Lectures 11

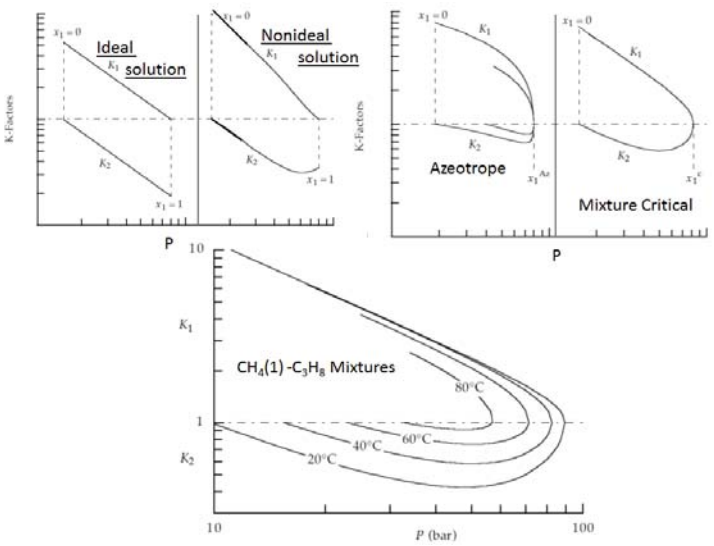
Applications of Thermodynamics I.

O'Connell & Haile
Chapter 12.1-12.2

Topics:

- **Vapor-liquid Equilibria**
  - **K-factors, relative volatility**
- **Liquid-liquid Equilibria**
  - **Distribution coefficient**
- **Solubility**
  - **Gases in liquids**
  - **Solids in liquids**
  - **Near-critical systems**

Figures 12.1-3



SAMPLE APPLICATIONS I. (CHAPTER 12)

Vapor-Liquid Equilibria

Rearrange $f_i^v = f_i^l$ for *K*-factor, K_i, from various FFF See Figures 12.1-3

$$K_i \equiv \frac{y_i}{x_i} = \frac{\phi_i^l(T,v^l,\{x\})}{\phi_i^v(T,v^v,\{y\})} = \frac{\gamma_i(T,\{x\})f_i^{oL}(T)\exp\left(\int_{P_i^o}^{P}\left.\frac{\bar{V}_i(T,\pi,\{x\})}{RT}\right|_{T,\{x\}}d\pi\right)}{\phi_i^v(T,P,\{y\})P}$$

FFF#1 & #1 **FFF#1 & #5**

<u>Use</u> FFF#1 & #1 but <u>understand</u> with FFF#1 & #5 See Figures 12.1-3

Relative volatility, α_{ij}

$$\alpha_{ij} \equiv \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j} = \frac{\phi_i^l(T,v^l,\{x\})\phi_j^v(T,v^v,\{y\})}{\phi_j^l(T,v^l,\{y\})\phi_i^v(T,v^v,\{y\})} \quad \text{FFF\#1 \& \#1}$$

$$= \frac{\gamma_i(T,\{x\})}{\gamma_j(T,\{x\})}\frac{f_i^{ol}(T)}{f_j^{ol}(T)}\exp\left(\int_{P_i^o}^{P}\frac{\bar{V}_i}{RT}d\pi - \int_{P_j^o}^{P}\frac{\bar{V}_j}{RT}d\pi\right)\frac{\phi_j^v(T,v^v,\{y\})}{\phi_i^v(T,v^v,\{y\})}$$

FFF#1 & #5 See Figure 12-4.

Low *P* estimates for $\phi - \phi$, Lewis-Randall SS

- **$\cong$ Ignore Poynting Correction,**
- **$\approx$ Assume Lewis Rule $[\phi_i^v(T,v^v,\{y\}) \approx \phi^s_{pure\,i}(T,v^v)]$**
- **$\sim$ Assume ideal solution**

$$K_i \equiv \frac{y_i}{x_i} = \frac{\phi_i^l(T,v^l,\{x\})}{\phi_i^v(T,v^v,\{y\})} \cong \frac{\gamma_i(T,\{x\})\phi_i^s(T)P_i^s(T)}{\phi_i^v(T,P,\{y\})P} \approx \frac{\gamma_i(T,\{x\})P_i^s(T)}{P} \sim \frac{P_i^s(T)}{P}$$

