MONDAY REVIEW

* Compositions

Isomers PNA

- Components (N_2 CO_2 H_2S C_1 C_2 C_3 iC_4 nC_4 iC_5 nC_5 ... C_6 ... C_7 ... C_8 C_9 C_{N-1} C_{N+})
- Amounts (m_i n_i | w_i z_i y_i x_i)
  - GC (Baseline Shift | Internal Standard | M_i ±)
  - Distillation (TBP | Crude Assays) : m_i $\bar{\rho}_i \leftrightarrow \bar{M}_i$
  - EOS requires z_i (molar)
  - Lab measures w_i (mass)

$\bar{M}_i$ ±

KF | Lab | ...

$\bar{M}_i = 14 i + h$

$-20 < h < +2$

PVTsim: $h = -4$

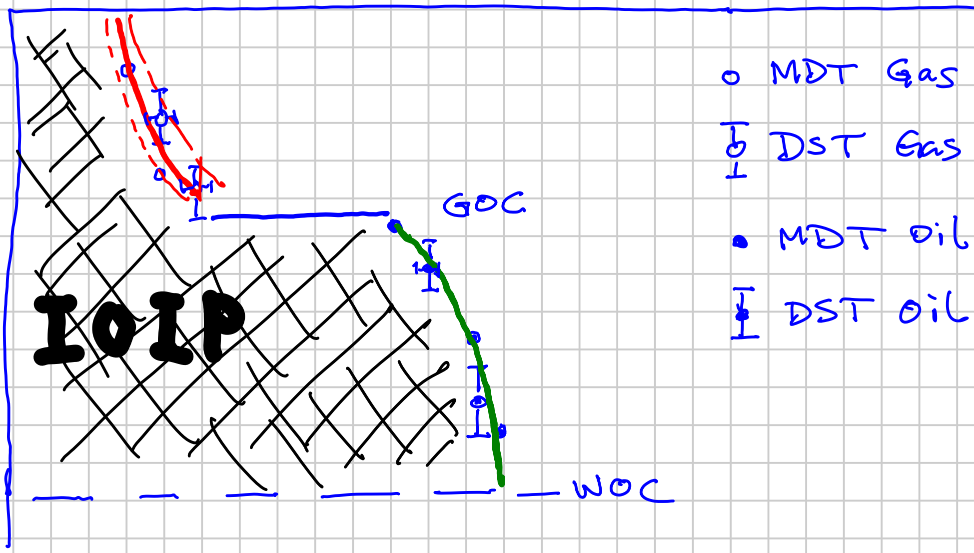
± Flash GOR

- Decontamination ± (particularly if molar dist. NOT Exp.)
- Molar Distribution Modeling
  - Discrete exponential ($\bar{M}_{n+}$, h)
  - Continuous Gamma ($\bar{M}_{n+}$, α, η, M_{Li})
  - Applications:
    - Extend C_{N+}
    - QC GC data, heavier w_i z_i & w_{N+} z_{N+}
    - Decontamination
    - Replace uncertain amounts (heavier w_i z_i & w_{N+} z_{N+})
    - Estimate all M_i for C_{n+}
  - Few (only PhazeComp ?) allow applications above except first (extending C_{N+})

* SAMPLING

- Methods
  - Surface Separator
  - Cased hole (traditional) BHS } Mobility-Average over Perf'd Interval
  - Openhole Formation Tester (MDT|RCI) - Depth-specific
  - Wellhead | Isokinetic $\bar{o} \sim C_{5+}\ C_{6+}$
  - Flashed stabilized STO $C_{5+}\ C_{6+}$

$$IOIP/HCPV = 1/B_{oi} = \overset{OGR}{r_{si}}/B_{gi} \propto \boxed{z_{n+}} \text{ mol-\%}$$



