

Definition of (a, b) : vdw CC ( $T_c, p_c$ )

$$a = \Omega_a \frac{R^2 T_c^2}{p_c} \quad \Omega_a = 27/64$$

$$b = \Omega_b \frac{R T_c}{p_c} \quad \Omega_b = 1/8$$

1949: Redlich Kwong

$$p = \frac{RT}{v-b} - \frac{a \cdot \alpha(T)}{[v(v+b)]} \quad \textcircled{2}$$

① Better (quite accurate) description of Methane also as a liquid

$$Z_{CEOS}^{RK} = 1/3$$

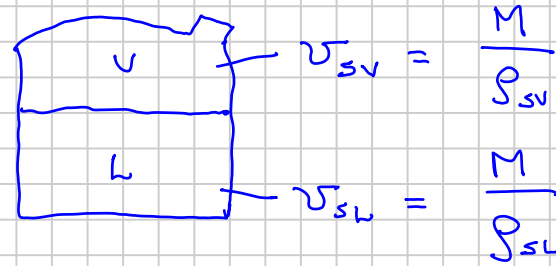
②  $\alpha(T)$  : Improve the  $f_v(T)$  for light HCs

$$\alpha = T_r^{-1/2} = \frac{1}{\sqrt{T_r}} \quad T_r \equiv \frac{T}{T_c}$$

How does an EOS "calculate" the  $f_v(T)$

H<sub>2</sub>O at 100°C / 1 atm

Given T, H<sub>2</sub>O  
 Same  $\phi$  with  
 (a) 2 v (Z)



$v_{sv} = \frac{M}{\rho_{sv}}$   
 $v_{sl} = \frac{M}{\rho_{sl}}$

$f_{sv}(v_{sv}, A, B)$   
 $\neq$   
 $f_{sl}(v_{sl}, A, B)$

(b)  $f_{sv} = f_{sl} \Rightarrow \mu_{sv} = \mu_{sl}$

Chemical Energy of a compound @ (P, T, v)

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

..... (4.13)