FFF#1 & #1 FFF#1 & #5

$$\alpha_{ij} \equiv \frac{y_i/x_i}{y_j/x_j} = \frac{\phi_i^l(T,v^l,\{x\})\phi_j^v(T,v^v,\{y\})}{\phi_j^l(T,v^l,\{y\})\phi_i^v(T,v^v,\{y\})} \text{ FFF\#1 \& \#1}$$

$$\cong \frac{\gamma_i(T,\{x\})}{\gamma_j(T,\{x\})}\frac{P_i^s(T)}{P_j^s(T)}\frac{\phi_i^s(T)\phi_j^v(T,P,\{y\})}{\phi_j^s(T)\phi_i^v(T,P,\{y\})} \text{ FFF\#1 \& \#5}$$

$$\approx \frac{\gamma_i(T,\{x\})}{\gamma_j(T,\{x\})}\frac{P_i^s(T)}{P_j^s(T)} \sim \frac{P_i^s(T)}{P_j^s(T)}$$

Low *P* estimates for $\phi - \phi$ or Henry's Law SS

- $\cong$ **Ignore Poynting Correction**
- $\approx$ **Assume Lewis Rule;**
- $\sim$ **Assume ideal solution**

FFF#1 & #5

$$K_i \equiv \frac{y_i}{x_i} \cong \frac{\gamma_i^*(T,\{x\})H_i(T)}{\phi_i^v(T,P,\{y\})P} \approx \frac{\gamma_i^*(T,\{x\})H_i(T)}{P} \sim \frac{H_i(T)}{P}$$

$$\alpha_{ij} \equiv \frac{y_i/x_i}{y_j/x_j} \cong \frac{\gamma_i^*(T,\{x\})}{\gamma_j(T,\{x\})}\frac{H_i(T)}{P_j^s(T)}\frac{\phi_j^v(T,P,\{y\})}{\phi_j^s(T)\phi_i^v(T,P,\{y\})}$$

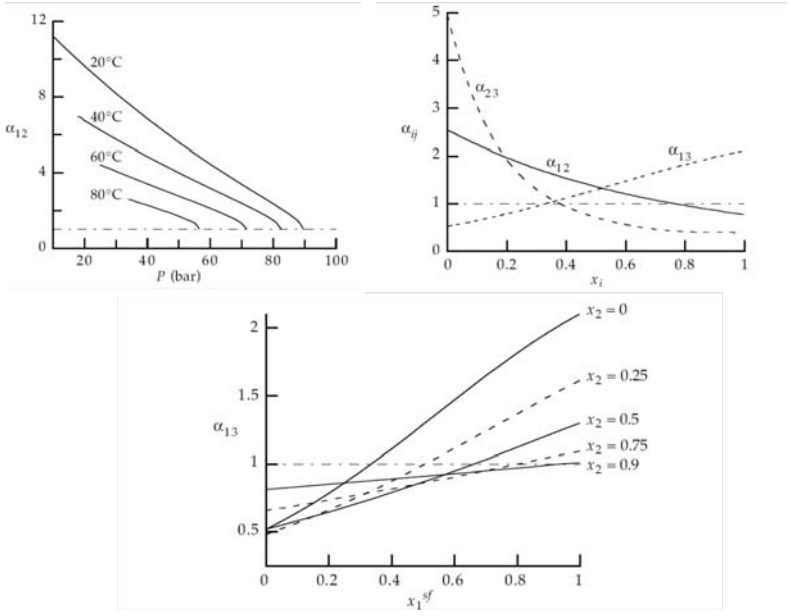
$$\approx \frac{\gamma_i^*(T,\{x\})}{\gamma_j(T,\{x\})}\frac{H_i(T)}{P_j^s(T)} \sim \frac{H_i(T)}{P_i^s(T)} \text{ FFF\#1 \& \#5}$$

α_{ij} is monotonic over compositions

Range of infinitely dilute *i* to pure *i*

$$\frac{\gamma_i^\infty(T,\{x_{SF}\})P_i^s(T,\{x_{SF}\})}{\gamma_j(T,\{x_{SF}\})P_j(T,\{x_{SF}\})} \le \alpha_{ij} \le \frac{P_i^s(T)}{\gamma_j^\infty(T,\{x_{SF}\})P_j^s(T,\{x_{SF}\})}$$

