Note Title 11/3/2016

$$\ln\frac{f}{p} = \ln\phi = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B}\ln\left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right]$$

and
$$\ln\frac{f_i}{y_i p} = \ln\phi_i = \frac{B_i}{B}(Z-1) - \ln(Z-B) + \frac{A}{2\sqrt{2}B}\left(\frac{B_i}{B} - \frac{2}{A}\sum_{j=1}^{N} y_j A_{ij}\right)\ln\left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right], \quad \ldots\ldots\ldots\ldots \quad (4.23)$$

Ch. 4

$\neq$

$$\ln\phi_1^L = \frac{b_1}{b^L}(Z^L - 1) - \ln(Z^L - B^L) - \frac{A^L}{2\sqrt{2}\,B^L}\left(\frac{2(x_1 a_{11} + x_2 a_{12})}{a^L} - \frac{b_1}{b^L}\right)\ln\left[\frac{Z^L + (1+\sqrt{2})B^L}{Z^L + (1-\sqrt{2})B^L}\right] \quad (8\text{-}12.28a)$$

Prausnitz

f ✓

PSU

$=$

Pure Substance

✓
$$\ln\phi = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B}\ln\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \quad (16.44)$$

Mixtures

$$\ln\phi_i = (BB)_i(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B}((AA)_i - (BB)_i)\ln\left[\frac{Z + (\sqrt{2}+1)B}{Z - (\sqrt{2}-1)B}\right]$$

(16.45)

TERNARY Problem 18 $C_1 - n\text{-}C_4 - n\text{-}C_{10}$

BIPs : k_{ij} $C_1 - C_{10} = 0$ in the problem

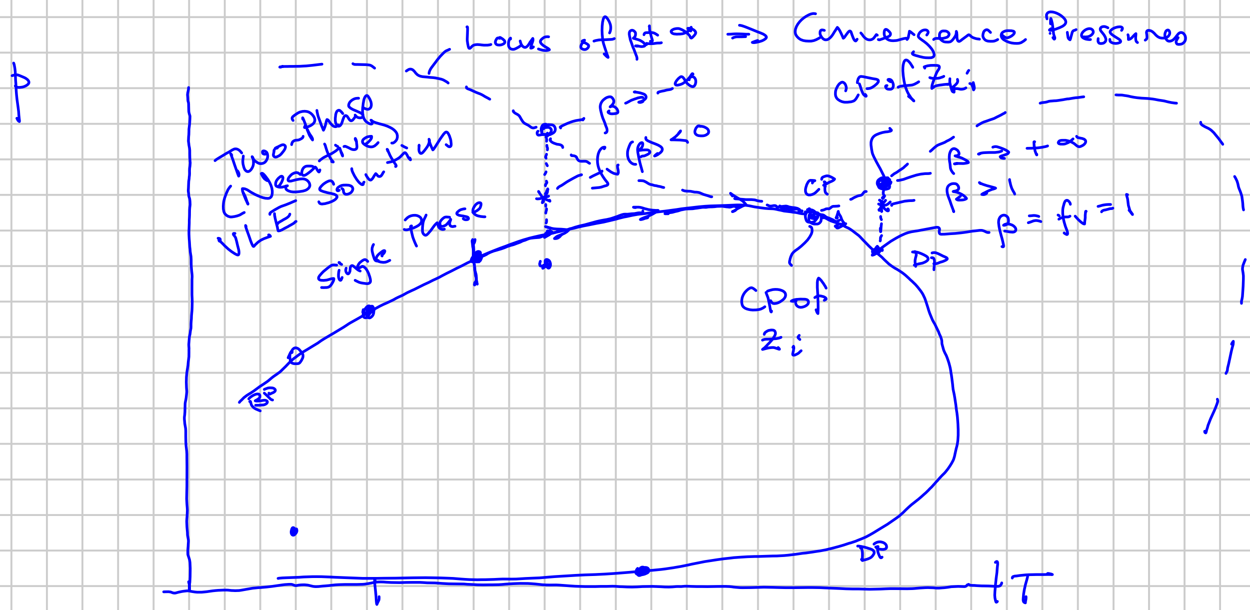
Any effect on VLE $k_{C_1-C_{10}} = 0$

$= 0.05$ (Chueh) ?

(1) At 500 psia same effect on all 3 components
mostly C_1 & C_{10} , little C_4
10%

(2) At low p (15 & 0.15 psia) same result
except no effect on C_4 & C_{10}
C_1 10%

What about near critical condition ?



$z_i = \beta y_i + (1-\beta) x_i$

$\beta \to \pm\infty$, $y_i \to x_i \Rightarrow Z_{ki} \neq Z_i$

Convergence

VLE (Vapor-Liquid Equilibria) Calculations

- Flash Calculation

  - Specify z_i, p, T
  - Determine : (1) # Phases [2 or 1 | ...]

