x p_{Ri} =

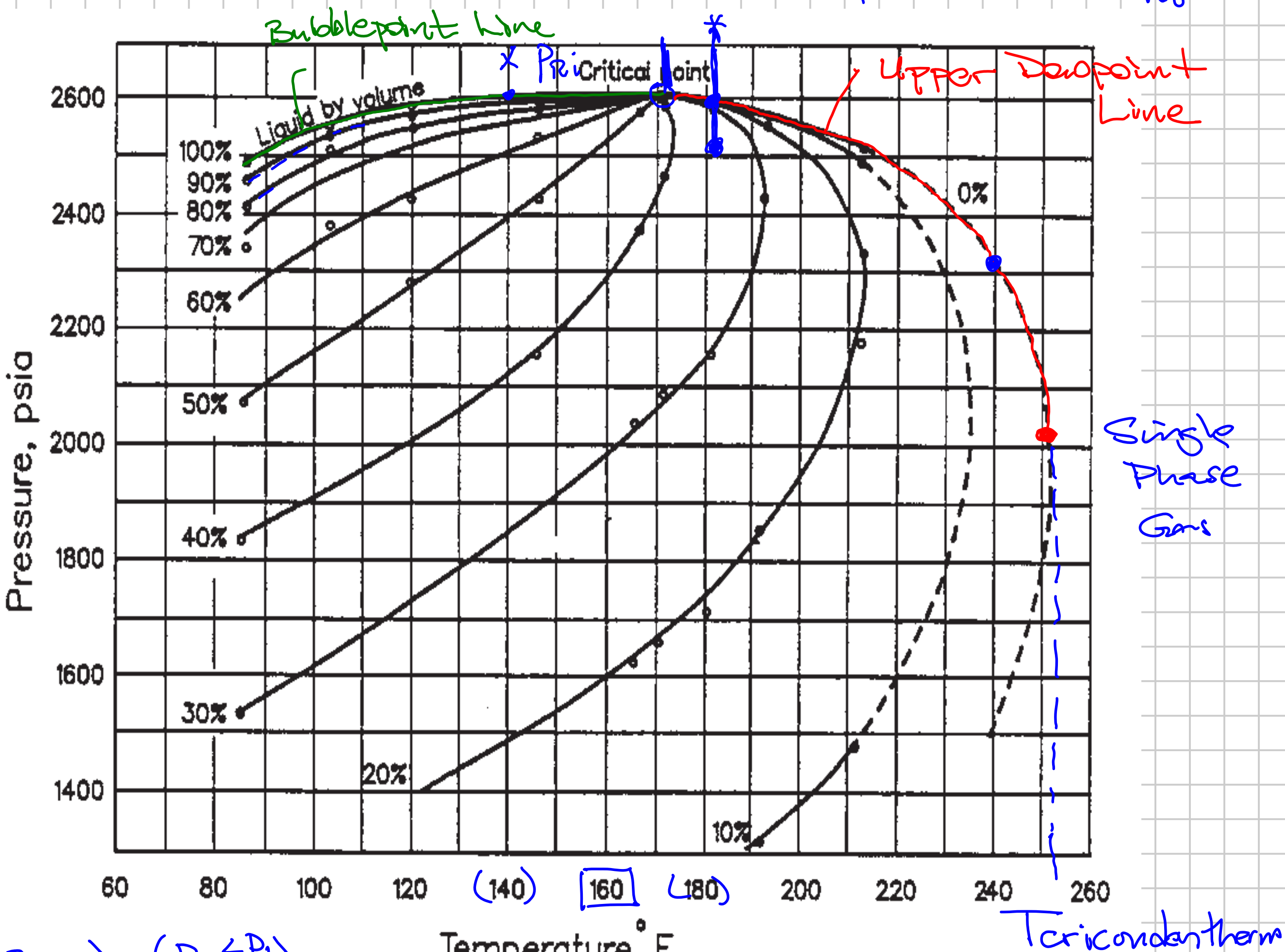
* p_{Ri}
$T_R > T_{cric}$

Note Title

1/30/2018

Multicomponent Phase Diagrams (p–T, p–V, p–x) [Ch. 2]

