Lectures 8

Phase Equilibrium Calculations

O'Connell & Haile
Chapter 10.1-10.2

Topics:

- Setting up phase equilibrium problems
- Methods
  - Phi-Phi
  - Gamma-Phi
    - Standard states
      - Lewis-Randall & Henry's Law

SOLVING PHASE EQUILIBRIA

The PSALMS approach:

1. What is to be solved for; what is known; Is problem well-posed? (PS)
2. Choose the ideality & nonideality (ALM)
3. Set strategy for solving (S)

General equilibrium criteria	⇒	Situation-specific equilibrium criteria	⇒	Particular methods of implementation
$f_i' = f_i'' = \ldots$		*FFF*	⇒	Solve & Check

Phase Equilibrium Relations

2-phase problems are $\mathcal{F}$ in 2*C* variables ($T,P,\{x^\alpha\},\{x^\beta\}$) with $\{x^\alpha\}$, $\{x^\beta\}$ = phase compositions, not overall

Gibbs Phase Rule: total variables - equations = independent variables

For 2-phase ($\mathcal{P}$ = 2) $\mathcal{F} = C + 2 - \mathcal{P} = C$

Thus, must solve *C* equations in *C* variables

- Write always true $f_i^\alpha = f_i^\beta$ $i = 1, \ldots, C$
- Select FFF for each component in phases
- Select models for properties in FFF
- Provide required information:
  - Values for independent variables
  - Model parameters & SS (for FFF #2-5
  - Solve for dependent variables & check

2-PHASE VLE METHODS

"Phi-Phi" - FFF# 1 for components in both phases $y_i\varphi_i^V P = x_i\varphi_i^L P \Rightarrow y_i/x_i = \varphi_i^L/\varphi_i^V$

Used for all fluid phases (not solids)Fig. 10.1

Advantages:

- No model (γ, ϕ) mismatch at critical point (ϕ same for both phases)
- No standard state decisions needed

Disadvantages:

- EoS models explicit in v^L, not P, *i.e.*, $\varphi_i^L(T, v^L, \{x\})$
- Complex EoS evaluations of φ_i^V, φ_i^L & derivatives from multiple v roots

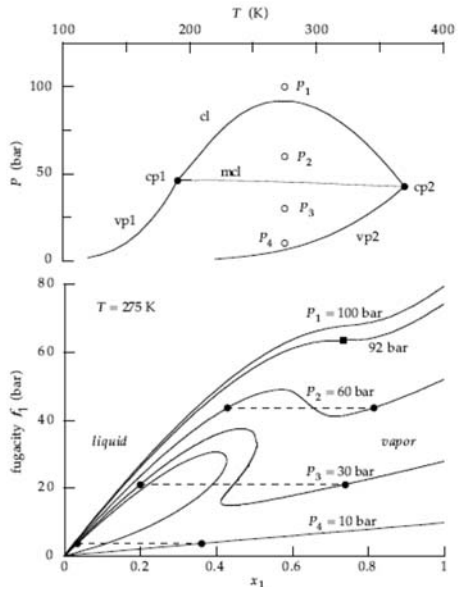


Figure 10.1

"Gamma-Phi" -Use FFF# 1 for vapor
FFF#2 / FFF#3 / FFF#4 / FFF#5 for liquid

$$y_i \varphi_i^V(T,P,\{y\})P = x_i \gamma_i(T,\{x\}) f_1^o(T) \exp\left(\int_{P_i^o}^{P} \frac{\bar{V}_i(T,\pi,\{x\})}{RT} d\pi\right)$$

Simultaneously match all fugacities for phase equilibria (Fig. 10.2 binary)

Advantage:
- **Accounts separately for *P* domination of vapor, {*x*} domination of liquid**

Disadvantages:
- **Mismatch at critical**
- **Requires decision about & data for standard state fugacity,** $f_1^o(T;P_i^o)$

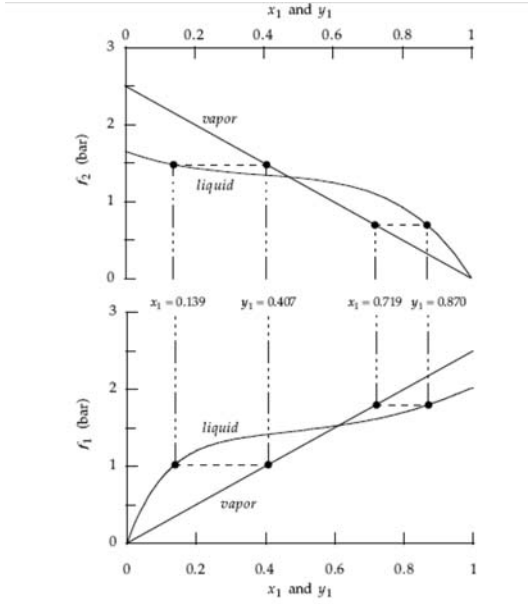


Figure 10.2

"Gamma-Gamma"- FFF# 2-5 for condensed phases (Ignore *P* dependence)

$$x_i^\alpha \gamma_i^\alpha(T,\{x^\alpha\}) f_i^{o\alpha}(T) = x_i^\beta \gamma_i^\beta(T,\{x^\beta\}) f_i^{o\beta}(T)$$

