CM 3230 Thermodynamics, Fall 2016

Lecture 24

1. Brief Summary of Chapter 6

- Criteria for nonreactive multiphase equilibria

  Example: 2-components (A and B) in 2-phases (α-phase and β-phase)

  $$T^\alpha = T^\beta \;;\; P^\alpha = P^\beta \;;\; \mu_A^\alpha = \mu_A^\beta \;;\; \mu_B^\alpha = \mu_B^\beta$$

  Special case: pure component in two phase

  $$T^\alpha = T^\beta \;;\; P^\alpha = P^\beta \;;\; g_A^\alpha = g_A^\beta$$

  - Clapeyron equation : (along saturation curve)

  $$\frac{dP}{dT} = \frac{h_A^\alpha - h_A^\beta}{(v_A^\alpha - v_A^\beta)T}$$

  - Claussius Clapeyron: (if α is vapor phase and β is liquid phase, Δh_{vap} is constant, $v_{vap} \gg v_{liq}$, and vapor approximated by ideal gas behavior)

  $$\ln\left(\frac{P_{sat,2}}{P_{sat,1}}\right) = \frac{-\Delta h_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

  - Antoine Equation: (empirically-fit equation for vapor-liquid saturation curve)

- Multiple components, single phase, constant T and P
  - Partial molar properties:

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

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

  - Identities:

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

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

- Property change of mixing:

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

  - Special case: mixture of ideal gases

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

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

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

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

- Additional identities for μ_i

$$\frac{\partial \mu_i}{\partial T} = -\bar{S}_i \text{ ; } \quad \frac{\partial\left(\frac{\mu_i}{T}\right)}{\partial T} = -\frac{\bar{H}_i}{T^2} \quad ; \quad \frac{\partial \mu_i}{\partial P} = \bar{V}_i$$

2. Introduction to Fugacity

- *Development:*
  - Consider the isothermal process for a mixture of ideal gases, with P allowed to change.

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

  - Integrating, and let μ_i^o be a reference value,

$$\mu_i - \mu_i^o = RT\ln\left(\frac{P}{P^o}\right) = RT\ln\left(\frac{y_i P}{y_i P^o}\right) = RT\ln\left(\frac{p_i}{p_i^o}\right)$$

  - G.N. Lewis proposes a new property called "fugacity", denoted $\hat{f}_i$, that will yield the same form as that of ideal gas mixtures, but would work for other conditions, including real gas mixtures, liquid solutions and solid solutions.

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

    Or more generally,

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

- Notation of various terms (some to be discussed later):

  $\hat{f}_i$ = fugacity of component i in the mixture
  f_i = fugacity of pure i
  f_i^o = fugacity of pure i at a chosen reference state
  $\hat{\phi}_i = \dfrac{\hat{f}_i}{y_i P_{sys}}$ = fugacity coefficient of i (often used in gas phases… but can also be used in liquid and solid phases)
  $\phi_i = \dfrac{f_i}{P_{sys}}$ = fugacity coefficient of pure i
  $\gamma_i = \dfrac{\hat{f}_i}{x_i f_i^o}$ = activity coefficient (often used in liquid and solid phases)
  $a_i = x_i \gamma_i = \dfrac{\hat{f}_i}{\hat{f}_i^o}$ = activity (often used in liquid reaction equilibrium)

Remarks:

a) In liquid systems, there will be many different reference conditions used, e.g. the Lewis-Randall reference state, Henry's law reference state, infinite dilution reference state.
b) For vapor-liquid equilibrium, the key equation (e.g. for use in distillation) will be:

$$\hat{f}_i^{vap} = \hat{f}_i^{liq} \qquad \rightarrow \qquad y_i \hat{\phi}_i P_{sys} = x_i \gamma_i f_i^o \qquad i = 1, \cdots, N$$

Thus, we need to know how to find $\hat{\phi}_i$, γ_i and f_i^o.