For a fixed composition z_{Ri}



$\left(\frac{0.3}{0.8}\right)^3 = \frac{\lambda_o (p_R < p_b)}{\lambda_{oi}} = 0.05$

$p_s(T_R)$: BP

scf/STB

$\boxed{T_R < T_c(z_{Ri})}$: OIL Reservoir

High-Shrinkage Oil ← – "Volatile Oil"

Higher API

– "Black Oil"

– "Low-GOR Oil"

– Dead-Oil

Heavy Oil

Solution Gas-Oil Ratio 1500+ – 3500

500 – 1000

100 – 500

GOR < 100 $\frac{scf}{STB}$

$\lambda = \frac{k_o}{\mu_o} = \frac{k \cdot k_{ro}}{\mu_o}$

$k_{ro} \propto S_o^{2-5}$

Low API

S_{OR}

$S_{OR} > S_w$, $\mu_o > 100\,cp$

$\Rightarrow 10^6\,cp$

$T_R > T_c$: GAS Reservoir

See HC Liquid in the R : Gas Condensate $T_c < T_R < T_{cric}$

@STC

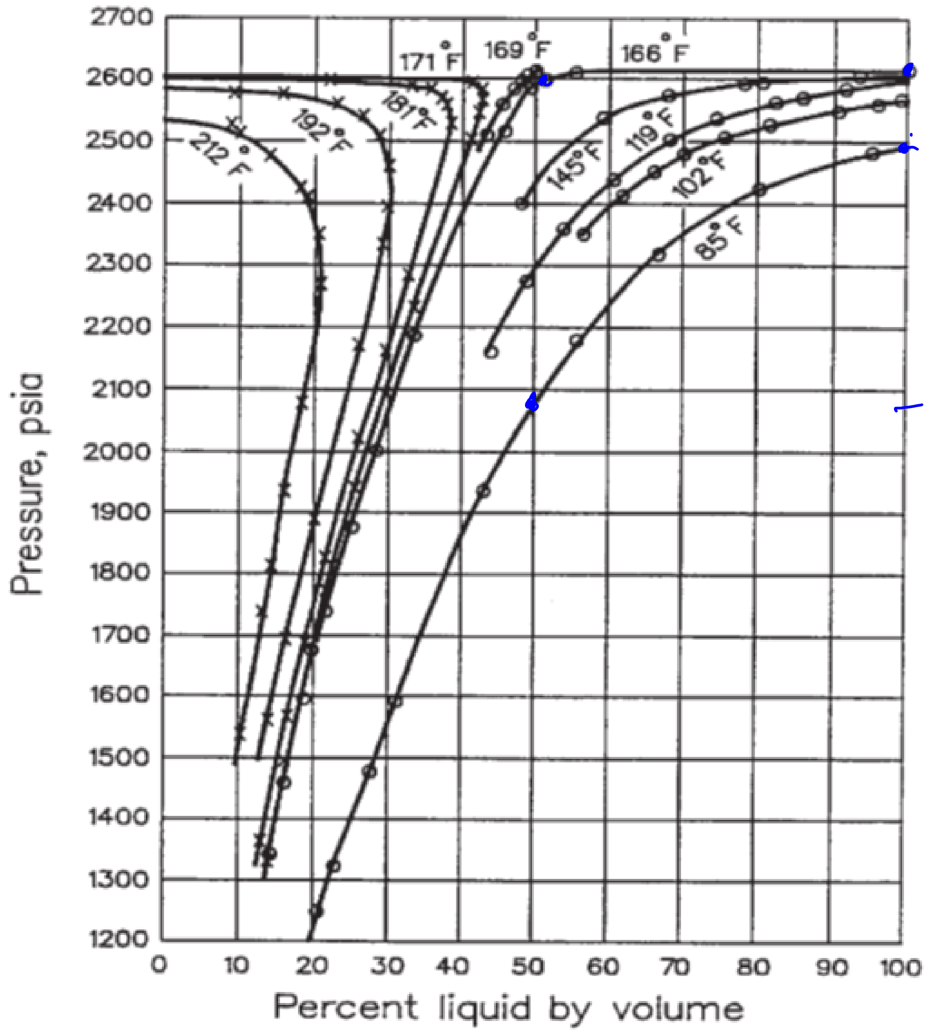
– (Wet) Gas

– (Dry) Gas

$T_R > T_{cric}$

GOR < ∞

GOR ≐ ∞



Liquid Relative Volume Curve (s)