- Why Sample?
  1. PVT data to develop | verify | modify an EOS model
  2. Fluid Initialization : spatial fluid variations

z_i R_s r_s $(p_b\ p_d)$ I J K

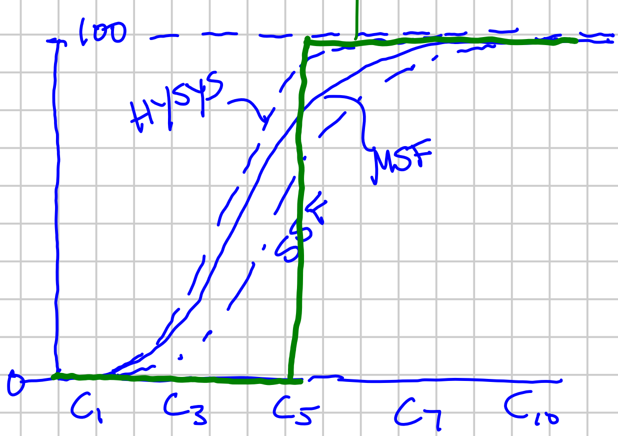
$$\boxed{GOR} = \frac{(1-z_{5+})\left(\frac{RT_{sc}}{p_{sc}}\right)}{z_{5+}\left(\frac{M}{\rho}\right)_{5+}} = \boxed{C \cdot \frac{1-z_{5+}}{z_{5+}}}$$

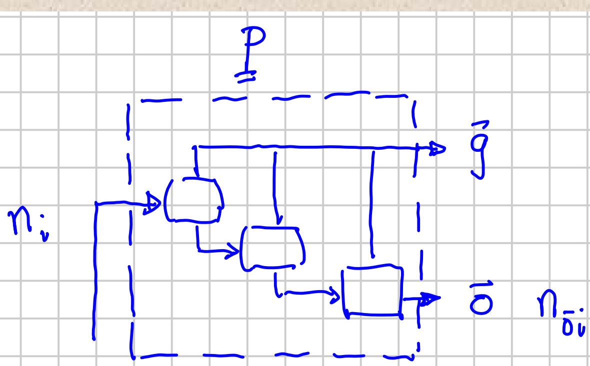
- **Monday**
  - Compositions. ✓
    - Sampling. ✓
    - Measurement. ✓
    - Ch. 5 Heptanes-Plus Characterization. (✓)

$RF_{\bar{o}i} = \dfrac{n_{\bar{o}i}}{n_i}$

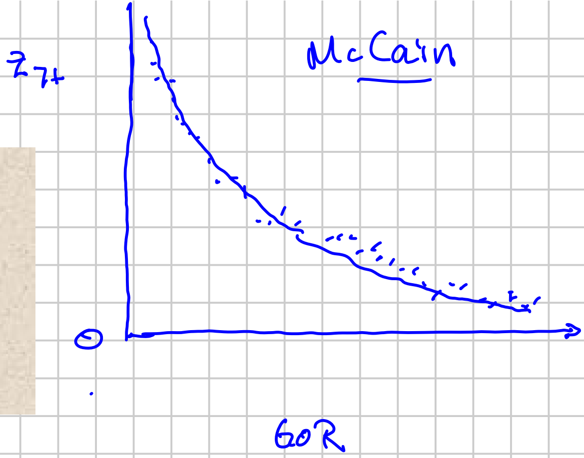
$RF_{oi} = 1$ C_{5+}

$RF_{oi} = 0$ C_{4-}





EQUATION OF STATE (EOS)



- **Tuesday**
  - Equations of State (EOS) Introduction.
  - Phase Behavior Review.
  - EOS Calculations with PhazeComp.
  - C_{7+} Characterization, Part B

8 T_b { T_c p_c ω s } C_{7+} fractions

EOS

CUBIC EOS

(1) Which EOS: { vdW 186x | RK 1949 }

{ ZJRK, Amoco RK 1980s vintage }

99% – SRK } : w/ w/out* Volume Translation – 3rd Constant "c"
– PR }

- Original 1977 } ≠
- Modified 1978/79 }

>90% (Modified 1978/79)

* w/ VT 99% since 2000

⇒ Vast majority of EOS < SRK / PR79 w/ VT (3-const EOS)

(2) What does an EOS do?

