CM 3230 Thermodynamics, Fall 2016

Lecture 26

1. Fugacity in Liquid Phase (at T_{sys} and P_{sys})

A) <u>Liquid of Pure Component i</u> (Note: $P_{sys} \geq P^{sat}$)

Case 1: $P_{sys} = P_i^{sat}$ (where P_i^{sat} can be found from Antoine's equation at T^{sat})

→ vapor and liquid coexist (we include marker "sat" to indicate that this value occurs for V-L coexistence of pure component i)

$$\left(f_i^{liq}\right)^{sat} = \left(f_i^{vap}\right)^{sat} = \phi_i^{sat} P_i^{sat}$$

Case 2: $P_{sys} > P^{sat}$ (only liquid phase exist)

<u>Common approach</u>: use the path from saturation to "sub-cooled" condition, i.e. look for the "Poynting Correction", $\mathcal{P}_{corr}$, such that

$$f_i^{liq} = \left(f_i^{liq}\right)^{sat} \mathcal{P}_{corr}$$

Recall general identity of fugacity,

$$\mu_i^{\textcircled{2}} - \mu_i^{\textcircled{1}} = RT \ln\left(\frac{\hat{f}_i^{\textcircled{2}}}{\hat{f}_i^{\textcircled{1}}}\right) = \int_{P^{\textcircled{1}}}^{P^{\textcircled{2}}} \bar{V}_i \; dP$$

- Pure component: $\mu_i = g_i$ and $\bar{V}_i = v_i = v_i^{liq}$.
- ②:condition at (T_{sys}, P_{sys}) and ①:condition at $\left(T_{sys}, P^{sat}\right)$, then: .
- Also, assume $v_i^{liq} \approx$ constant (i.e. incompressible),

$$RT \ln\left(\frac{f_i^{liq}}{\left(f_i^{liq}\right)^{sat}}\right) = v_i^{liq}\left(P_{sys} - P^{sat}\right)$$

or

$$\mathcal{P}_{corr} = \frac{f_i^{liq}}{\left(f_i^{liq}\right)^{sat}} = \exp\left(v_i^{liq} \, \frac{P_{sys} - P^{sat}}{RT}\right)$$

$$\rightarrow \quad f_i^{liq} = \phi_i^{sat} P_i^{sat} \exp\left(v_i \, \frac{P_{sys} - P^{sat}}{RT}\right)$$

B) <u>Liquid Mixture, Ideal Solution</u> (e.g. chemical behavior of all components similar):

These are solution where,

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

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

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

Implications for liquid solution:

$$\Delta_{mix} g^{\text{ideal soln}} = g - \sum_{i=1}^{N} x_i g_i$$

$$= \sum_{i=1}^{N} x_i (\mu_i^{\text{ideal soln}} - g_i) = RT \sum_{i=1}^{N} x_i \ \ln\left(\frac{\left(\hat{f}_i^{liq}\right)^{\text{ideal soln}}}{f_i^{liq}} \right)$$

Thus, we get the Lewis-Randall rule:

$$\ln\left(\frac{\left(\hat{f}_i^{liq}\right)^{\text{ideal soln}}}{f_i^{liq}} \right) = \ln(x_i) \qquad \rightarrow \qquad \left(\hat{f}_i^{liq}\right)^{\text{ideal soln}} = x_i f_i^{liq}$$

C) <u>Liquid Mixture, nonideal Solution</u> :

use another correction factor known as “activity coefficient”γ_i:

$$\hat{f}_i^{liq} = \gamma_i \left(\hat{f}_i^{liq}\right)^{\text{ideal soln}} = \gamma_i x_i f_i^{liq}$$

Where γ_i can be obtained using different methods and models (to be discussed next)

2. Activity Coefficients (γ_i)

A) Main approach:

- Use “excess property”=deviation of the mixing property of the real solution from mixing of ideal solutions

$$\begin{aligned} g^E &= \text{excess Gibbs energy} \\ &= \Delta_{mix}g - \Delta_{mix}g^{\text{ideal soln}} \\ &= \left(g - \sum_{i=1}^{N} x_i g_i\right) - RT\sum_{i=1}^{N} x_i \ln(x_i) \\ &= \sum_{i=1}^{N} x_i\,[\mu_i - g_i] - \sum_{i=1}^{N} x_i\,[RT\ln(x_i)] \\ &= \sum_{i=1}^{N} x_i\left[RT\ln\left(\frac{\hat{f}_i^{liq}}{f_i^{liq}}\right)\right] - \sum_{i=1}^{N} x_i\,[RT\ln(x_i)] \\ &= \sum_{i=1}^{N} x_i\left[RT\ln\left(\frac{\hat{f}_i^{liq}}{x_i f_i^{liq}}\right)\right] = \sum_{i=1}^{N} x_i\,[RT\ln(\gamma_i)] \end{aligned}$$

Or in terms of partial molar excess Gibbs energy, i.e. $\bar{G}_i^E = (\partial(n_{total}g^E)/\partial n_i)_{T,P,n_j\neq i}$

$$g^E = \sum_{i=1}^{N} x_i\,\bar{G}_i^E \qquad \rightarrow \qquad \bar{G}_i^E = RT\ln(\gamma_i)$$

Thus,

$$\gamma_i = \exp\left(\frac{\bar{G}_i^E}{RT}\right)$$

Q: So where does one get g^E ?