$$\left(\frac{S_o}{1-S_w}\right)$$

$$q_o = \lambda_o \, \Delta P$$

$$q_o = \frac{k \, k_{ro}}{\mu_o} \, \Delta P$$

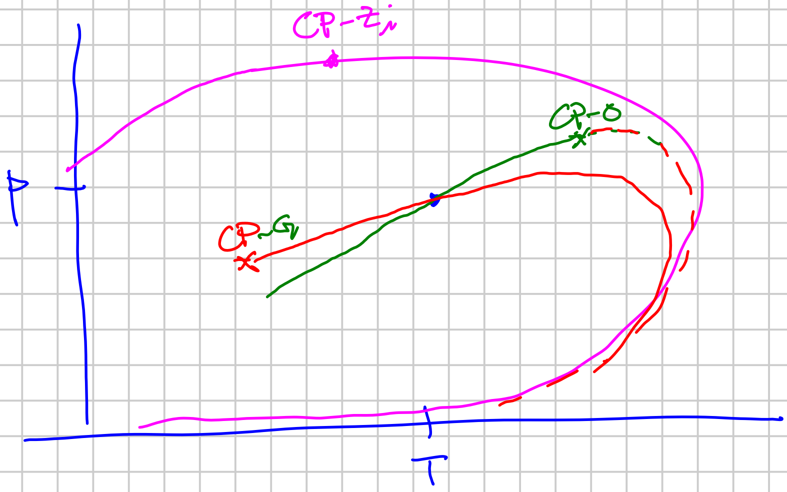
$$k_{ro} \propto S_o^{3.5}$$

z_i @ (p, T)

Saturated System is two phase with Gas & Oil Equilibrium

Saturated Gas $y_i(p,T)$ @ $p = p_d(T)$

Saturated Oil $x_i(p,T)$ @ $p = p_b(T)$



Phase Equilibrium Calculations

Ch. 3
Starting
3.6 +
(4.3.1)

– Vapor-Liquid Equilibrium (only)

Know: z_i

Calculate: At (p, T)

- Single phase
- Two Phase
  - Amount (n, m, V) of each phase
  - Composition (y_i, x_i), molar
    - y_i: Vapor / Gas
    - x_i: Liquid / Oil
  - Bubblepoint: $z_i = x_i$, $n_L = 1 - \epsilon$; Bubble y_i, $n_v = \epsilon$
  - Dewpoint: $z_i = y_i$, $n_V = 1 - \epsilon$; Dew x_i, $n_L = \epsilon$