PVT Calcs of Gas & Oil & Critical/Undefined Phases at any (p, T)
{ also water phase }

Phase Amounts (V, m, n)
Phase Density
Phase Compositions (y_i x_i)

③ What is required to use an existing EOS

3rd const. (c_i)

EOS Model
- (a) Table 1 : i $\quad \underline{M_i}$ $\quad T_{ci}$ $\quad p_{ci}$ $\quad \omega_i$ $\quad s_i$ $\quad 5 \cdot N$
- (b) Table 2 : BIP Binary Interaction Parameters

k_{ij} = correction terms ($=0$ No corr.)

$-0.1 < k_{ij} < 0.2$

$k_{ij} = k_{ji} \qquad k_{ii} = 0$

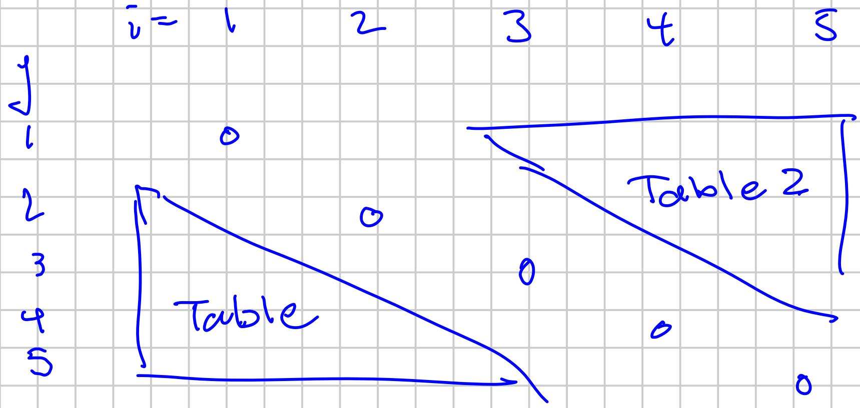
MAY BE:

Multiple EOS models:

e.g. $\underbrace{\text{R1 R2 S} \dots}$

Deal with component 'slates' in each EOS $\neq = ?$

$$\frac{N^2 - N}{2}$$



10 BIPs

(c) Molar composition z_i

Same components as in the two tables (EOS model)

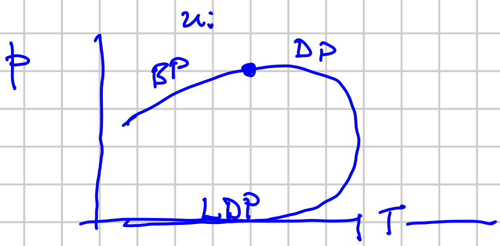
or mapping

④ <u>How does the EOS do calculations?</u>

SATURATION PRESSURE

$\left.\begin{matrix} z_i \\ y_i \\ x_i \end{matrix}\right\} (u_i, T) \rightarrow p_s(T)$ BP or DP or both or none

$\rightarrow$ 2nd incipient phase composition



$(z_i, T, p) \rightarrow$ # phases exist $(1, 2, 3, \ldots)$

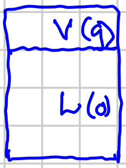
phase amount (n, m, V)

phase densities ρ

phase compositions y_i x_{i1} $x_{i2} \ldots$

FLASH

Two Phases



$$E_{iV} = E_{iL}$$

$$\underbrace{\mu_{iV} = \mu_{iL}}$$

Gibbs Energy

Minimizing the Total Chemical Energy of the System (z_i, p, T)

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

$$\mu_{iV}(y_i, p, T) \qquad \mu_{iL}(x_i, p, T)$$

$$\uparrow \qquad\qquad \uparrow$$

$$n_V \qquad\qquad n_L$$

$$\mu_{iV}(n_{iV}, p, T) \overset{\checkmark}{=} \mu_{iL}(n_{iL}, p, T)$$

$$\min \quad \mu_t = \sum n_V \cdot \mu_{iV} + n_L \mu_{iL}$$

Gibbs Stability Test

$$\Delta \mu_t = \sum \epsilon \, \mu_{iz}(u_{iz}, p, T) + (1-\epsilon)\mu_i$$

Search

Michael Michelsen 1980–82

⑤ How to validate an EOS ?