Figures 12.5-6



For liquid-liquid equilibria (ignore *P*),

$$f_i^\alpha = f_i^\beta = x_i^\alpha \gamma_i^\alpha(T,x_i^\alpha) f_i^{0\alpha}(T) = x_i^\beta \gamma_i^\beta(T,x_i^\beta) f_i^{0\beta}(T)$$

Gives "distribution coefficient"

$$C_i \equiv x_i^\beta / x_i^\alpha \text{ ~ } \textbf{\textit{K}}\textbf{-factor}$$

For same SS in phases, $C_i \approx \gamma_i^\alpha/\gamma_i^\beta$

Also use selectivity, $\beta_{ij} \equiv C_i/C_j \approx \frac{\gamma_i^\alpha \gamma_j^\beta}{\gamma_i^\beta \gamma_j^\alpha}$ **~** α_{ij}

Infinite dilution values for design of extraction separation of solutes *i, j*

$$C_i^\infty(T) \equiv \lim_{x_i \to 0} \frac{x_i^\beta}{x_i^\alpha} = \frac{\gamma_i^{\infty\alpha}(T)}{\gamma_i^{\infty\beta}(T)} \quad \textbf{(Fig. 12.7)}$$

$$\beta_{ij}^\infty(T) \equiv \lim_{x_i,\, x_j \to 0} \frac{C_i^\infty}{C_j^\infty} = \lim_{x_k^\alpha,\, x_l^\beta \to 1} \frac{x_i^\alpha/x_i^\beta}{x_j^\alpha/x_j^\beta} = \frac{\gamma_i^{\infty\alpha}/\gamma_i^{\infty\beta}}{\gamma_j^{\infty\alpha}/\gamma_j^{\infty\beta}}$$

Solid-solid is like liquid-liquid (Fig. 12.8)

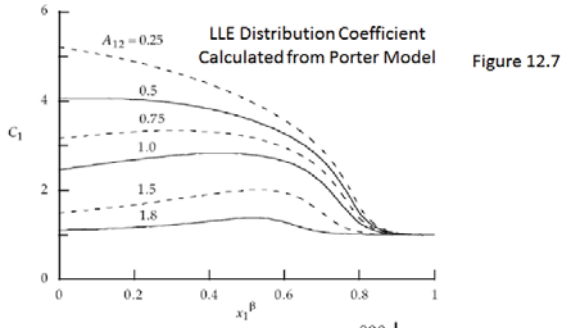


Figure 12.7

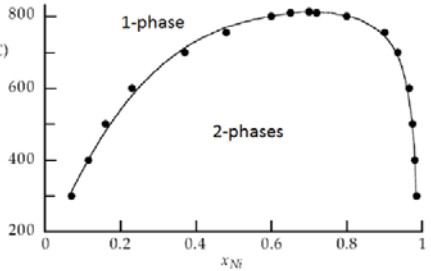


Figure 12.8
Ni-Au Alloy

SOLUBILITY

Gases in Liquids -

Often high P, want to <u>use</u> $\phi - \phi$ method so no model discontinuity at critical

<u>Understanding</u> best with $\gamma - \phi$, Henry's Law SS

For solute, rearrange $f_1^v = f_1^l$ with FFF #5

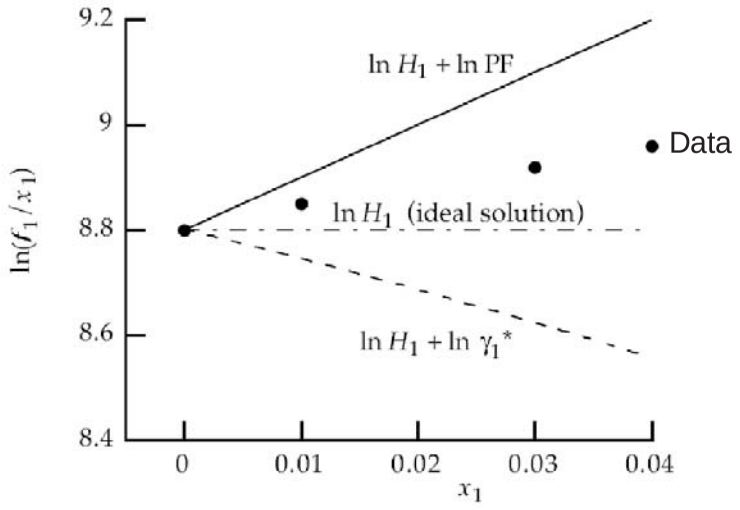
$$\ln\left(\frac{f_1}{x_1}\right) = \ln\left(\frac{y_1\phi_1^v P}{x_1}\right) = \ln\gamma_1^*(T,\{x\}) + \left(\int_{P_1^o}^{P} \frac{\bar{V}_1}{RT}\, d\pi\right) + \ln H_1(T)$$