Thermodynamics: What do we know

e.g. C_1 Two phases in equilibrium: ① $\mu_{i,v} = \mu_{i,L}$ all i

Chemical Energy (Gibb's energy) μ_i

② Total mixture Chemical Energy

$$\mu = \sum n_{Li}\mu_{iL} + n_{vi}\mu_{iv}$$

at a minimum

Ch. 4 gives the equations to solve this problem using cubic EOS (eq. of state)
~ Peng-Robinson | Soave-Redlich-Kwong

van der Waals : 18xx

$$p = \underbrace{\frac{RT}{v-b}}_{\sim \text{repulsive forces}} - \underbrace{\frac{a}{v^2}}_{\sim \text{attractive forces}}$$

$$\text{EOS} \Rightarrow \overset{n_V}{\mu_{iV}}(y_i, p, T) = \overset{n_L}{\mu_{iL}}(x_i, p, T)$$

z_i

Complicated Solution not knowing what x_i & y_i look like

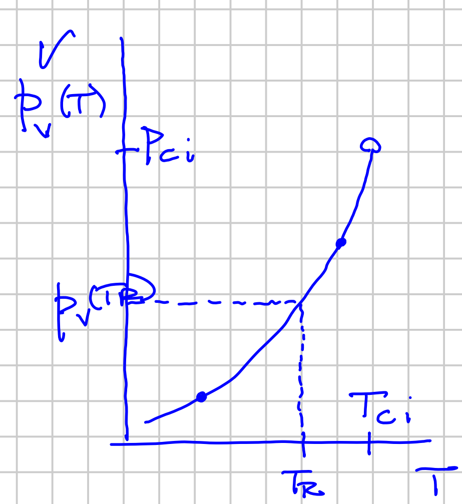
Guidelines on how to search for y_i and x_i
Ch. 3.6

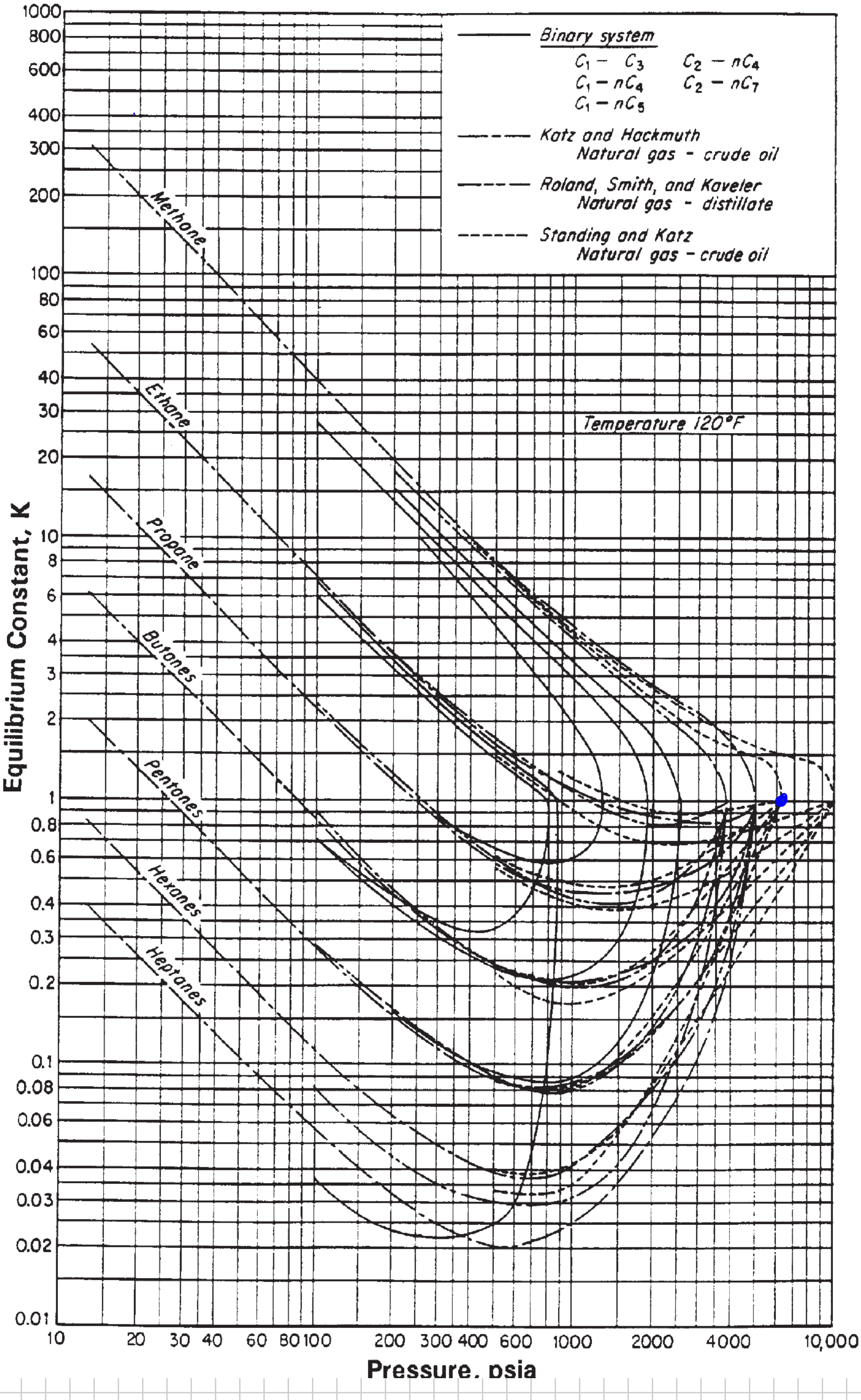
Quantity $K_i \equiv \frac{y_i}{x_i}$ Equilibrium K-values

