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

A) Liquid of Pure Component \( i \) (Note: \( P_{\text{sys}} \geq P_{\text{sat}} \))

Case 1: \( P_{\text{sys}} = P_{i \text{sat}} \)

\[
(f_i^{\text{liq}})^{\text{sat}} = (f_i^{\text{vap}})^{\text{sat}} = \phi_i^{\text{sat}} P_i^{\text{sat}}
\]

Case 2: \( P_{\text{sys}} > P_{\text{sat}} \) (only liquid phase exist)

*Common approach*: use the path from saturation to “sub-cooled” condition, i.e. look for the “Poynting Correction”, \( P_{\text{corr}} \), such that

\[
f_i^{\text{liq}} = (f_i^{\text{liq}})^{\text{sat}} P_{\text{corr}}
\]

Recall general identity of fugacity,

\[
\mu_i^{(2)} - \mu_i^{(1)} = RT \ln \left( \frac{f_i^{(2)}}{f_i^{(1)}} \right) = \int_{P_i^{(1)}}^{P_i^{(2)}} V_i dP
\]

- Pure component: \( \mu_i = g_i \) and \( V_i = v_i^{\text{liq}} \).
- (2):condition at \((T_{\text{sys}}, P_{\text{sys}})\) and (1):condition at \((T_{\text{sys}}, P_{\text{sat}})\), then:

- Also, assume \( v_i^{\text{liq}} \approx \text{constant} \) (i.e. incompressible),

\[
RT \ln \left( \frac{f_i^{\text{liq}}}{(f_i^{\text{liq}})^{\text{sat}}} \right) = v_i^{\text{liq}} (P_{\text{sys}} - P_{\text{sat}})
\]

or

\[
P_{\text{corr}} = \frac{f_i^{\text{liq}}}{(f_i^{\text{liq}})^{\text{sat}}} = \exp \left( v_i^{\text{liq}} \frac{P_{\text{sys}} - P_{\text{sat}}}{RT} \right)
\]

\[
\Rightarrow f_i^{\text{liq}} = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left( v_i \frac{P_{\text{sys}} - P_{\text{sat}}}{RT} \right)
\]
B) Liquid Mixture, Ideal Solution (e.g. chemical behavior of all components similar):
These are solutions where,

\[ \Delta_{mix} h^{ideal soln} = 0 \]

\[ \Delta_{mix} s^{ideal soln} = -RT \sum_{i=1}^{N} x_i \ln(x_i) \]

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

Implications for liquid solution:

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

\[ = \sum_{i=1}^{N} x_i (\mu_i^{ideal soln} - g_i) = RT \sum_{i=1}^{N} x_i \ln \left( \frac{f_i^{liq}}{f_i^{liq}} \right)^{ideal soln} \]

Thus, we get the Lewis-Randall rule:

\[ \ln \left( \frac{f_i^{liq}}{f_i^{liq}} \right)^{ideal soln} = \ln(x_i) \rightarrow \left( f_i^{liq} \right)^{ideal soln} = x_i f_i^{liq} \]

C) Liquid Mixture, nonideal Solution:

use another correction factor known as “activity coefficient” \( \gamma_i \):

\[ f_i^{liq} = \gamma_i \left( f_i^{liq} \right)^{ideal soln} = \gamma_i x_i f_i^{liq} \]

Where \( \gamma_i \) can be obtained using different methods and models (to be discussed next)
2. Activity Coefficients \( (\gamma_i) \)

A) Main approach:

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

\[
g^E = \text{excess Gibbs energy} \\
= \Delta_{\text{mix}} g - \Delta_{\text{mix}} g_{\text{ideal soln}} \\
= \left( g - \sum_{i=1}^{N} x_i g_i \right) - RT \sum_{i=1}^{N} x_i \ln(x_i) \\
= \sum_{i=1}^{N} x_i [\mu_i - g_i] - \sum_{i=1}^{N} x_i [RT \ln(x_i)] \\
= \sum_{i=1}^{N} x_i \left[ RT \ln \left( \frac{f_i^{\text{liq}}}{x_i f_i^{\text{liq}}} \right) \right] - \sum_{i=1}^{N} x_i [RT \ln(x_i)] \\
= \sum_{i=1}^{N} x_i \left[ RT \ln \left( \frac{f_i^{\text{liq}}}{x_i f_i^{\text{liq}}} \right) \right] = \sum_{i=1}^{N} x_i \left[ RT \ln(\gamma_i) \right]
\]

