Lecture 3.2

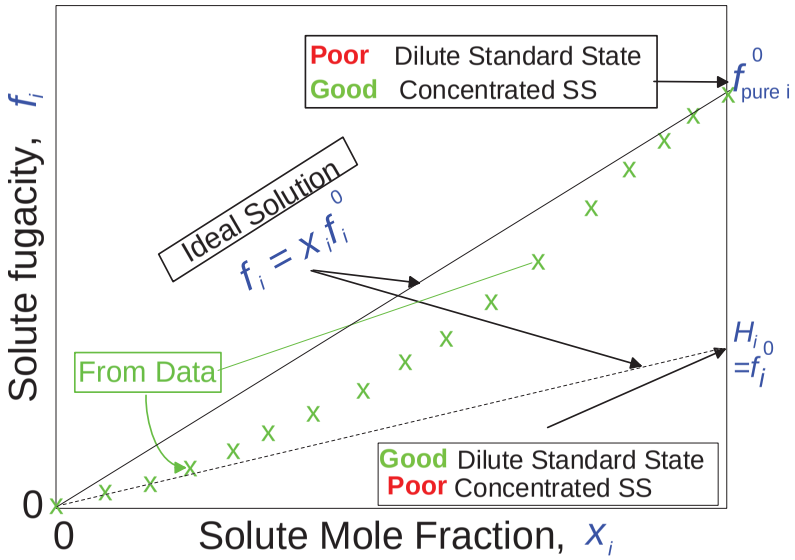
Properties Relative to Ideal Solution

O'Connell & Haile
Chapter 5

Topics:

Ideal Solutions: Properties & Standard States
Deviations from Ideal Solution:
- **Difference - Excess Properties**
- **Ratio - Activity Coefficient**

Equations of State
- **Using for Values of Conceptuals**
- **Some Models & Comparisons**



IDEAL SOLUTIONS

Ideal gases have no intermolecular forces
Ideal solutions have same intermolecular forces (in liquids, overall attractive)
Get simple composition effect, *e.g.*, fugacity

$$f_i^{is}(T,P,\{x\}) = \varphi_i^{is}(T,P)\, f_i^{ig}(T,P,\{x\}) = x_i \varphi_i^{is}(T,P)\, P \qquad \textbf{(5.1.1)}$$

Define *standard state* ° where

$$f_i^o(T,P) \equiv \phi_i^{is}(T,P)P = \phi_i^o(T,P)P$$

so $f_i^{is}(T,P,\{x\}) = x_i\, f_i^o(T,P)$ **(5.1.2)**

Convenient if can get $f_i^o(T,P)$**,**
e.g., $\approx P_i^{sat}(T)$ **,** $\lim_{x_i \to 0}(y_i \varphi_i P / x_i) \equiv H_i$

Traditional approach of condensed phases; used less now with current EoS models
Sec. 5.1: *is* total, partial molar properties
First Law Properties, *e.g.*,

$$v^{is}(T,P,\{x\}) = \sum_{i=1}^{C} x_i v_i^o(T,P) \qquad \textbf{(5.1.14)}$$

$$\overline{V}_i^{is}(T,P,\{x\}) = v_i^o(T,P) \qquad \textbf{(5.1.8)}$$

Second Law Properties, *e.g.*,

$$s^{is}(T,P,\{x\}) = \sum_{i=1}^{C} x_i s_i^o(T,P) - R\sum_{i=1}^{C} x_i \ln x_i > \sum_{i=1}^{C} x_i s_i^o(T,P) \qquad \textbf{(5.1.18)}$$

$$\overline{G}_i(T,P,\{x\}) = g_i^o(T,P) + RT\ln x_i < g_i^o(T,P) \qquad \textbf{(5.1.7)}$$

Also defines <u>mixing</u> properties

$$F^m(T,P,\{N\}) \equiv F(T,P,\{N\}) - \sum_{i=1}^{C} N_i f_i^0(T,P) \quad \textbf{(5.1.21)}$$

Initial illustrative purposes <u>only</u>, will use standard state as

- → **pure *i***
- → **in "natural" phase (liquid, solid)**
- → **<u>mixed system *T, P*</u>**

Then all properties set such that

$$f_i^o(T,P) \Rightarrow f_{pure\ i}(T,P)$$

<u>DEVIATIONS FROM IDEAL SOLUTIONS</u>
<u>I. DIFFERENCES</u>

Difference Measures - Excess Properties

$$F^E(T,P,\{N\}) \equiv F(T,P,\{N\}) - F^{is}(T,P,\{N\}) \quad \textbf{(5.2.1)}$$