$K_i(p, T)$?

(1) "Low" Pressures ($0 \rightarrow 100$ bar)

$$K_i \simeq \frac{p_{vi}(T)}{p}$$





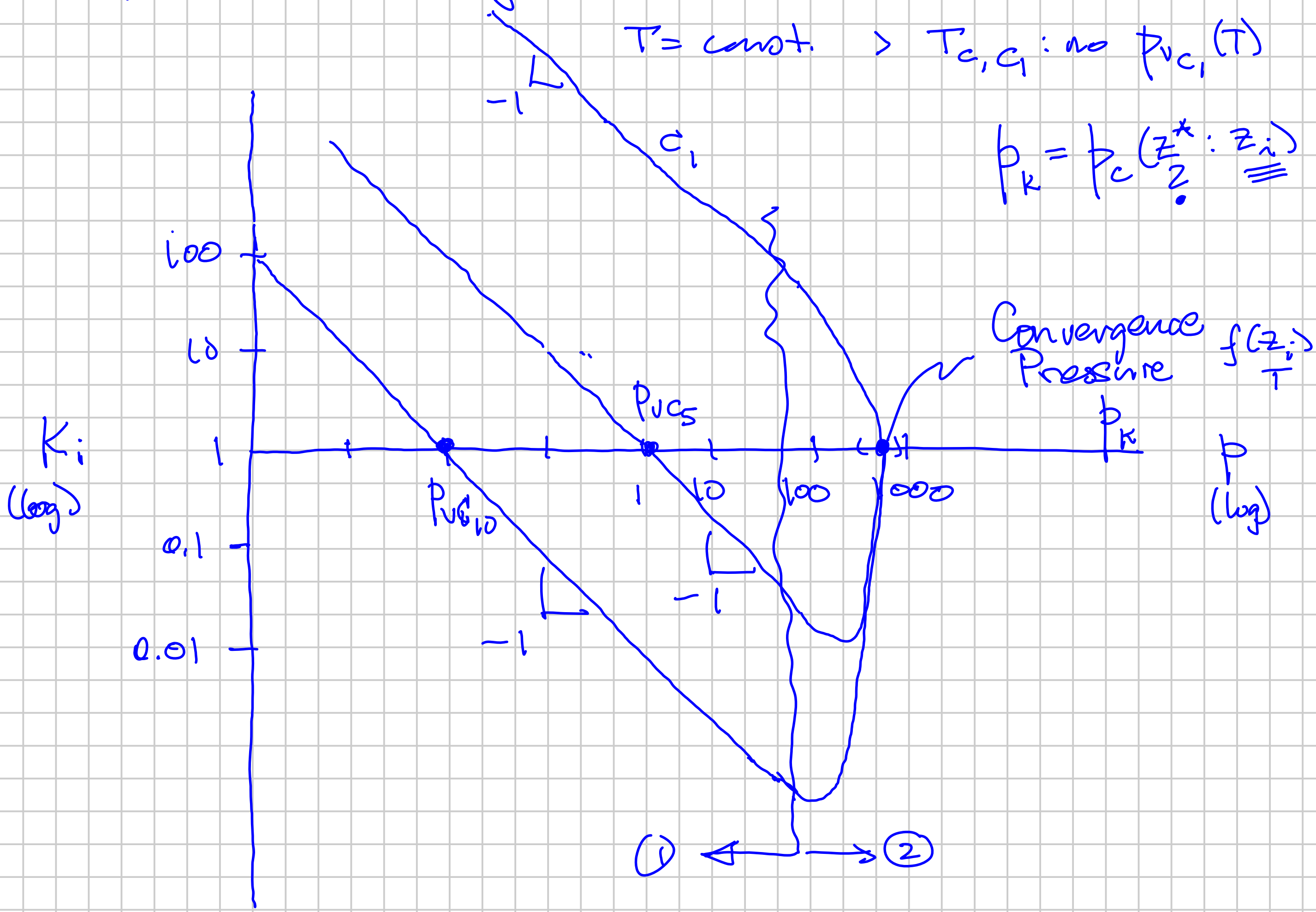
Binary system
$C_1 - C_3$ $C_2 - nC_4$
$C_1 - nC_4$ $C_2 - nC_7$
$C_1 - nC_5$
Katz and Hackmuth
Natural gas - crude oil
Roland, Smith, and Kaveler
Natural gas - distillate
Standing and Katz
Natural gas - crude oil
Temperature 120°F
Methane
Ethane
Propane
Butanes
Pentanes
Hexanes
Heptanes
Equilibrium Constant, K
1000
800
600
400
300
200
100
80
60
40
30
20
10
8
6
4
3
2
1
0.8
0.6
0.4
0.3
0.2
0.1
0.08
0.06
0.04
0.03
0.02
0.01