- Is it thermodynamically kosher (consistent)

Check list (4)

PR (3)
SRK (3) } starting point

VT

Cubic EOS

van der Waals 187x

$$p = \underbrace{\frac{RT}{v-b}}_{\text{Repulsive}} - \underbrace{\frac{a}{v^2}}_{\text{Attractive}}$$

Two constants a & b
Different for each component

$$v = \frac{V}{n}$$

same term different b's { vdW, RK, SRK, PR } different

$$p = \frac{RTv^2 - a(v-b)}{(v-b)v^2} = \frac{RTv^2 - a(v-b)}{v^3 - bv^2}$$

$$\Rightarrow \quad v^3 + \underline{\quad\quad} v^2 + \underline{\quad\quad} v + \underline{\quad\quad} = 0$$

what is a, b

How to get a, b ?

H_2O : Steam Table

p	T	v
One Phase		

Two Phases

p_v	T	v_{sL}	v_{sV}
Vapor Pressure			
$T_{min} < T < T_c$			

Excel

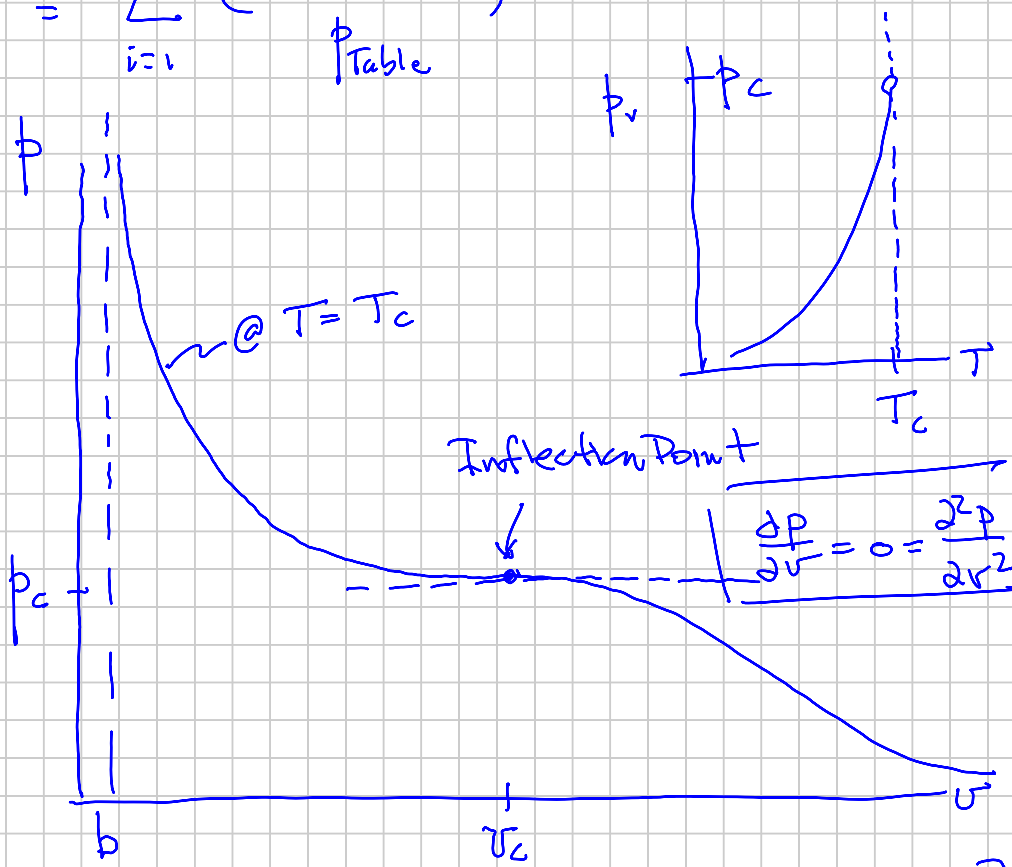
$\boxed{a}$ ✓
$\boxed{b}$ ✓
$\Big\}$ Guess $\Rightarrow$ min SSQ