$\mu \approx \ln f$   
 Gibbs  
 Chemical  
 Potential

$$A = a \cdot \frac{p}{RT^2}$$

$$B = b \frac{p}{RT}$$

$$a = \Omega_a \frac{R^2 T_c^2}{p_c} \alpha$$

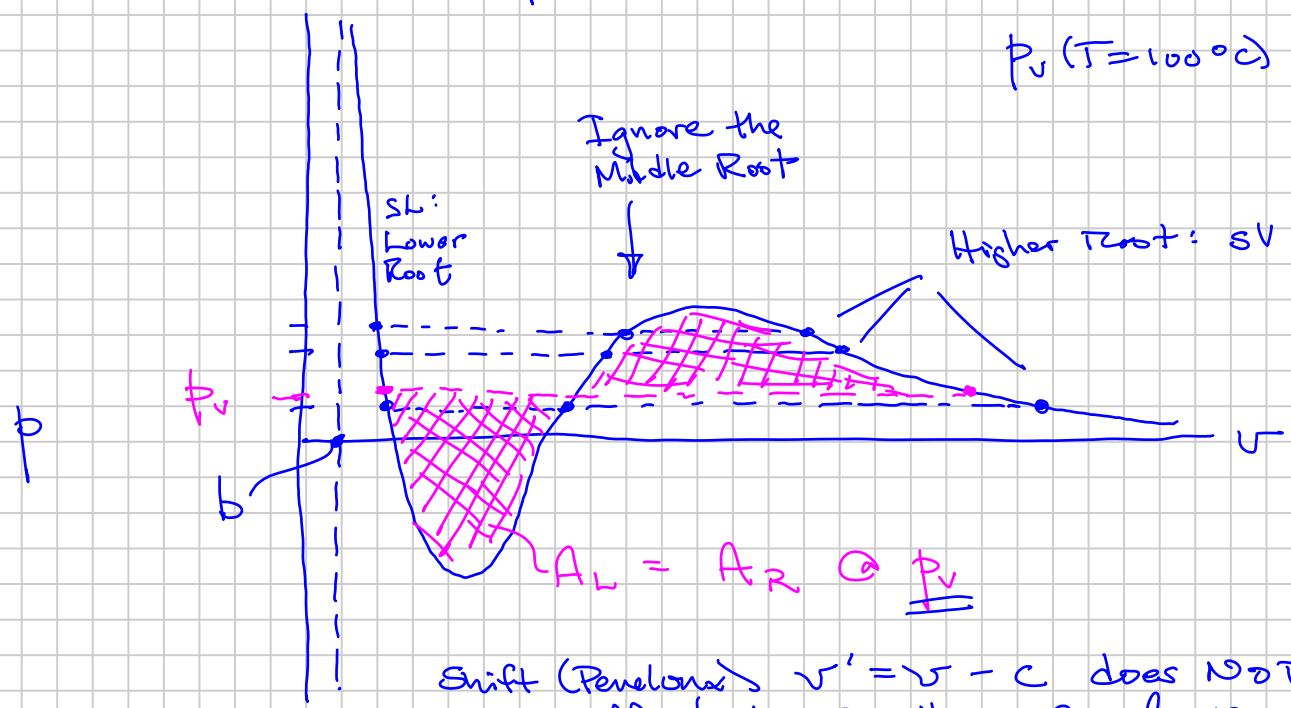
$$b = \frac{RT_c}{p}$$

$$A = \Omega_a \frac{p_r}{T_r^2} \alpha$$

$$B = \Omega_b \frac{p_r}{T_r}$$

H<sub>2</sub>O T=100°C p-v

- EOS



Same pressure,  $P_i$ , where  $f_{SV}(V_{SV}, A, B) = f_{SL}(V_{SL}, A, B)$

Lower ( $P, T$ ) Surface Gas Processing

$$K_i(P, T) \approx \frac{P_{vi}(T)}{P}$$

EOS w/  $\alpha$

Soave (1972) : SRK

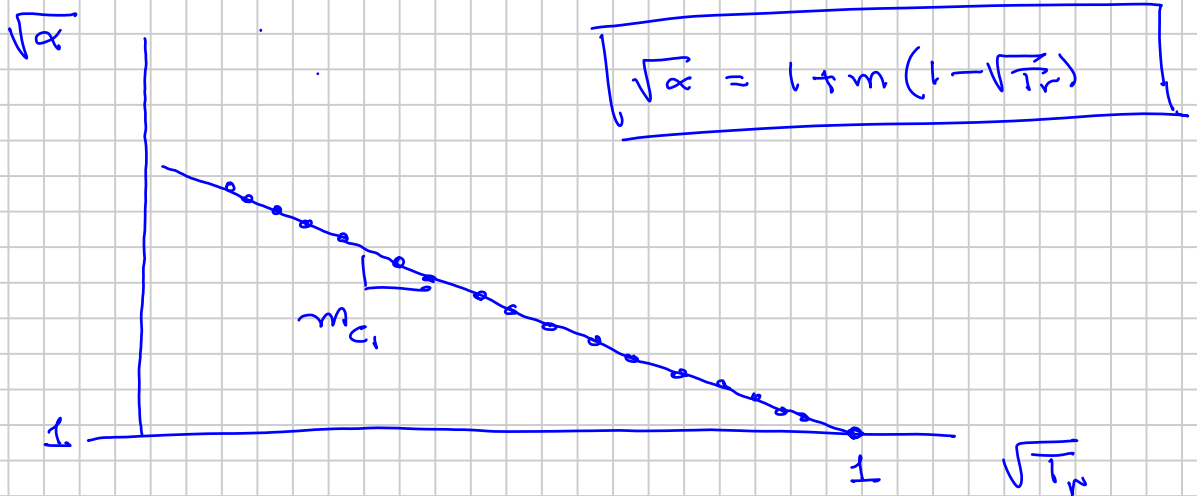
RKS

We want accurate  $P_{vi}(T)$  for all compounds

⇒ Need a special  $\alpha_i(T)$

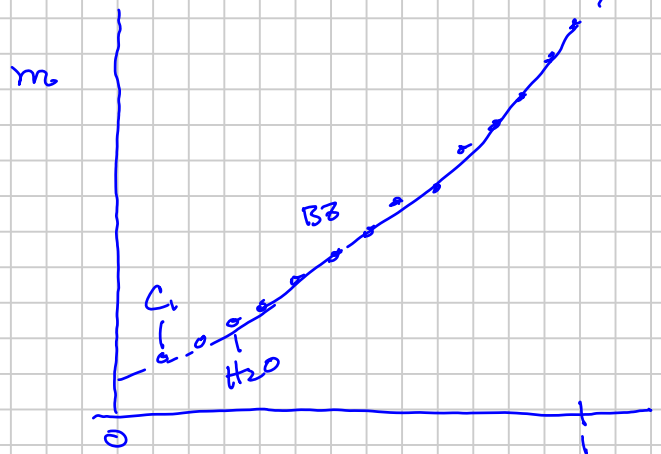