10 20 30 40 60 80 100 200 300 400 600 1000 2000 4000 10,000
Pressure, psia

② At "some" higher pressure ($\rightarrow$ 4000 – 15,000 psig
250 – 1000 bar

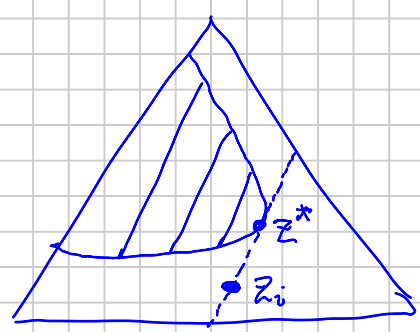
ALL K_i converge to 1

$T = \text{const.} > T_{c,C_1}$: no $p_{vC_1}(T)$

$p_K = p_c(z^*_2 : z_i)$



$p = p_K$, T



Know: z_i

Estimate: $K_i(p, T)$

$$T_{ri} \equiv \frac{T}{T_{ci}}$$

$$p_{ri} \equiv \frac{p}{p_{ci}}$$

Acentric Factor

Guess

$$K_i = \left(\frac{p_{ci}}{p_K}\right)^{A_1 - 1} \frac{\exp\left[5.37 A_1 (1 + \omega_i)\left(1 - T_{ri}^{-1}\right)\right]}{p_{ri}},$$

. . . . (3.159)

