}_i^{\text{①}}} \right)$$

   b. **Notations and terms:**

      i) f_i^{α} = fugacity of pure i in the α phase (e.g. f_i^{vap}, f_i^{liq})

      ii) $\hat{f}_i^{\alpha}$= fugacity of component i in the α phase mixture/solution

      iii) $\hat{\phi}_i^{\alpha} = \hat{f}_i^{\alpha}/(y_i P_{sys})$ and $\phi_i^{\alpha} = f_i^{\alpha}/P_{sys}$ = fugacity coefficient

      iv) $\gamma_i = \hat{f}_i^{\alpha}/(x_i f_i^{\alpha})$ = activity coefficient

   c. **Lewis / Lewis-Randall rule** : (interaction with other molecule species is similar to interaction with other i molecules): $\hat{f}_i^{\alpha} = x_i f_i^{\alpha}$

   d. **Evaluation:**

      i) f_i^{vap} (fugacity of pure i)

      - If property tables exist: $f_i^{vap} = P_{\text{low}} \exp[(g_i - g_i^{o})/(RT)]$
      - Equation of state:

$$RT \ln\left(\frac{f_i^{vap}}{P_{\text{low}}} \right) = \int_{P_{\text{low}}}^{P} v \; dP$$

or with $z = Pv/(RT)$

$$\ln(\phi_i^{vap}) = \ln\left(\frac{f_i^{vap}}{P} \right) = \int_{P_{\text{low}}}^{P} (z-1)\frac{1}{P} \; dP$$

- Example: virial equation of state explicit in v

$$z = \frac{Pv}{RT} = 1 + B'P + C'P^2 + \cdots$$

$$\rightarrow \ln(\phi_i^{vap}) = \ln\left(f_i^{vap}/P\right) = B'P + \frac{C'}{2}P^2 + \cdots$$

      - Via generalized correlations, e.g. Lee-Kesler charts

$$\log(f_i/P) = \log(\phi_i) = \log(\phi_i)^{(0)} + \omega \log(\phi_i)^{(0)}$$

ii) $\hat{f}_i^{vap}$ (fugacity in gas mixtures)

- Rough estimate: ideal gas behavior

$$\hat{\phi}_i^{vap} = 1 \rightarrow \hat{f}_i^{vap} = y_i P$$

- Moderate estimate: Lewis Rule → ideal solution behavior

$$\gamma_i^{vap} = 1 \rightarrow \hat{f}_i^{vap} = y_i f_i^{vap}$$

- Better estimate: Equation of state together with mixing rules

$$RT \ln\left(\frac{\hat{f}_i^{vap}}{y_i P_{\text{low}}}\right) = -\int_{V_\infty}^{V} \left(\frac{\partial P}{\partial n_i}\right)_{V,T,n_{j\neq i}} dV$$

→ see Table 7.1 on page 408 for various examples

iii) f_i^{liq} (fugacity in of pure i liquid)

$$f_i^{liq} = \phi_i^{sat} P_i^{sat} \mathcal{P}_{corr}$$

where,

$$\mathcal{P}_{corr} = \exp\left(v_i^{liq} \frac{P_{sys} - P^{sat}}{RT}\right) = \text{Poyting correction factor}$$

iv) $\hat{f}_i^{liq}$ (fugacity in of i in liquid solution)

- Ideal solution behavior: $\hat{f}_i^{liq} = x_i f_i^{liq}$
- Real solution behavior: $\hat{f}_i^{liq} = \gamma_i x_i f_i^{liq}$
- Based on Henry's Law (property at dilute concentrations):

$$\hat{f}_i^{liq} = \gamma_i^{\mathcal{H}} x_i \mathcal{H}_i$$

where

$$\mathcal{H}_i = \gamma_i^{\infty} f_i^{liq} \qquad \text{and} \qquad \gamma_i^{\mathcal{H}} = \frac{\gamma_i}{\gamma_i^{\infty}}$$

3. Activitiy Coefficients and Excess Molar Gibbs Energy

$$\bar{G}_i^E = \left(\frac{\partial [n_T g^E]}{\partial n_i}\right)_{T,P,n_{j\neq i}} = RT \ln(\gamma_i)$$

where, g^E models need to satisfy "thermodynamic consistency", e.g. satisfy Gibbs-Duhem relationships.

Models available: Margules, Van Laar, Wilson, NTRL, UNIQUAC, UNIFAC (see Table 7.2, page 438)

4. Phase Equilibrium (N components, π phases)

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

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

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

$$\vdots$$

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

Or

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

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

$${\hat{f}_1}^{\alpha_1} = {\hat{f}_1}^{\alpha_2} = \cdots = {\hat{f}_1}^{\alpha_\pi}$$

$$\vdots$$

$${\hat{f}_N}^{\alpha_1} = {\hat{f}_N}^{\alpha_2} = \cdots = {\hat{f}_N}^{\alpha_\pi}$$

5. Vapor Liquid Equilibrium

$$\hat{f}_i^{vap} = \hat{f}_i^{liq}$$

a) With activity coefficients based on ideal solution behavior

$$y_i \hat{\phi}_i^{vap} P_{sys} = x_i \gamma_i \phi_i^{sat} P^{sat} \exp\left(v_i^{liq} \frac{P_{sys} - P^{sat}}{RT} \right)$$

Special case: vapor is ideal gas, liquid is ideal solution,
Poynting correction is 1 → **Raoult's Law**

$$y_i P_{sys} = x_i P^{sat}$$

b) With activity coefficients based on Henry's law behavior

$$y_i \hat{\phi}_i^{vap} P_{sys} = x_i \gamma_i^{\mathcal{H}} \mathcal{H}_i$$

Special case: vapor is ideal gas, component i is near dilute condition in liquid solution

$$y_i P_{sys} = x_i \mathcal{H}_i$$