First Law properties ($F = V, U, H$):

$$F^E = F^m \qquad \textbf{(5.2.3)-(5.2.5)}$$

Second Law properties ($F = S, A, G$):

$$F^E = F^m + K_F \sum_{i=1}^{C} N_i \ln x_i, \qquad \textbf{(5.2.6)-(5.2.8)}$$

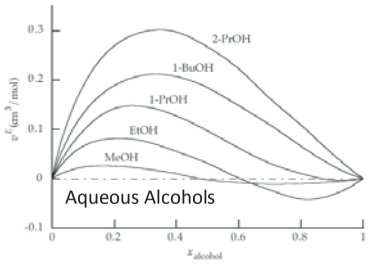
where $K_F = R, (-RT)$

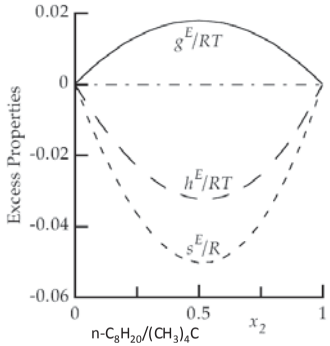
Partial Molar *Excess* Properties exist

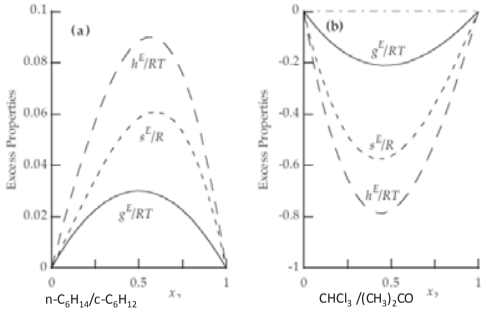
$$\overline{G}_i^E(T,P,\{x\}) = \left(\frac{\partial \boldsymbol{G}^E}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \overline{G}_i(T,P,\{x\}) - \overline{G}_i^{is}(T,P,\{x\})$$

Examples of $V^E, G^E, H^E, S^E = (H^E - G^E)/T$

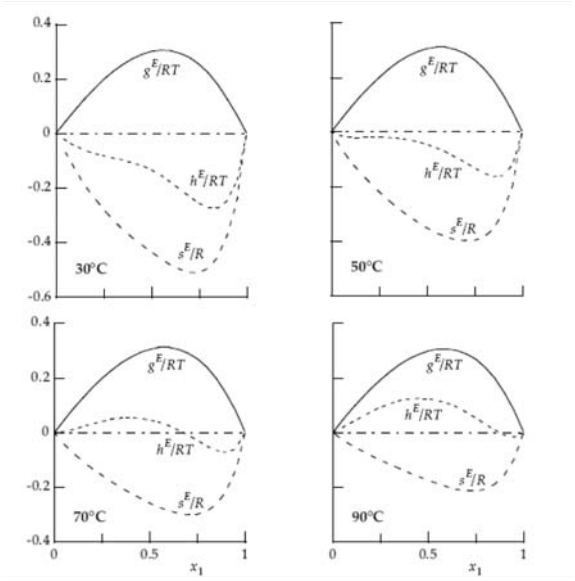
Figs. 5.1-4: Nature shows many variations!







H_2O/C_2H_5OH at various *T*



Do not normally define F^E for gases
Section 5.3 shows F^E relations for virial EoS
Only for pedagogical not practical purposes!

Relationship of ^{E} and ^{res} is

$$f^E(T,P,\{x\}) = f^{res}(T,P,\{x\}) - \sum_{i=1}^{C} x_i f_i^{o,res}(T,P) \quad \textbf{(5.3.1)}$$

