

CM 3230 Thermodynamics, Fall 2014

Lecture 26

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

A) Liquid of Pure Component i (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)

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

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

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

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

Recall general identity of fugacity,

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

- 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 (T_{sys}, P^{sat}) , then: .
- Also, assume $v_i^{liq} \approx \text{constant}$ (i.e. incompressible),

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

or

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

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

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

These are solution where,

$$\begin{aligned}\Delta_{mix}h^{\text{ideal soln}} &= 0 \\ \Delta_{mix}s^{\text{ideal soln}} &= -R \sum_{i=1}^N x_i \ln(x_i) \\ \rightarrow \Delta_{mix}g^{\text{ideal soln}} &= RT \sum_{i=1}^N x_i \ln(x_i)\end{aligned}$$

Implications for liquid solution:

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

Thus, we get the Lewis-Randall rule:

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

C) Liquid Mixture, nonideal Solution :

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

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

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. $\bar{G}_i^E = (\partial(n_{total}g^E)/\partial n_i)_{T,P,n_j \neq i}$

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

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	$-RT \sum_i x_i \ln(x_i + \sum_{j \neq i} \Lambda_{ij} x_j)$
NRTL (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

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

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

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

$$\begin{aligned} \bar{G}_2^E &= \frac{\partial}{\partial n_1} ((n_1 + n_2)g^E) = g^E - \frac{dg^E}{dx_1} (x_1) \\ &= 4Bx_1^3 + (A - 3B)x_1^2 = RT \ln \gamma_2 \end{aligned}$$

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 $(\hat{f}_i^{liq})^o$ fixed), along a path of changing composition,

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

Recall Gibbs-Duhem for μ_i 's:

$$\begin{aligned} 0 &= x_1 d\mu_1 + x_2 d\mu_2 + \dots + x_N d\mu_N \\ 0 &= x_1 \left[RT d(\ln(\gamma_1)) + \frac{RT}{x_1} dx_1 \right] + \dots + x_N \left[RT d(\ln(\gamma_N)) + \frac{RT}{x_N} dx_N \right] \\ 0 &= (x_1 d(\ln(\gamma_1)) + \dots + x_N d(\ln(\gamma_N))) + d(x_1 + \dots + x_N) \\ 0 &= x_1 d(\ln(\gamma_1)) + \dots + x_N d(\ln(\gamma_N)) \end{aligned}$$

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,

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

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

$$\begin{aligned} &RT [x_1 d \ln(\gamma_1) + x_2 d \ln(\gamma_2)] \\ &= [-12B(x_1 x_2^2 + x_2 x_1^2 - x_1 x_2) + 2A(x_1 x_2 - x_2 x_1)] dx_2 \\ &= -12Bx_1 x_2 (x_2 + x_1 - 1) dx_2 = 0 \end{aligned}$$

→ 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.