• Using RK EOS, abandon  $\alpha_{RK}$

make new, special  $\alpha_i(T)$



Table

Compound Name	$m$

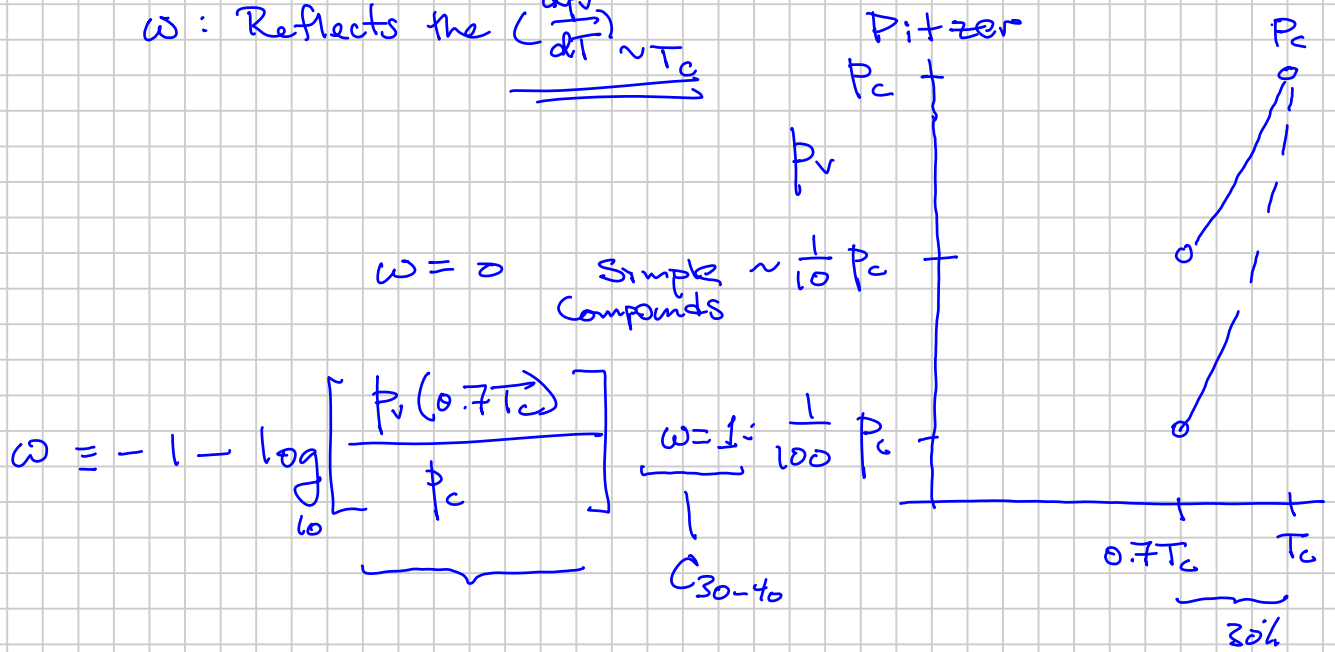


$$m \approx m_0 + m_1 \omega + m_2 \omega^2$$

$\omega = 0$

Acentric Factor

$\omega$ : Reflects the  $\left(\frac{dp_v}{dT}\right)_{T_c} \sim T_c$



1977 Peng-Robinson

1976  $m_{PR} = m_0' + m_1' \omega + m_2' \omega^2$

$$p = \frac{RT}{v-b} - \frac{a \cdot \alpha(T_r, \omega)}{v(v+b) + b(v-b)}$$

1977: 1976 Eq  $m \checkmark$   $\omega < 0.49$

Cubic for  $\omega > 0.49$

$m_0'' \cdot m_1'' \cdot m_2'' \cdot m_3''$

$Z_{CR} = 0.3074 \dots$

Best  $\{ Z_c, \rho_c, v_c \}$  for  $n-C_6$

$\int_0^{PR}$  still 5-20% high

$\int_0^{SRK}$  10-30% high

not good enough!