Cancel standard state fugacities if same state

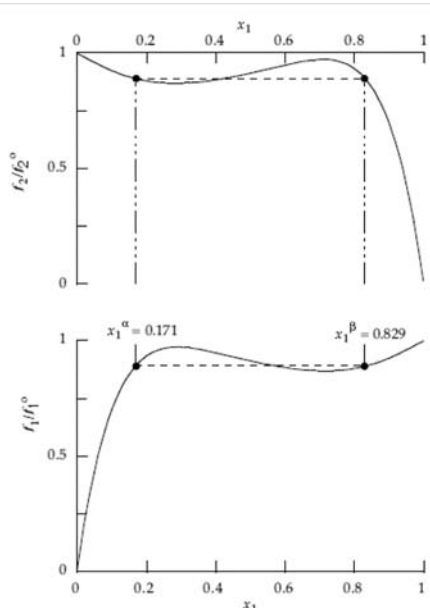
$$f_i^{o\alpha}(T) = f_i^{o\beta}(T)$$

$$\Rightarrow x_i^\alpha / x_i^\beta = \gamma_i^\beta(T,\{x^\beta\}) / \gamma_i^\alpha(T,\{x^\alpha\})$$

***All* behavior in $\gamma_i(T,\{x\})$ from g^E (*T*,{*x*}); some models will not work**

Simultaneously match all fugacities for phase equilibria (Fig. 10.3 binary)

Figure 10.3



THE "STANDARD STATE" (SS) I.

Ideal Solution gives $f_i^{is}(T, P_i^o, \{x\}) = x_i f_i^o(T; P_i^o)$

***f₁* vs. *x₁* has** $f_i^o(T; P_i^o)$ **= intercept at *xᵢ* = 1**

Figure 10.5

Common SS choices made for *convenience*

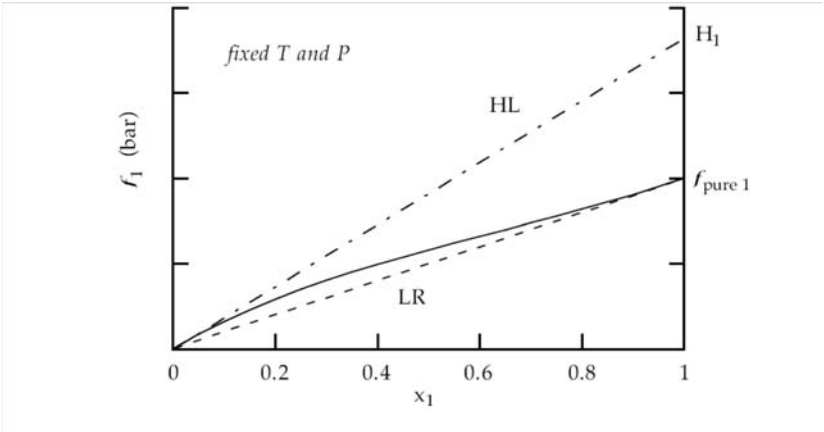
Lewis -Randall (pure component) has $f_i^o = f_{pure\ i}$ (real or hypothetical) so

$$f_i^{LR}(T, P_i^o, \{x\}) = x_i f_{pure\ i}(T; P_i^o)$$

Variations of γ_i for different FFF, but always

$$\lim_{x_i \to 1}(\gamma_i) = 1 \text{ and } \lim_{x_i \to 1}\left(\frac{\partial \gamma_i}{\partial x_i}\right)_{T,P} = 0$$

Figure 10.5



Note approximations for VLE (Sec. 10.2.2)

Choose LR SS, $P^o_i = P_i^s(T)$

$$f_i^{LR} = f_{pure\ i}^{sL}(T, P_i^s) = f_{pure\ i}^{sV}(T, P_i^s) = \varphi_{pure\ i}^s P_i^s$$

Assume "low" *P* (FFF# 2-5 equivalent)

$$x_i \gamma_i \varphi_{pure\ i}^s P_i^s \cong y_i \varphi_i P$$

Assume "lower" *P* so have ^{ig} ($\varphi_i = \varphi_{pure\ i}^s = 1$),

$$x_i \gamma_i P_i^s \approx y_i P$$

Assume ^{is} ($\gamma_i = 1$), Raoult's "Law", $x_i P_i^s \sim y_i P$

Note: $P = \sum_{i=1}^{C} y_i P \cong \sum_{i=1}^{C} x_i \gamma_i \varphi_i^s P_i^s / \varphi_i \sim k \sum_{i=1}^{C} x_i P_i^s$

Needs:

***T*; {*x*}; EoS for** φ_i^s, φ_i**;** $g^E(T, \{x\})$ **for** $\{\gamma\}$**;** $\{P^s(T)\}$

THE "STANDARD STATE" (SS) II.

If component k only found at small x_k (e.g., $T_k^c < T$ (gas), $T_k^{melt} > T$ (solid), $f^o_{pure\ i}$ = ?