Depend on which data used

i	p_{Table}	T_{table}	v_{Table}	$p^{EOS}(T, v)_{Table}$
	100s			
	1000s			

$$\min \quad SSQ = \sum_{i=1}^{1000} \left(\frac{p_{Table} - p^{EOS}}{p_{Table}} \right)^2$$

Every Compound



vdW : Find a, b such that $\left[\frac{\partial p}{\partial v} = \frac{\partial^2 p}{\partial v^2} = 0 \text{ at } (T_c, p_c) \right]$

T_c, p_c

$$\boxed{\begin{aligned} a &= \underbrace{\Omega_a}_{\sim 0.4} \left(\frac{R^2 T_c^2}{p_c} \right) \\ b &= \underbrace{\Omega_b}_{0.1} \left(\frac{R T_c}{p_c} \right) \end{aligned}}$$

$\Omega_a^{vdW} = 27/64$

$\Omega_b^{vdW} = 1/8$

$v_c^{vdW} \neq v_c$ most components

$$Z \equiv \frac{pv}{RT} \qquad Z_c^{RK} = 1/3 \qquad Z_c^{PR} = 0.3074\ldots$$

$$Z_c = \frac{p_c v_c}{RT_c} \qquad Z_c^{vdW} = \frac{3}{8}$$

$$v_c^{\underline{SRK},\ \underline{PR},\ \underline{vdW}} \neq v_c^{Actual}$$

5-40%

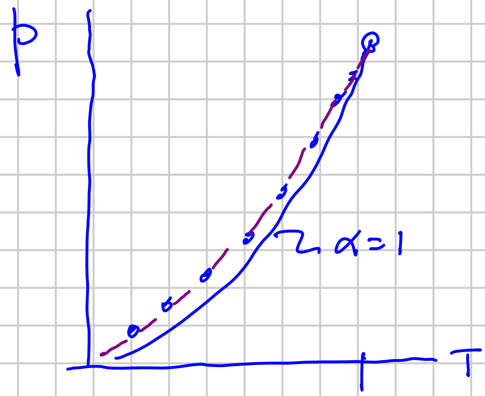
$$b^{EOS} \neq b^{Actual}$$

5-40%

Cubic EOS overpredict v of liquids and critical state

$\Rightarrow \rho^{EOS} = \frac{M}{v}$ underpredict 5-40% oil densities

1949 : Redlich-Kwong



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

$$\alpha = \underbrace{1/\sqrt{T_r}}$$: Improved $p_v(T)$ lighter HCs

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

Equilibrium K-values

Know $\{ \underline{z_i}, \underline{K_i}(p,T) \} \Rightarrow$ Accurately calc. n_v y_i / n_L x_i

$p < 1000$ psia (sep. conditions)

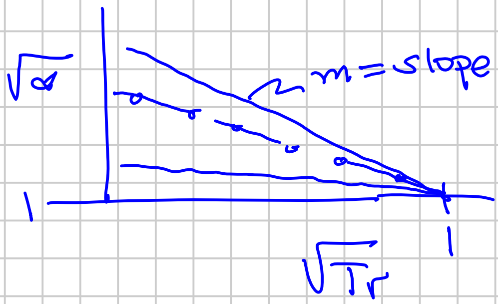
$$\underbrace{K_i \cong \frac{p_{vi}(T)}{p}}$$

Getting $p_{vi}(T) \Rightarrow K_i^{\checkmark} \Rightarrow V_{STO}^{\checkmark}$

1970: Process Industry was ~~starting~~ to use EOS for Gas Processing optimization