A: From real data and/or models of g^E: (see Table 7.2, page 438)

Types	Model for g^E
Margules (2-suffix)	Ax_1x_2
Margules (3-suffix, form 1)	$x_1x_2(A + B(x_1 - x_2))$
Margules (3-suffix, form 2)	$x_1x_2(A_{21}x_1 + A_{12}x_2)$
Van Laar	$x_1x_2AB/(Ax_1 + Bx_2)$
Wilson	$-RT\ \sum_i x_i \ln\left(x_i + \sum_{j\neq i}\Lambda_{ij}\,x_j\right)$
NTRL (non-random two-liquid)	$-RT\ x_1x_2(q_1 + q_2)$ where $q_1 = \frac{\tau_{21}e^{-\alpha\tau_{21}}}{x_1+x_2e^{-\alpha\tau_{21}}}$; $q_2 = \frac{\tau_{12}e^{-\alpha\tau_{12}}}{x_2+x_1e^{-\alpha\tau_{12}}}$

In addition, there are models based on molecular principles:

a) UNIQUAC (Universal Quasi-Chemical) : see Table 7.4 for model
b) UNIFAC (Universal Functional Activity Coefficient)

Partial List of Recommendations:

(based on S. Sandler, *Chemical, Biochemical and Engineering Thermodynamics 4th Ed.*", J. Wiley, 2006, p.475-476):

Let *NP*=nonpolar,*WP*=weakly polar, *SP*=strongly polar, *H2O*=water, *CA*=carboxylic acid

a) For *NP-NP*, *NP-WP*, *NP-SP*, *WP-WP* and *WP-SP* : all models adequate but UNIQUAC/UNIFAC and Wilson better for nonideal behaving solutions (except Wilson model not good for solutions with partially miscible liquid-liquid solutions)
b) For *SP-SP* and *H2O-SP*: UNIQUAC/UNIFAC has best correlation
c) For *H2O-NP* and *H2O-WP*: Wilson is not appropriate, other models need to add partial miscibility property into model, e.g. UNIFAC needs improved interaction parameters.
d) For *CA* solutions: Wilson appears best if mutually soluble. If not then UNIQUAC/UNIFAC, NTRL and van Laar should be adequate.

Example: Find the activity coefficient based on Margules 3-suffix, form 1 model for a binary mixture.

Solution:

First note that

$$g^E = x_1x_2(A + B(x_1 - x_2)) = -2Bx_1^3 + (3B - A)x_1^2 + (A - B)x_1$$

$$\frac{dx_1}{dn_2} = \frac{1}{n_1 + n_2}(-x_1)$$

$$\frac{dg^E}{dx_1} = -6Bx_1^2 + (6B - 2A)x_1 + (A - B)$$

$$\bar{G}_2^E = \frac{\partial}{\partial n_1}\left((n_1 + n_2)g^E\right) = g^E - \frac{dg^E}{dx_1}(x_1)$$

$$= 4Bx_1^3 + (A - 3B)x_1^2 = RT \ln \gamma_2$$

Interchanging roles of components,

$$\bar{G}_1^E = -4Bx_2^3 + (A + 3B)x_2^2 = RT \ln \gamma_1$$

Q: Are there some constraints on allowable models for g^E ?

A: Yes, the model should satisfy "thermodynamic consistency" condition, i.e. it should not violate the Gibbs-Duhem relation.

For each component i (with T, μ_i^o and $\left(\hat{f}_i^{liq}\right)^o$ fixed), along a path of changing composition,

$$\begin{aligned} d\mu_i &= RTd\left(\ln \hat{f}_i^{liq}\right) = RTd(\ln(\gamma_i x_i f_i)) \\ &= RTd(\ln(\gamma_i) + \ln(x_i) + \ln(f_i)) \\ &= RT\, d(\ln(\gamma_i)) + RT\frac{1}{x_i}dx_i + 0 \;\; (f_i \text{ does not change with composition}) \end{aligned}$$

Recall Gibbs-Duhem for μ_i's:

$$0 = x_1 d\mu_1 + x_2 d\mu_2 + \cdots + x_N d\mu_N$$

$$0 = x_1\left[RT\, d(\ln(\gamma_1)) + \frac{RT}{x_1}dx_1\right] + \cdots + x_N\left[RT\, d(\ln(\gamma_N)) + \frac{RT}{x_N}dx_N\right]$$

$$0 = (x_1\, d(\ln(\gamma_1)) + \cdots + x_N\, d(\ln(\gamma_N))) + d(x_1 + \cdots + x_N)$$

$$0 = x_1\, d(\ln(\gamma_1)) + \cdots + x_N\, d(\ln(\gamma_N))$$

Remark: This means only $(N-1)$ activity coefficients are independent values.

Example: Check whether the Margules 3-suffix, form 1 satisfies the thermodynamic consistency condition.

Recall the prior result,

$$\begin{aligned} RT\ln\gamma_1 &= -4Bx_2^3 + (A+3B)x_2^2 \\ &\rightarrow\;\; RTd\ln\gamma_1 = [-12Bx_2^2 + (2A+6B)x_2]\, dx_2 \\ RT\ln\gamma_2 &= 4Bx_1^3 + (A-3B)x_1^2 \\ &\rightarrow\;\; RTd\ln\gamma_2 = [(12Bx_1^2 + (2A-6B)x_1)]dx_1 \end{aligned}$$

With $x_1 = 1 - x_2$ and $dx_1 = -dx_2$,

$$RT\,[x_1 d\ln(\gamma_1) + x_2 d\ln(\gamma_1)]$$

$$\begin{aligned} &= [-12B(x_1x_2^2 + x_2x_1^2 - x_1x_2) + 2A(x_1x_2 - x_2x_1)]dx_2 \\ &= -12Bx_1x_2(x_2 + x_1 - 1)dx_2 = 0 \end{aligned}$$

→ thus, the Margules 3-suffix model is thermodynamically consistent.

Remark: Equation (7.50) used for "area test" is the based on consistency condition for a binary solution:

$$\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right)dx_1 = 0$$

→ should be used as a constraint when curve-fitting experimental data.