Note: *P* & x_1 not independent if vary at fixed *T*

Also, $\gamma_1^* < 1$ while $\bar{V}_1 \approx \bar{V}_1^\infty > 0$, so 1st & 2nd terms tend to cancel (Fig. 12.9)

***For $T/T_{c2} << 1$*, nonideality small, PF OK; near solvent critical, nonideality exceeds volumetric effect!**

Gas in Liquid Figure 12.9



FFF #4 Combines Terms

$$\ln\left(\frac{f_1}{x_1}\right) = \ln\left(\frac{y_1\phi_1^v P}{x_1}\right) = \ln\gamma_1^*(T,P,\{x\}) + \ln H_1(T)$$

***H_1* has maximum in *T* ⇔ P^s (Fig. 12.10)**

Figure 12.11 shows naive assumption: false apparent line of *P* vs. x_1 has intercept of (0,<0), not (0, P_2^s>0)

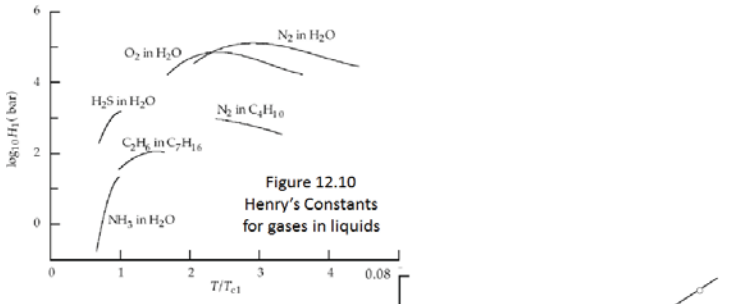


Figure 12.10
Henry's Constants
for gases in liquids

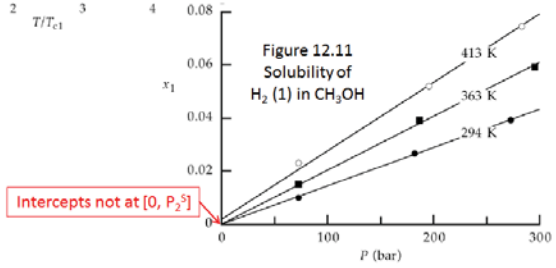


Figure 12.11
Solubility of
H_2 (1) in CH_3OH

SOLID PHASE STANDARD STATES

Phase equilibrium (to get solubility, x_i^L) using FFF# 2-5, hypothetical f_i^{oL} ($T<T_i^{melt}$)

$$x_i^L \gamma_i^L f_i^{oL} = x_i^s \gamma_i^s f_i^{oS}$$

Rearrange to $x_i^L = x_i^s(\gamma_i^s/\gamma_i^L)(f_i^{oS}/f_i^{oL})$ & use Gibbs-Helmholtz Equation on f_i^{oS}/f_i^{oL}

$$0 > \ln\left(\frac{f_i^{oS}(T)}{f_i^{oL}(T)}\right) = \frac{g_i^{oS} - g_i^{oL}}{RT} =$$

$$= \left[\frac{g_i^{oS}(T)}{RT} - \frac{g_i^{oS}(T_i^m)}{RT_i^m}\right] + \left[\frac{g_i^{oS}(T_i^m)}{RT_i^m} - \frac{g_i^{oL}(T_i^m)}{RT_i^m}\right] + \left[\frac{g_i^{oL}(T_i^m)}{RT_i^m} - \frac{g_i^{oL}(T)}{RT}\right]$$

$$= \frac{-\Delta h_i^{melt}}{R}\left(\frac{1}{T} - \frac{1}{T_i^m}\right) - \frac{1}{RT}\int_{T_i^m}^{T}\left(c_{pi}^{ol} - c_{pi}^{os}\right)d\tau + \int_{T_i^m}^{T}\frac{\Delta c_{pi}^o}{R\tau}d\tau$$