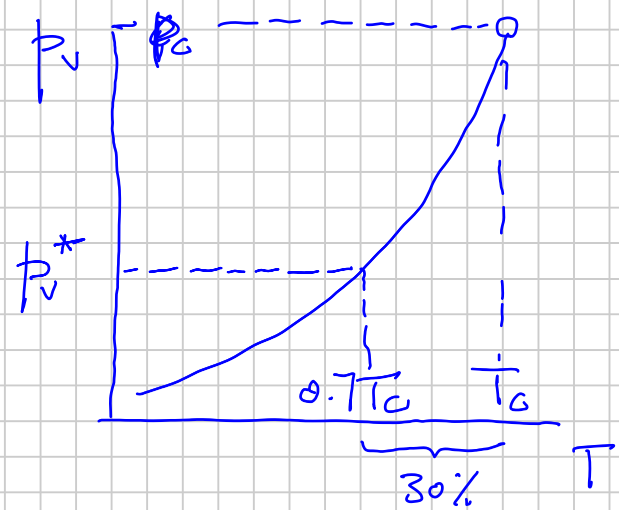
where A_1 = a function of pressure, with $A_1 = 1$ at $p = p_{sc}$ and $A_1 = 0$ at $p = p_K$. The key characteristics of K values vs. pressure

$$\omega \equiv -1 - \log_{10}\left(\frac{p_v^*}{p_c}\right)$$

CH_4 $\omega \sim 0$

C_{30} $\omega \sim 1$

C_{50} 2



z_i, K_i known

$$K_i \equiv \frac{y_i}{x_i}$$

Component Material Balance

$$n z_i = n_v y_i + n_L x_i$$

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

$$z_i = f_v\, y_i + (1 - f_v)\, x_i$$

$$K_i = y_i / x_i$$

$$y_i = K_i\, x_i$$

$$z_i = f_v\, K_i\, x_i + x_i - f_v\, x_i$$

$$= f_v\, (K_i - 1)\, x_i + x_i$$

Given $\sum z_i = 1$

$$z_i = x_i \left[f_v\, (K_i - 1) + 1 \right]$$

$$x_i = \frac{z_i}{f_v\, (K_i - 1) + 1} \quad \checkmark$$

Know z_i, K_i
Unknown f_v

$$y_i = K_i\, x_i = \frac{z_i\, K_i}{f_v\, (K_i - 1) + 1} \quad \checkmark$$

Mole Fractions must sum to 1

$$\underbrace{\sum y_i = 1 \qquad \sum x_i = 1}$$

$$\sum (y_i - x_i) = 0 = \underset{1}{\sum y_i} \; \underset{-}{-} \; \underset{1}{\sum x_i}$$

Rachford Rice ~1960

$$\sum_{i=1}^{N} \frac{z_i\, (K_i - 1)}{f_v (K_i - 1) + 1} = 0$$

One Unknown
One Equation

Muskat & McDowell 1949 footnote

$$h(f_v) = \sum \frac{z_i}{\underbrace{f_v + c_i}_{T_i}} = 0 \qquad \text{Find } f_v \checkmark$$