    (2) Phase Amounts (molar) f_v F_v F_g β

    (3) Equilibrium molar compositions y_i x_i

  - Level of Difficulty finding the thermodynamically-correct answer

    99% { (1) Easy at low p ($\lesssim$ 1000 psia)

    (ii) Challenge

    1% (*) Very difficult - near critical point

    - (RR|MM) : Some extreme low-p calculations

      $z_i \to \epsilon$

      $K_i \to \epsilon$ or $1/\epsilon$

    - More than 2-phase solutions

- Saturation Pressure : Orientation "Data" 1-phase / 2-phase

  - Specify : z_i T
  - Calculate : $\underline{\underline{p_s}}$, incipient phase composition

    Type: BP : y_i ; DP : x_i

  - Special case of Flash where $f_v \to$ 1, 0 ; $1-\epsilon$, ϵ
  - Level of Difficulty

    ✓ • Easy for lower dewpoints (usually)

    ✓ • Difficult many cases — mostly not knowing if a solution exists

    ✓ • Very Challenging near critical point

- Phase Stability Test (Gibbs)
  - Given z_i P T
  - Calculate – Will a new phase lower the total mixture chemical energy from the current total mixture energy that we have in our current equilibrium state.

The Current Equilibrium State is (probably) Stable

no – current equilibrium state is the correct state (Maybe)

yes: –(1) a new equilibrium state with one more phase from our current state EXISTS and will lead to a lower total system energy. (Guaranteed)

The Current Equilibrium State is UNSTABLE (for sure)

(2) identify the ~ nature (composition) of the new phase.

Level of Difficulty:

- Assuming a reasonable guess of the new phase composition ($\hat{u}_i$) (guesses) ($\hat{u}_i^H$, $\hat{u}_i^L$)
  - → Easy to Challenging (Easier than a Flash Calculation)

First State: Single Phase

$$z, p, T \Rightarrow (Z \ v \ \rho) \Rightarrow (f_i \ \mu_i) \Rightarrow \mu_t = \sum z_i \mu_i$$

Test Phase is introduced as an ϵ amount

$$\mu_t' = (1-\epsilon)\sum z_i \mu_i(z_i) + \epsilon \sum u_i \cdot \mu_i(u_i)$$

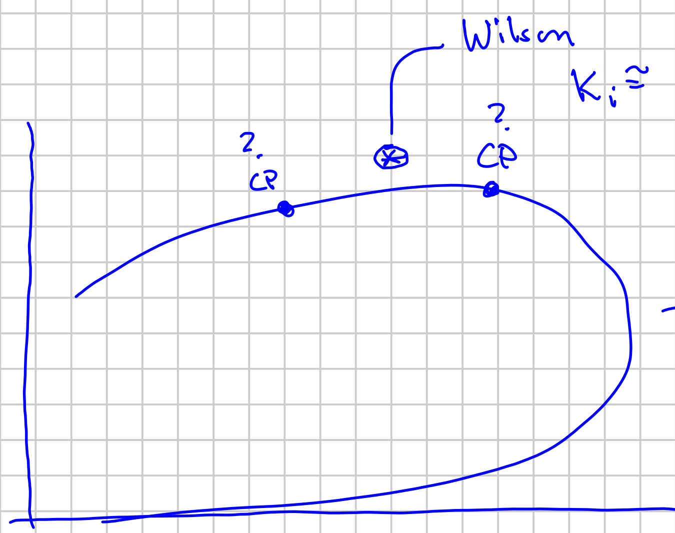
Find u_i where $\mu_t' < \mu_t$

and where

$$\Rightarrow \underline{\mu_i(z) = \mu_i(u)} + \underbrace{\overset{C}{\text{constant}}}_{\text{same for all } i}$$

$C > 0$: $\mu_t' > \mu_t$ STABLE currently as single phase

$C \le 0$: $\mu_t' < \mu_t$ UNSTABLE currently as single phase



$$K_i \simeq \frac{P_{vi}(T)}{P} = \frac{y_i}{x_i}$$

$$K_i^{Wilson} = \frac{\hat{u}_i^v}{z_i}$$

Test (1) $u_i^v = z_i K_i^{wilson}$

$$K^{wilson} = \frac{z_i}{u_i^L}$$

$$u_i^L = \frac{z_i}{K_i^{wilson}}$$

Test 1: C_v u_i^v

Test 2: C_L u_i^L

C_V and/or $C_L < 0 \Rightarrow$ UNSTABLE

Both C_V & $C_L > 0 \Rightarrow$ STABLE