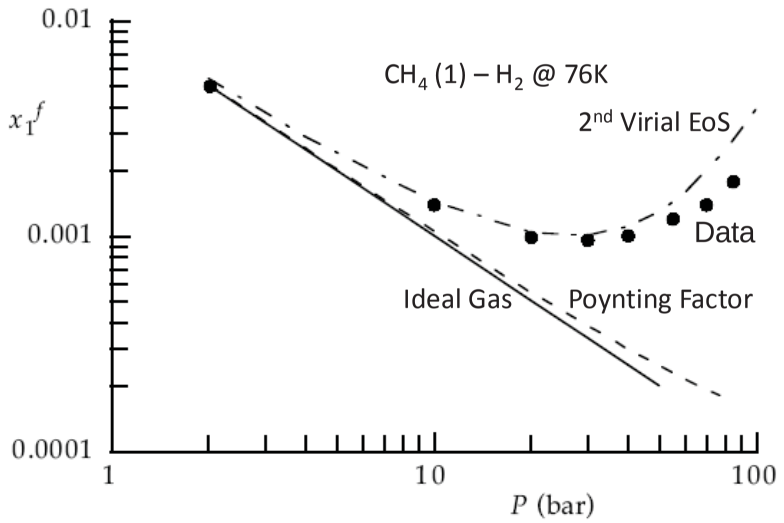
Treat Δc_{pi}^o terms as on p. 547: ~0 to $\Delta h_i^{melt}/T_m$

NEAR-CRITICAL SYSTEMS

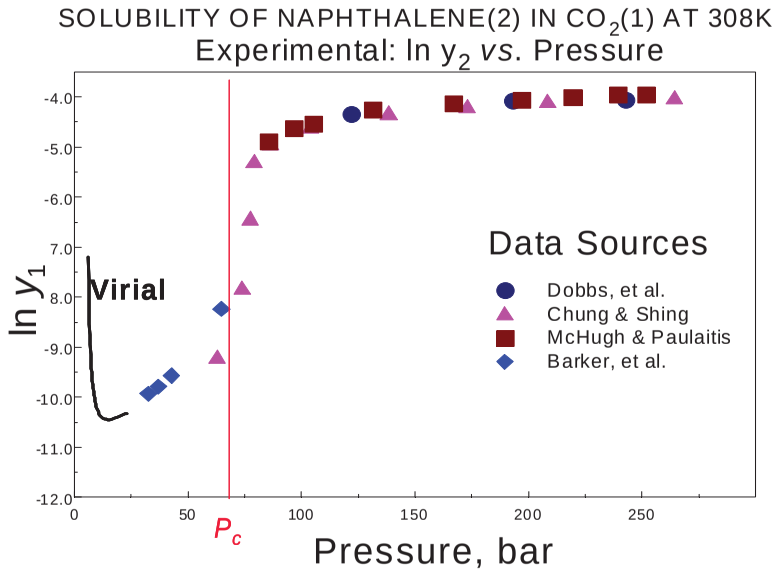
- **Possible separation technique for low volatility substances to avoid organic solvents, high *T* (food / flavor / odor species pharmaceuticals)**
- **Use high pressure CO_2, C_2H_6, C_3H_8, etc. to remove solute from S/L into "fluid (*f*)" Fig. 12.12 has *P* variation; better to use ρ^f**
- **Consider pure component 1 (solid) dissolved in fluid; use LR for solute, FFF #5, rearrange $f_1^f = f_1^s$ to**

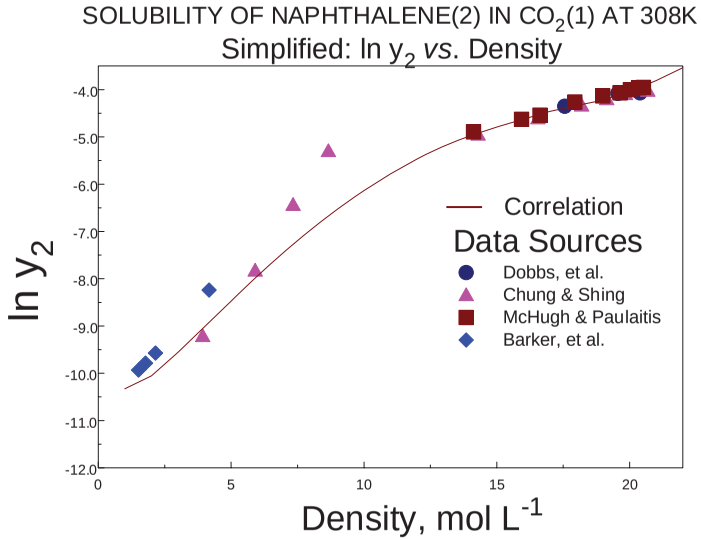
$$\ln x_1^f \cong \ln(P_1^{sub}(T)/\rho RT) + \frac{v_2^s P}{RT} - \ln[\phi_1^f(T,P,x_1)Z]$$