Models of f^{res} give models for f^E & reverse

But must have a model in one form or the other

DEVIATIONS FROM IDEAL SOLUTIONS
II. RATIOS

Activity, a_i ; relates desired state to standard state

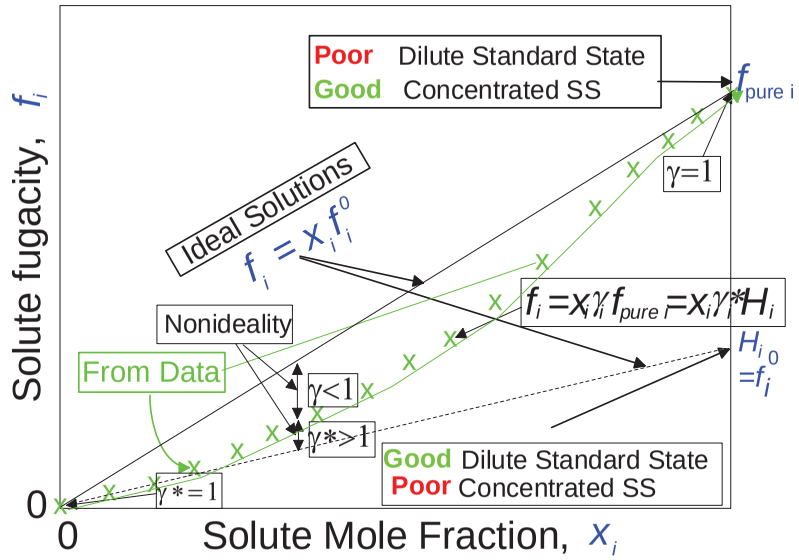
$$\overline{G}_i(T,P,\{x\}) - \overline{G}_i^o(T,P_i^o) = RT\ln\frac{f_i(T,P,\{x\})}{f_i^o(T,P_i^o)} \quad \textbf{(5.4.1&3)}$$
$$\equiv RT\ln a_i(T,P,\{x\};P_i^o,f_i^o)$$

Activity coefficient, γ_i, ratio deviation

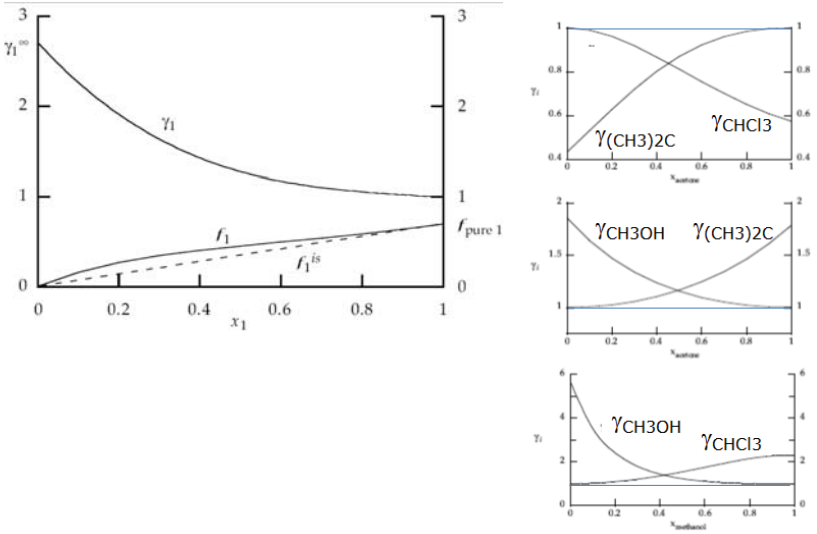
$$\gamma_i(T,P,\{x\};P_i^o,f_i^o) \equiv f_i(T,P,\{x\})/f_i^{is}(T,P_i^o,\{x\}) \quad \textbf{(5.4.5&7)}$$
$$= a_i(T,P,\{x\};P_i^o,f_i^o)/x_i$$
$$= f_i(T,P,\{x\})/x_i\, f_i^o(T,P_i^o)$$

γ_i has Gibbs-Helmholtz, Gibbs-Duhem Equations

Nonlinearity of fugacity is nonideality of γ_i



Figures 5.6-7 show behaviors of γ_i



Activity Coefficient Relations

Partial molar excess properties

$$\overline{G}_i^E = RT\ln\gamma_i \qquad \textbf{(5.4.10)}$$

***P, T* derivatives** **(5.4.17-18)**

Fugacity coefficients,

$$\gamma_i(T,P,\{x\};f_i^o(T,P_i^o)) = \frac{\varphi_i(T,P,\{x\})P}{\varphi_i^o(T,P_i^o)P_i^o} \qquad \textbf{(5.5.4)}$$