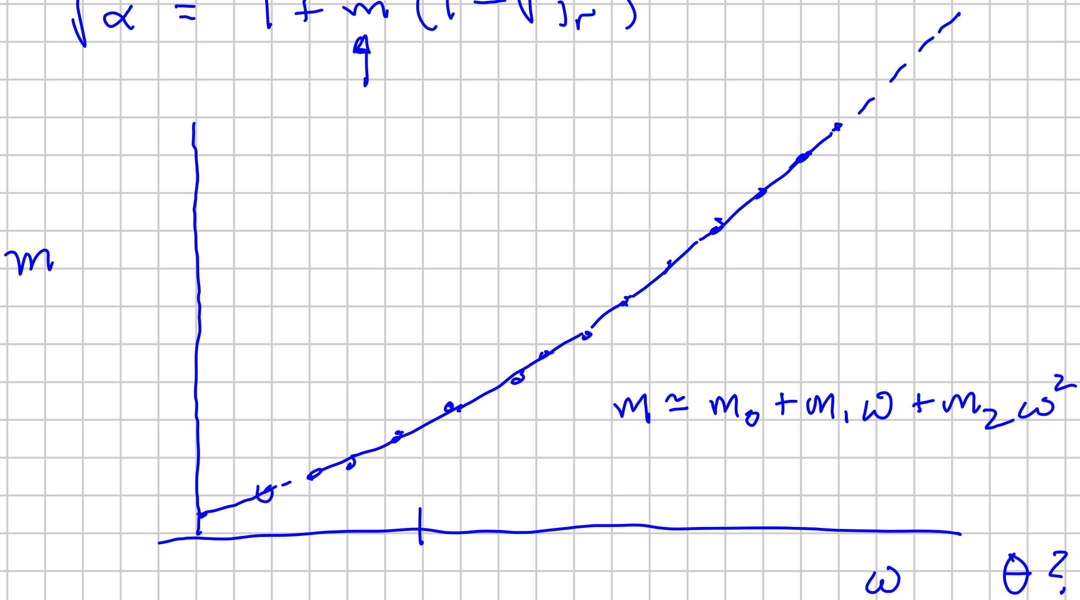
$p_{vi}(T)$ accurate for <u>all</u> components

Soave Find $\alpha_i(T_r)$



Tabulated m all components

$$\sqrt{\alpha} = 1 + m(1 - \sqrt{T_r})$$



Acentric Factor (Pitzer)

SRK = RK except $\alpha(T_r, \omega)$ $\Rightarrow$ $p_{vi}(T)$

Any Component

$\Downarrow$

Accurate (Process - Crude)

K_i

$\underbrace{1972 \to 1977\ (1980)}$

$\rho_o \sim 10-40^+\%$ too low

Oil density correlation $\underline{\text{COSTALD}}$

$\rho_o(x_i, \underbrace{p, T}_{T_{sc}, p_{sc}})$ $\pm 1\%$

$\cancel{\rho_o^{EOS}}$

1977 Peng - Robinson

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

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2$$

1977 $m = m_0^{PR} + m_1^{PR}\,\omega + m_2^{PR}\,\omega^2$

78-79 original m eq. $\omega \lesssim 0.49$

$$m = \sum_{k=0}^{3} \tilde{m}_k^{PR}\,\omega^k \qquad \omega > 0.49$$

ρ_o^{PR} only off ~ -5 to 25%

1978 Katz — Bergman (PhD), Firoozabadi — PR EOS

SPE JPT

PE.: PR

Process: SRK

1980 Coats EOS Simulator

Miscible Processes

ρ_o^{EOS} ρ_g^{EOS}

ZJRK ARK Universities a, b, c ...

1982 Peneloux et al. "c" Volume Translation shift

$$\boxed{v = v^{EOS2} - c}$$

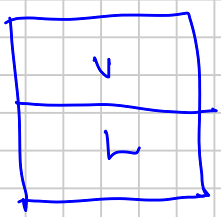
No effect on K_i μ_i

$$c = \sum u_i c_i$$

$$\mu_{iV} + \cancel{c_i} = \mu_{iL} + \cancel{c_i}$$

c_i of the components?