1980: Keith Coats EOS-based reservoir simulation

R: approaching critical conditions

$f_g(y_i) \Rightarrow f_0(x_i)$  as  $y_i \rightarrow x_i$

R&Z: Peneloux Volume Shift Solution

$\int_0^{EOS} g$  Still good  $\pm 2\%$

$\int_0^{EOS} g$  Became good  $\pm 2\%$

Didn't require any change in Flash,  
Saturation Pressure Calcs for SRK / PR code  
that existed.

$K_i(P, T, z)$

1978 KF

↑  
Wide  
Range  
of  
Composition



Near-Critical

Retrograde Condensation

Vaporization

⇒ Binary Interaction Parameters (BIPs)

Potentially  
EVERY pair of  
components

↓  
Correction Terms  
(little physical meaning)

# EOS applied to Mixtures

(1) Same EOS  $p-v-T$  of mixtures as pure compounds

(2) Average  $\bar{a} \neq \bar{b} (\neq \bar{c})$  :  $u_i = \text{molar fraction}$

Quadratic  $\bar{a} = \sum_{i=1}^N \sum_{j=1}^N u_i u_j (a_i a_j)^{1/2} (1 - k_{ij})$   $(z_i, y_i, x_i)$   
Total  $V$   $L$

Linear  $\bar{b} = \sum_{i=1}^N u_i b_i$

$\bar{c} = \sum_{i=1}^N u_i c_i$

$(z_i, K_i)$

$\Rightarrow$  All phase equilibrium  