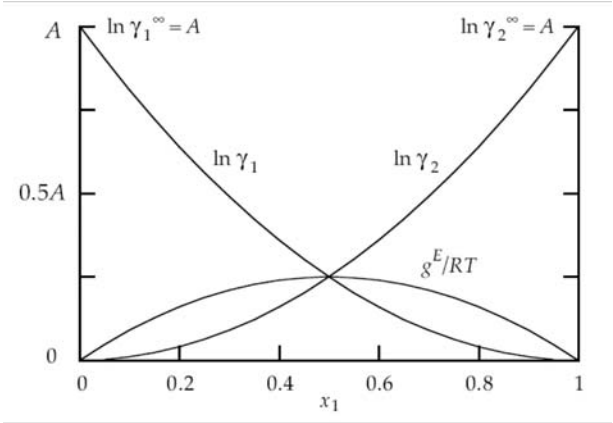
Cases:

$$P_i^o \equiv P \Rightarrow RT\ln\gamma_i(T,P,\{x\};f_i^o(T,P)) = \overline{G}_i^E(T,P,\{x\}) \qquad \textbf{(5.4.10)}$$

$$P_i^o \neq P, \varphi_i(T,P,\{x\}) \Rightarrow RT\ln\gamma_i(T,P,\{x\};f_i^o(T,P_i^o)) = \overline{G}_i(T,P,\{x\}) - \overline{G}_i^{is}(T,P^o,\{x\}) \qquad \textbf{(5.4.9)}$$

$$P_i^o \neq P, \varphi_i(T,P^o,\{x\}) \Rightarrow RT\ln\gamma_i(T,P^o,\{x\};f_i^o(T,P_i^o)) = \overline{G}_i^E(T,P^o,\{x\}) \qquad \textbf{(5.5.12)}$$

Figure 5.8



Note: Symmetry in g^E & $\ln\gamma_1^\infty = \ln\gamma_2^\infty =$

Has implications for V^E, H^E, {x} variations

SIMPLE EXCESS FUNCTION MODELS

Empirical series expressions for binary g^E

Redlich-Kister Expansion

$$\frac{g^E}{RTx_1x_2} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots \qquad \textbf{(5.6.3)}$$

where *A, B, C* parameters (from data fits)

Note: Pure component limit of g^E=0 $\Rightarrow$ SS

For *B, C, . . .* = 0, becomes

"Porter" Equation(1 parameter/binary)

$$g^E(T,P,x_1;f_{pure\,i})/RT = A(T,P)x_1x_2 \Rightarrow \ln\gamma_1 = Ax_2^2$$

Note: Sign of *A* can be + or - ; Table E.1

For *C, . . .* = 0, becomes "Margules" Equation (2 parameters per binary)

$$g^E(T,P,x_1;f_{pure\,i})/RT = [A_1(T,P)x_1 + A_2(T,P)x_2]x_1x_2 \Rightarrow$$

$$\ln\gamma_1 = [A_2 + 2x_1(A_1 - A_2)]x_2^2$$

$$\ln\gamma_2 = [A_1 + 2x_2(A_2 - A_1)]x_1^2$$

Note: Symmetry in A_i dependence but asymmetry in composition behavior;

$\gamma_2^\infty =$, $\gamma_1^\infty =$ **Values in Table E.2**

Multicomponent systems (*C* > 2)

assume g^E pairwise additive

$$g^E(T,P,\{x\}) = \sum_i \sum_j g_{ij}^E(T,P,\{x\}_{ij})$$

SEMITHEORETICAL MODELS

"Local composition" models (2,3 params per pair -Wilson, NRTL, UNIQUAC)

Wilson Equation for multicomponents

$$\frac{g^E(T,\{x\};f^o_{pure\,i})}{RT} = -\sum_{i=1}^{C} x_i \ln\left(\sum_{j=1}^{C} x_j \Lambda_{ij}(T)\right) \Rightarrow$$

Binary

$$\ln\gamma_1(T,x_1) = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left[\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}\right]$$

Note:asymmetric $\Lambda_{ij} \neq \Lambda_{ji}, \Lambda_{ii} = 1$**, no *P* effect**

$\ln\gamma_1^\infty = 1 - \ln\Lambda_{12} - \Lambda_{21}$**, interchange 1 & 2 for** γ_2^∞

"Theory" for *T* variation, H^E:

$\Lambda_{ij} = \frac{\rho_{purei}}{\rho_{purej}}\exp\left(\frac{-\lambda_{ij}}{RT}\right), \lambda_{ij} \neq \lambda_{ji}$ **constant or *f* (*T*)**

Commonly used in process simulators