$$c_i = \frac{1}{K_i - 1} \quad ; \quad T_i = 0 \quad \text{for} \quad K_i = 1$$

$N-1$ solutions

* Only $\underbrace{\text{one solution}}$ that gives all $y_i, x_i > 0$

$$\downarrow$$

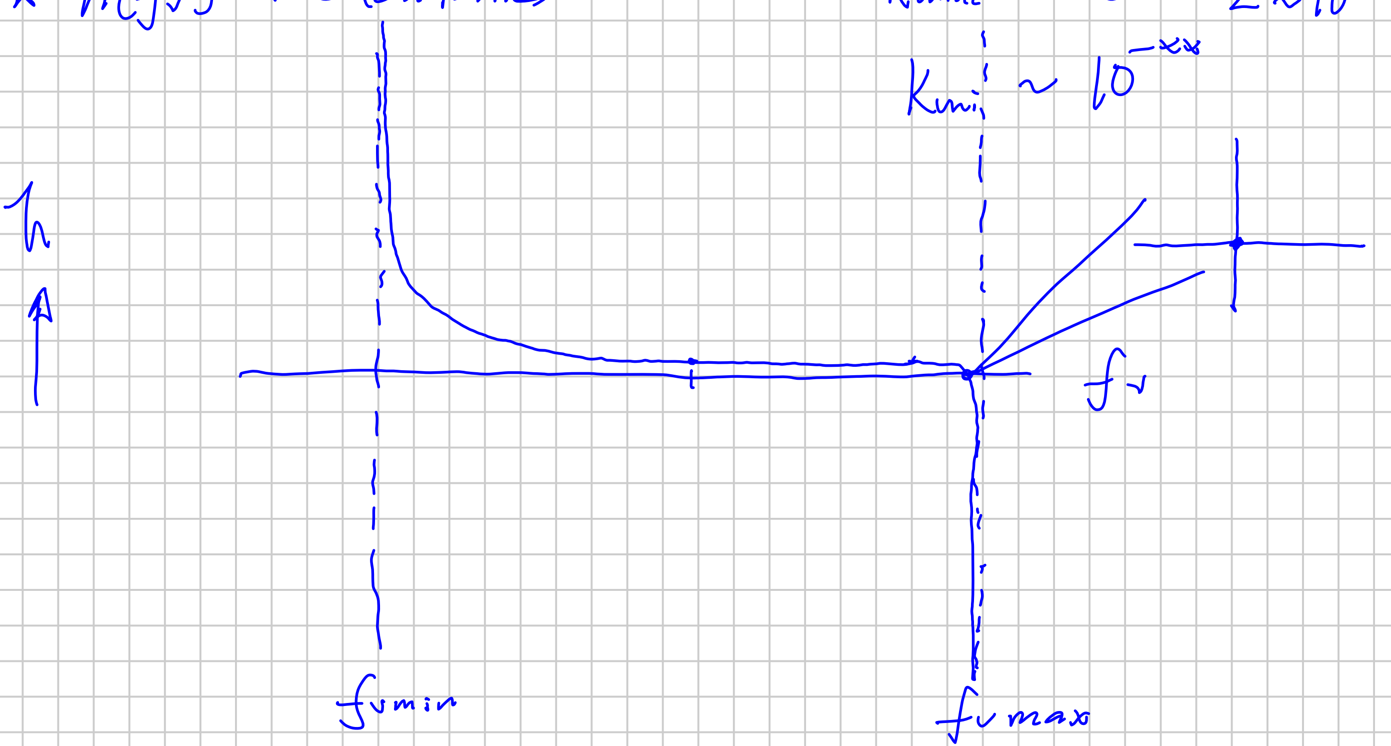
$$f_{v\,min} < f_v < f_{v\,max}$$

$$f_{v\,min} = \underbrace{\frac{1}{1-K_{max}}}_{<0} \qquad f_{v\,max} = \underbrace{\frac{1}{1-K_{min}}}_{>1}$$

* $h(f_v)$ monontonic

$K_{max} \sim 10^{xx}$ $\quad z \sim 10^{-xx}$

$K_{min} \sim 10^{-xx}$



Find a solution for assumed K_i

$$\mu_{iV}^{EOS}(y, p, T) \stackrel{?}{=} \mu_{iL}^{EOS}(x, p, T) \quad \text{all } i$$

yes ✓ done with tol. 10^{-10}

No : try new set K_i ↻ iterations

10, 100, 1000

How to solve for saturation pressure? p_s p_d / p_b

- Specify z_i, T
  - Guess p
  - Solve RR (MM)
  - Solve $\mu_{iV} = \mu_{Li}$

K_i^{est}

$\Rightarrow f_v$

$1 - f_v = 0 \, (\epsilon)$

$f_v = 1$: Dewpoint

Change p until

$f_v = 0 \, (\epsilon)$: Bubblepoint

(More efficient methods)

Ch. 4. only required reading 4.3.1