10 − 0.2 = 10



y_i $v_V^{EOS2} \Rightarrow v_V^{EOS3}$ little change

x_i $v_L^{EOS2} \Rightarrow v_L^{EOS3}$ just the right change

1 − 0.2 = 0.8

ρ_o ±1-2 %

ρ_g ±1-2 % as before

TABLE 4.3—VOLUME-TRANSLATION COEFFICIENTS ($s_i = c_i/b_i$) FOR PURE COMPOUNDS FOR THE PR EOS AND SRK EOS

Component	PR EOS	SRK EOS
N_2	−0.1927	$\boxed{-0.0079}$
CO_2	−0.0817	0.0833
H_2S	−0.1288	0.0466
C_1	−0.1595	$\boxed{0.0234}$
C_2	−0.1134	0.0605
C_3	−0.0863	0.0825
$i\text{-}C_4$	−0.0844	0.0830
$n\text{-}C_4$	−0.0675	0.0975
$i\text{-}C_5$	−0.0608	0.1022
$n\text{-}C_5$	−0.0390	0.1209
$n\text{-}C_6$	−0.0080	0.1467
$n\text{-}C_7$	0.0033	0.1554
$n\text{-}C_8$	0.0314	0.1794
$n\text{-}C_9$	0.0408	0.1868
$n\text{-}C_{10}$	0.0655	0.2080

b_i, c_i: $\frac{m^3}{kg\text{-mole}}$ $\frac{ft^3}{lb\text{-mole}}$

$$s_i = \frac{c_i}{b_i}$$ dimensionless shift factor

These s_i numbers ~(−deviation error) in liquid density without using s_i

HYSYS: uses

$$v = v^{EOS2} + c$$

Input the negative of the actual c value

Peneloux recommends for C_{7+} fractions:

$$\boxed{\gamma_i} = \frac{\rho_{Li}(T_{sc}, P_{sc})}{\rho_{\bar{w}}} = \frac{\rho_{Li}^{EOS}(T_{sc}, P_{sc}, a, b, \underline{\underline{c}})}{\rho_{\bar{w}}}$$

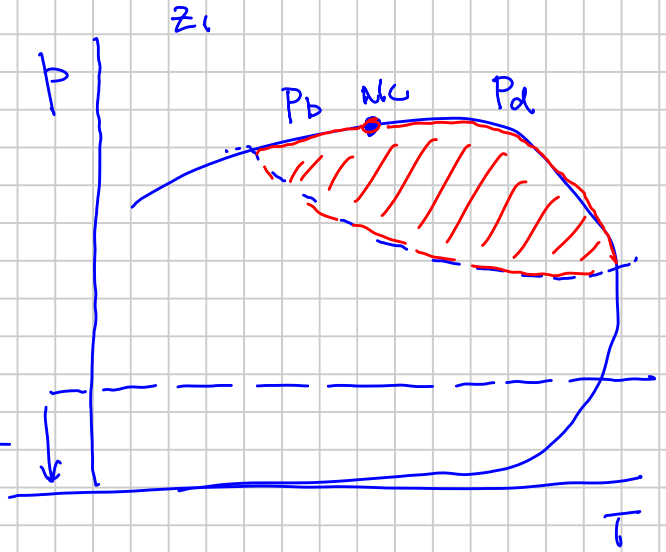
Regress Find

$$\rho_L^{EOS} = \frac{M}{v_L^{EOS2} - \boxed{c}}$$

Getting s_i (c_i) for C_{7+} fractions accurate (i.e. $\gamma_i^{lab} = \gamma_i^{EOS}$) will ensure accurate reservoir oil densities also.

Reservoir EOS calculation are difficult to predict accurately because

$K_i(\underline{\underline{p}}, \underline{\underline{T}}, \underline{\underline{z_i}})$ are wrong.