3. Alternative for Chemical Criteria for Equilibrium

Recall the original criteria : $\mu_i^\alpha = \mu_i^\beta$. Then

$$(\mu_i^o)^\alpha + RT\ln\left(\frac{\hat{f}_i^\alpha}{\left(\hat{f}_i^o\right)^\alpha}\right) = (\mu_i^o)^\beta + RT\ln\left(\frac{\hat{f}_i^\beta}{\left(\hat{f}_i^o\right)^\beta}\right)$$

$$\left(\left[(\mu_i^o)^\alpha - (\mu_i^o)^\beta\right] - RT\ln\left(\frac{\left(\hat{f}_i^o\right)^\alpha}{\left(\hat{f}_i^o\right)^\beta}\right)\right) = RT\ln\left(\frac{\hat{f}_i^\beta}{\hat{f}_i^\alpha}\right)$$

$$0 = RT\ln\left(\frac{\hat{f}_i^\beta}{\hat{f}_i^\alpha}\right)$$

$$\rightarrow \qquad \hat{f}_i^\alpha = \hat{f}_i^\beta$$

4. Fugacity in Vapor Phase

A) Pure component : ($\mu_i = g_i$, $y_i = 1$ and $\hat{f}_i = f_i$)

$$g_i - g_i^o = RT \ln\left(\frac{f_i}{f_i^o}\right)$$

Choose ideal gas as reference, $f_i^o = P_{\text{low}}$:

$$g_i - g_i^o = RT \ln\left(\frac{f_i}{P_{\text{low}}}\right)$$

- Three possible approaches to finding f_i (given T and P)

  i) Using property tables of pure components, e.g. steam table
    - Evaluate $g(T,P) = h(T,P) - Ts(T,P)$ and $g(T,P_{\text{low}}) = h(T,P_{\text{low}}) - Ts(T,P_{\text{low}})$, where P_{low} is the lowest value of P available in the table.
    - Calculate $f_i = P_{\text{low}} \exp([g_i - g_i^o]/RT)$
    - See example 7.1 (page 397)

  ii) Using equations of state: (e.g. Van der Waals, Peng-Robinson, etc.)
    - Recall that for constant temperature, pure component,

$$dg = vdP$$

$$\rightarrow \quad g_i - g_i^o = \int_{P_{\text{low}}}^{P} v\, dP = RT \ln\left(\frac{f_i}{P_{\text{low}}}\right)$$

    - For cubic EOS, one could first convert $dP = (?)dv$. Then, for the limits of integration, will again need to use cube root equations to evaluate v at the given T, P, while for the reference state of ideal gas, $v_{P_{low}} = v_\infty$. (see example 7.2, page 398)
    - For virial EOS, take the form that is explicit for v, i.e.

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

(Note: the coefficients B', C', etc. are often functions only of temperature)

$$\rightarrow \int_{P_{low}}^{P} v\, dP \; = RT \int_{P_{low}}^{P} \left(\frac{1}{P} + B' + C'P + \cdots\right) dP$$

$$\ln\left(\frac{f_i}{P_{\text{low}}}\right) = \int_{P_{low}}^{P} \left(\frac{1}{P} + B' + C'P + \cdots\right) dP$$

$$= \ln\left(\frac{P}{P_{\text{low}}}\right) + B'(P - P_{\text{low}}) + \frac{C'}{2}\left(P^2 - P_{\text{low}}^2\right) + \cdots$$

Taking the limit as $P_{\text{low}} \rightarrow 0$,

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

see example 7.2, page 399, for $B' = (bRT - a)/(RT)^2$, dropping higher order terms, then

$$f_i = P \exp\left(\left(b - \frac{a}{RT}\right)\frac{P}{RT}\right)$$

iii) Using generalized correlations for compressibility factor z

$$g_i - g_i^o = \int_{P_{\text{low}}}^{P} v\, dP = RT \ln\left(\frac{f_i}{P_{\text{low}}}\right)$$

Next, divide by RT and subtract the term $\int_{P_{\text{low}}}^{P} (1/P)\, dP$ from both sides

$$\int_{P_{\text{low}}}^{P} \left(\frac{v}{RT} - \frac{1}{P}\right) dP = \ln\left(\frac{f_i}{P_{\text{low}}}\right) - \ln\left(\frac{P}{P_{\text{low}}}\right)$$

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

Graphs on page 401 : $\log(\phi)^{(0)}$ vs. P_r and $\log(\phi)^{(1)}$ vs. P_r

$$\log(\phi) = \log(\phi)^{(0)} + \omega \log(\phi)^{(1)}$$

Also can use tables in appendices C.7 and C.8 , pp. 672-675.