 # phases  
 Amount phases  
 $y_i, x_i$

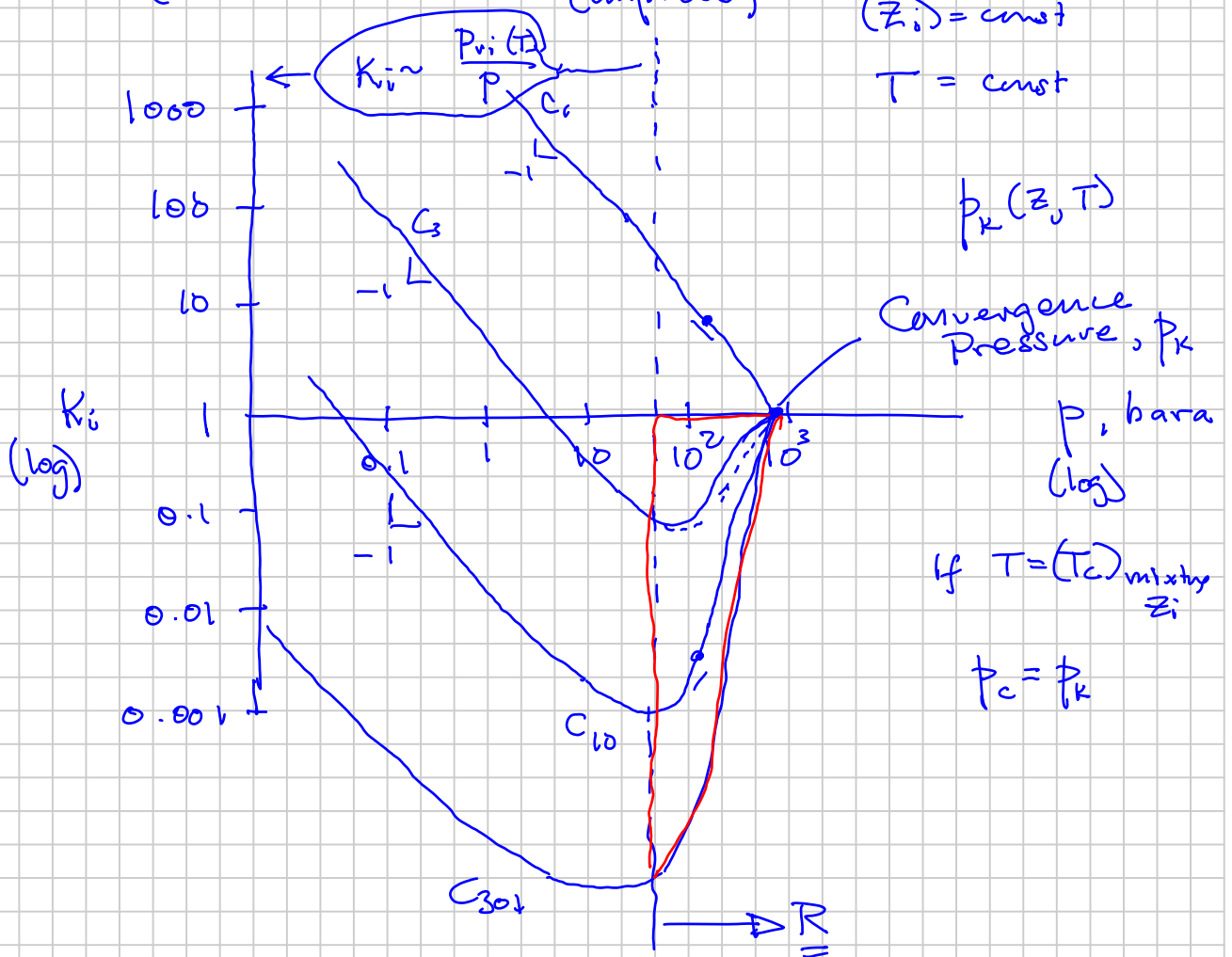
1960s Prausnitz - Chueh : BIPs

$k_{ij}$  could dramatically affect (and all other K-values) (improve)

$K_i = \frac{y_i}{x_i} \neq K_j = \frac{y_j}{x_j}$

$(z_i) = \text{const}$

$T = \text{const}$



# BIPs

SRK & PR

(1)  $k_{ij} = k_{ji}$

(2)  $k_{ii} = 0$

(3) non-HC ( $H_2S, CO_2, N_2$ ) - HC  $\sim 0.05 - 0.15$  SRK & PR

(4) HC-HC  $-0.1$  to  $+0.2$   
( $-0.05$  to  $+0.15$ ) most studies

(5)  $H_2O$  - (Petroleum Mixtures)

Conventional BIP in Quasibinary mixing rule

-  $H_2O$  amount in the HC (G or O) phase:  $k_{H_2O-HC} \sim 0.5$

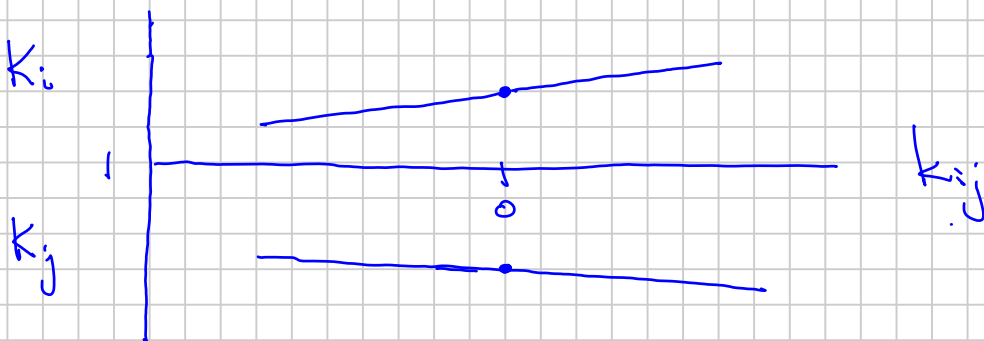
- HC(s) amounts in the Aqueous Phase:  
 $k_{iH_2O}(T, i, \text{salinity})$   $\begin{matrix} > 0 \\ < 0 \end{matrix}$

- Can't predict mutual solubilities right

## Ch. 9

- To get mutual solubilities use  
Huron-Vidal mixing rule (PVTsim)  
w/ Cubic EOS (not in PhaseComp)

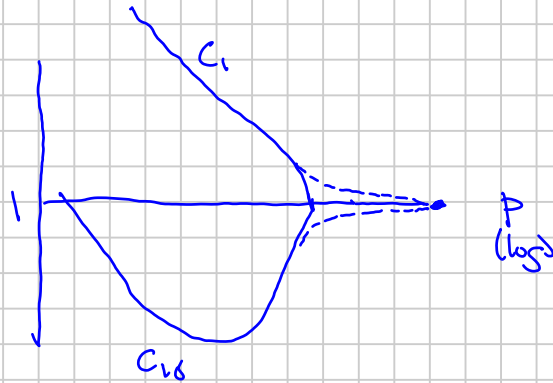
(7)