Henry's Law ("infinite dilution") - $f_i^o = H_{1s}$ (Fig. 10.5)

(always hypothetical) so

$$f_i^{HL}(T, P_i^o, \{x\}) = x_i H_i(T; P_i^o)$$

1 option for pure solvent (binary system)

2 options for >2 solvent components (ternary+)

"Solute-free" $\{x^{sf}\}$ is set of mole fractions without "solutes" (k) $P_k^o = P_{sf}^s$

(saturation pressure over solute-free liquid)

$$H_{ks}(T, P_{sf}^s, \{x^{sf}\}) \equiv \lim_{x_k \to 0}\left(\frac{f_k}{x_k}\right)_{T, P_{sf}^s, x^{sf}}$$

Pressure correction of FFF# 3 has $\exp\left(\int_{P_{sf}^s}^{P} \frac{\bar{V}_{ks}^{\infty}}{RT} d\pi\right)$

FFF# 4 has $\lim_{x_k \to 0} \gamma_k^* = 1$

$$f_k(T, P, \{x\}) = x_k \gamma_k^*(T, P, \{x\}) H_{ks}(T, \{x^{sf}\})$$

$\bar{V}_{ks}^{\infty}, H_{ks}(T, \{x^{sf}\})$ **depend on solvent state**

"Reference Solvent" Henry's Constant for solute k with solvent r, $H_{kr} \equiv \lim_{x_r \to 1}\left(\frac{f_k}{x_k}\right)_{T,P}$

Pressure correction for FFF #3 is $\exp\left(\int_{P_{sf}^s}^{P} \frac{\bar{V}_{kr}^{\infty}}{RT} d\pi\right)$

FFF# 4 has $\lim_{x_r \to 1} \gamma_k^+ = 1$, $\lim_{x_{j \neq r} \to 1} \gamma_k^+ = H_{kj}(T)/H_{kr}(T)$

$$f_k(T, P, \{x\}) = x_k \gamma_k^+(T, P, \{x\}) H_{kr}(T)$$

THE "STANDARD STATE" (SS) III.

Note various γ_i^* & γ_i^+ **for FFF but always**

$$\lim_{x_k \to 0} \gamma_k^* = 1 \text{ and } \lim_{x_k \to 0}\left(\frac{\partial \gamma_k^*}{\partial x_k}\right)_{T,P} \neq 0$$

When $\gamma_k^*, \gamma_k^+ \neq 1$**, solutes "interact";**

$\gamma_k^* = 1 \Rightarrow$ **solute "alone" in solvent**

Note levels of approximation for VLE for HL* SS, $P^o_k = P_s^s(T, \{x^{sf}\})$; HL$^+$ SS, $P^o_k = P_r^s(T)$

$$f_k^{oHL} = H_{kr}(T, P_r^s) \text{ or } H_{ks}(T, P_s^s, \{x^{sf}\})$$

Assume "low" P (FFF# 2-5 equivalent)

$$x_k \gamma_k^* H_{ks} = x_k \gamma_k^+ H_{kr} \cong y_k \varphi_k P \qquad x_i \gamma_i \varphi_i^s P_i^s \cong y_i \varphi_i P$$

Assume dilute k but mixed nonideal solvents

$$x_k H_{ks} = x_k \gamma_k^+ H_{kr} \approx y_k \varphi_k P \qquad x_i \gamma_i \varphi_i^s P_i^s \approx y_i \varphi_i P$$

If assume ^{ig} ($\varphi_i = \varphi_k = 1$),

$$x_k H_k = x_k \gamma_k^+ H_{kr} \approx y_k P \qquad x_i \gamma_i P_i^s \approx y_i P$$

If assume ^{is} ($\gamma_i = 1 = \gamma_k^+$), get Henry's" Law"

$$x_k H_k = x_k \gamma_k^+ H_{kr} \approx y_k P \qquad x_i P_i^s \approx y_i P$$

Note: $P = \sum_{i=1}^{C} y_i P \cong \sum_k x_k \gamma_k^* H_k / \varphi_k + \sum_i x_i \gamma_i \varphi_i^s P_i^s / \varphi_i$

Need T; $\{x\}$; EoS for φ_i^s, φ_i; $\{H_k(T)\}, \{P^s(T)\}$;

$g^{E*}(T, \{x\})$ **for** $\{\gamma^*\}, \{\gamma\}$ **or** $g^{E+}(T, \{x\})$ **for** $\{\gamma^+\}, \{\gamma\}$

Often need P dependence in f_i^L, choose FFF #4 or #5

The Fugacity is the Same Regardless of the Formula

Example 10.2.6 shows that with same g^E model & consistent f_i^0, get same fugacity, *i.e.*,

$$
\begin{aligned}
f_1 &= x_1 \gamma_1(T, \{x\})\, f_{pure1}(T) \\
&= x_1 \gamma_1^*(T, \{x\})\, H_{1s}(T, \{x^{sf}\}) \\
&= x_1 \gamma_1^+(T, \{x\})\, H_{1r}(T)
\end{aligned}
$$