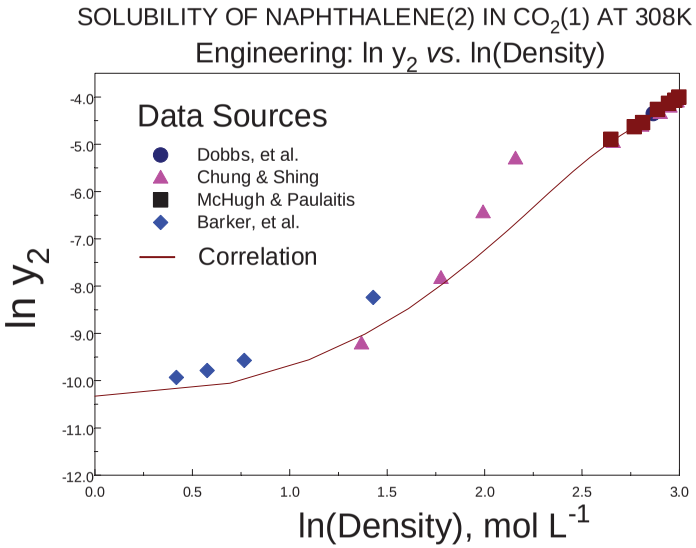
Figure 12.12



Example Thermodynamic Analysis







Rearrange fugacity equation for SVE of

$$x_1^f \phi_1^f P = P_1^{sub} \exp\left[\frac{v_1^s P}{RT}\right] \text{ to}$$

$$\ln(P_1^{sub}(T)/x_1^f \rho RT) + \frac{v_1^s P}{RT} = \ln[\phi_1^f Z] \approx$$

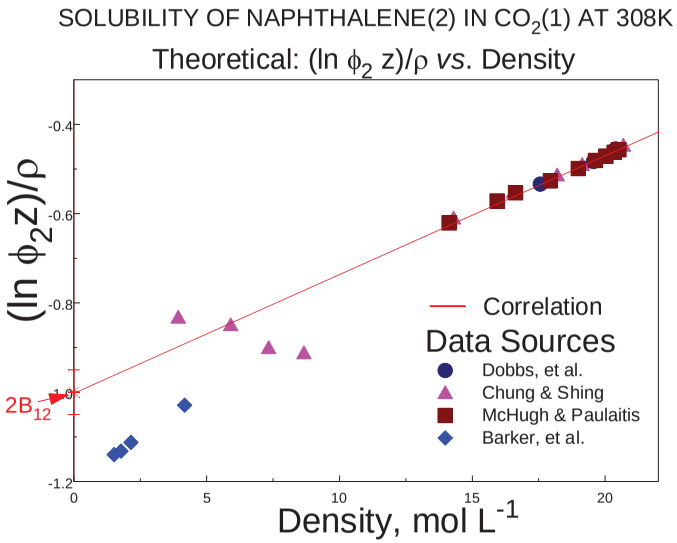
$$\ln\left[\phi_1^{\infty} Z_{pure\,2}\right] = 2\left(\rho_{pure\,2}\right)B_{12} + 3\left(\rho_{pure\,2}\right)^2 C_{122}$$

If have values of P_1^{sub} and v_1^s make linear plot of

$$\left[\ln(P_1^{sub}(T)/x_1^f \rho RT) + \frac{v_1^s P}{RT}\right]/\rho_{pure\,2} \text{ vs. } \rho_{pure\,2}$$

with intercept $2B_{12}$

Since variations of $\ln \phi_1^f z$ with $\rho_{pure\,2} \Rightarrow$ line, maybe not C_{122}


SOLUBILITY OF NAPHTHALENE(2) IN CO2(1) AT 308K
Theoretical: (ln ϕ2 z)/ρ vs. Density
(ln ϕ2z)/ρ
-0.4
-0.6
-0.8
-1.0
-1.2
2B12
0
5
10
15
20
Density, mol L-1
Correlation
Data Sources
Dobbs, et al.
Chung & Shing
McHugh & Paulaitis
Barker, et al.