Or in terms of partial molar excess Gibbs energy, i.e. \( \bar{g}^E_i \):

\[
g^E = \sum_{i=1}^{N} x_i \bar{g}^E_i \quad \rightarrow \quad \bar{g}^E_i = RT \ln(\gamma_i)
\]

Thus,

\[
\gamma_i = \exp \left( \frac{\bar{g}^E_i}{RT} \right)
\]

Q: So where does one get \( g^E \) ?

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

<table>
<thead>
<tr>
<th>Types</th>
<th>Model for ( g^E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margules (2-suffix)</td>
<td>( Ax_1 x_2 )</td>
</tr>
<tr>
<td>Margules (3-suffix, form 1)</td>
<td>( x_1 x_2 (A + B(x_1 - x_2)) )</td>
</tr>
<tr>
<td>Margules (3-suffix, form 2)</td>
<td>( x_1 x_2 (A_{21} x_1 + A_{12} x_2) )</td>
</tr>
<tr>
<td>Van Laar</td>
<td>( x_1 x_2 AB / (Ax_1 + Bx_2) )</td>
</tr>
<tr>
<td>Wilson</td>
<td>( -RT \sum_i x_i \ln(x_i + \sum_{j \neq i} A_{ij} x_j) )</td>
</tr>
<tr>
<td>NTRL (non-random two-liquid)</td>
<td>( -RT x_1 x_2 (q_1 + q_2) ) ( \text{where } q_1 = \frac{e^{\tau_{21}} - e^{\tau_{21}}}{x_1 + x_2 e^{\tau_{21}}}; ) ( q_2 = \frac{e^{\tau_{12}} - e^{\tau_{12}}}{x_2 + x_1 e^{\tau_{12}}} )</td>
</tr>
</tbody>
</table>
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:**


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

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

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

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

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

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

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 \( T, \mu_i^0 \) and \( (\gamma_i^{liq})^0 \) fixed), along a path of changing composition,

\[
d\mu_i = RT d\ln(\gamma_i^{liq}) = RT d(\ln(y_i x_i)) \\
= RT d(\ln(y_i) + \ln(x_i) + \ln(f_i)) \\
= RT d(\ln(y_i)) + RT \frac{1}{x_i} dx_i + 0 \quad (f_i \text{ does not change with composition})
\]

Recall Gibbs-Duhem for \( \mu_i \)'s:

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

\[
0 = x_1 \left[ RT d(\ln(y_1)) + \frac{RT}{x_1} dx_1 \right] + \cdots + x_N \left[ RT d(\ln(y_N)) + \frac{RT}{x_N} dx_N \right]
\]

\[
0 = (x_1 d(\ln(y_1)) + \cdots + x_N d(\ln(y_N))) + d(x_1 + \cdots + x_N)
\]

\[
0 = x_1 d(\ln(y_1)) + \cdots + x_N d(\ln(y_N))
\]

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,

\[
RT \ln y_1 = -4Bx_2^3 + (A + 3B)x_2^2 \\
\rightarrow RT d \ln y_1 = [-12Bx_2^2 + (2A + 6B)x_2] dx_2 \\
RT \ln y_2 = 4Bx_1^3 + (A - 3B)x_1^2 \\
\rightarrow RT d \ln y_2 = [(12Bx_1^2 + (2A - 6B)x_1)] dx_1
\]

With \( x_1 = 1 - x_2 \) and \( dx_1 = -dx_2 \),

\[
RT \left[ x_1 d \ln(y_1) + x_2 d \ln(y_1) \right]
\]

\[
= [-12B(x_1x_2^2 + x_2x_1^2 - x_1x_2) + 2A(x_1x_2 - x_2x_1)]dx_2 \\
= -12Bx_1x_2(x_2 + x_1 - 1)dx_2 = 0
\]

\( \Rightarrow \) 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:

\[
\int_0^1 \ln \left( \frac{y_1}{y_2} \right) dx_1 = 0
\]

\( \Rightarrow \) should be used as a constraint when curve-fitting experimental data.