@(P,T,z)

# ⑧ HC-HC $C_{7+}$ - $C_{7+}$ BIPs

- Can have a huge (+ or -) effect on  $K_i$  of  $C_{7+}$
- Very sensitive ( $\pm 0.05$ ) shape of the nose / physical behavior
- Many of them
- Biggest impact on near-critical / extreme retrograde condensation

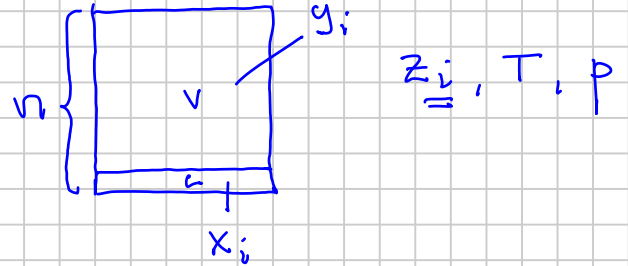




SRK vs PR  $\rightarrow$   $\{0.01 \rightarrow 0.1\}$  1978 KF  
 $C_1 - C_{7+} > 0$  (mainly to improve  $K_{ci}$ )  
 $\downarrow$  HC-HC BPs  $\sim 0$   $(\pm 0.05 \rightarrow 0.1)$

EOS for Mixtures:

Condition of phase equilibrium



$$\textcircled{1} n z_i = n_v y_i + n_L x_i$$

$$n = n_v + n_L \quad \checkmark$$

$$z_i = F_v y_i + (1 - F_v) x_i$$

$$F_v = \frac{n_v}{n}$$

$$\textcircled{2} \mu_{i,v}(y_i, p, T, v_v) = \mu_{i,L}(x_i, p, T, v_L) \quad \checkmark$$

same

Guarantee Total System

Minimum Chemical Energy

$$\sum_i (n_v \mu_{i,v} + n_L \mu_{i,L}) < \sum_i n \mu_i \quad \checkmark$$

$$\mu_i(z_i, p, T, v)$$

Phase Stability: Check your current system energy

$\rightarrow$  -1 phase  
 $\rightarrow$  -2 phase  
 $\downarrow$   
 $i$

Try Add another phase to lower the total system chemical energy

## FLASH CALCULATION

Know  $z_i$   $p$   $T$

Want (1) # Phases (1, 2, ...) Max 2  
(2) Phase Molar Amounts ( $n_v, n_L$ )  
(3) Phase Molar compositions ( $y_i, x_i$ )

Step 1. Guess (Estimate)  $K_i$ : Wilson K-value Eq.  
(Modified Wilson - Est  $p_r$ )

Step 2. Solve the component material balance

$$\checkmark z_i = F_v y_i + (1 - F_v) x_i = F_v K_i x_i + (1 - F_v) x_i$$

$$\checkmark K_i = y_i / x_i \quad y_i = K_i x_i$$

$$\sum z_i = 1 \Rightarrow \underbrace{\sum y_i = 1 = \sum x_i}$$

$$\sum (y_i - x_i) = 0$$

Muskat -  
McDowell  
1949

Rachford-Rice

$$\sum y_i - x_i$$

$$\sum K_i x_i - x_i = \sum (K_i - 1) x_i$$

$$\boxed{y_i = K_i x_i}$$

$$z_i = (F_v K_i + 1 - F_v) x_i$$

$$z_i = (F_v (K_i - 1) + 1) x_i$$

$$\boxed{x_i = \frac{z_i}{F_v (K_i - 1) + 1}}$$

$$0 = \sum \frac{(k_i - 1) z_i}{F_V (k_i - 1) + 1} = \sum \frac{z_i}{F_V + \frac{1}{(k_i - 1)}}$$

$$\text{MM: } c_i \equiv \frac{1}{k_i - 1}$$

$$0 = \sum \frac{z_i}{F_V + c_i}$$

Solve for  $F_V$

$$\checkmark F_{V\min} < F_V < F_{V\max} \Rightarrow \text{Guarantees } y_i > 0$$

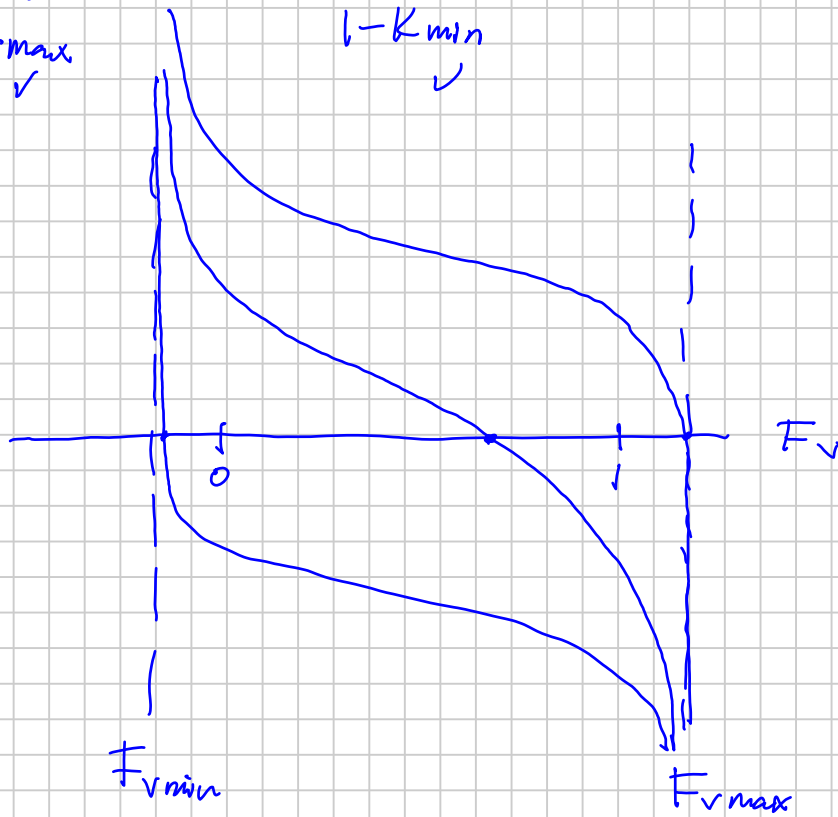
$$x_i > 0$$

$$= \frac{1}{1 - k_{\max}}$$

$$= \frac{1}{1 - k_{\min}}$$

$$k_{\max} > 1$$

$$k_{\min} < 1$$



Get  $F_V \Rightarrow$  Calc  $y_i, x_i$

$y_i \Rightarrow \text{EOS @ } (p, T) \quad U_v, Z_v, A_v, B_v \Rightarrow f_{iv} = \text{all } i \quad \bar{z}_i$   
 $x_i \Rightarrow \text{EOS @ } (p, T) \quad U_L, Z_L, A_L, B_L \Rightarrow f_{iL}$

yes  
(Iteration N)

$$\sum \left( \frac{f_{vi}}{f_{Li}} - 1 \right)^2 < \epsilon$$

$$> \epsilon$$

If no ( $\sum > \epsilon$ ) update  $K_i$  estimates

Simple :  $K_i^{\text{new}} = K_i^{\text{old}} \cdot \left( \frac{f_{Li}}{f_{vi}} \right)^n$  Successive Substitution (SS)

Better : Accelerated (SS)

- GDEM (Michelsen 1980-81)
- Zick

### TRIVIAL SOLUTION

$K_i = 1 \Rightarrow$  Satisfy all eqs above  $\bar{z}_i = y_i = x_i$

Unknowns :  $p, u_i^I$   $\left\{ \begin{array}{l} y_i \text{ BP} \\ x_i \text{ DP} \end{array} \right.$   
 Saturation Pressure :

$$\left. \begin{array}{l} N \text{ Eqs. } f_{Li} = f_{vi} \\ \sum u_i^I = 1 \end{array} \right\}$$

Unknowns  $u_i^I, p$

$$K_i = \frac{y_i}{x_i} \quad \left\{ \begin{array}{l} \frac{z_i}{x_i} \text{ DP} \\ \frac{z_i}{y_i} \text{ BP} \end{array} \right.$$

$$u_i = K_i z_i$$

If at the solution  $K_{c1} < 1$