$K_i \approx \frac{p_{vi}}{p}$

196x's Prausnitz

1978 KF PR $C_1 - C_{7+}$ $\underline{0.02 \to 0.08}$

SRK HC-HC ~ 0

Mixture :

$\ldots K_i \ldots K_j \ldots$

$$\bar{a} = \sum_i \sum_j u_i u_j (a_i a_j)^{1/2} \cdot \underline{(1 - k_{ij})}$$

$$\bar{b} = \sum_i u_i b_i$$

TABLE 4.1—BIP's FOR THE PR EOS AND SRK EOS

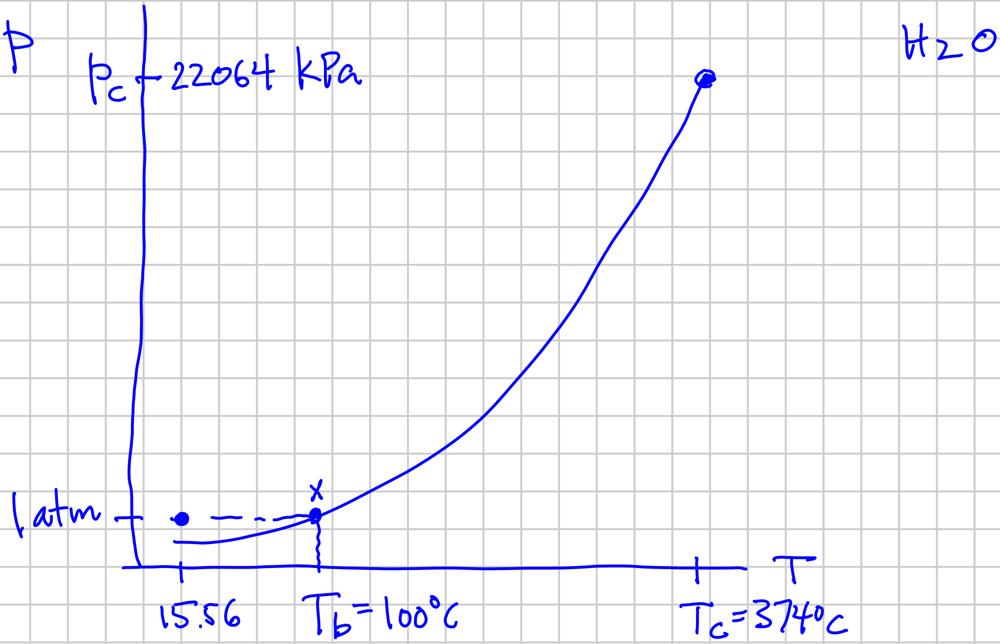
	PR EOS*			SRK EOS**		
	N_2	CO_2	H_2S	N_2	CO_2	H_2S
N_2	—	—	—	—	—	—
CO_2	0.000	—	—	0.000	—	—
H_2S	0.130	0.135	—	0.120†	0.120	—
C_1	0.025	0.105	0.070	0.020	0.120	0.080
C_2	0.010	0.130	0.085	0.060	0.150	0.070
C_3	0.090	0.125	0.080	0.080	0.150	0.070
i-C_4	0.095	0.120	0.075	0.080	0.150	0.060
C_4	0.095	0.115	0.075	0.080	0.150	0.060
i-C_5	0.100	0.115	0.070	0.080	0.150	0.060
C_5	0.110	0.115	0.070	0.080	0.150	0.060
C_6	0.110	0.115	0.055	0.080	0.150	0.050
C_{7+}	0.110	0.115	0.050‡	0.080	0.150	0.030‡

*Nonhydrocarbon BIP's from Nagy and Shirkovskiy.[24] Use for both the original PR EOS (Ref. 7) and modified PR EOS (Ref. 25).

**Nonhydrocarbon BIP's from Reid *et al.*[3]

†Not reported by Reid *et al.*[3]

‡Should decrease gradually with increasing carbon number.



$\boxed{\text{RK EOS}}$ Results:

SRK

$\rho_{\bar{w}}$ = 742 kg/m³ vs 1000 kg/m³ 1005 kg/m³

$P_s = P_v(T = T_b)$ = 2.94 bara vs 1.0 bara 0.93 bar ✓

$P_c(T = T_c)$ = 220.7 bar vs 220.6 bara

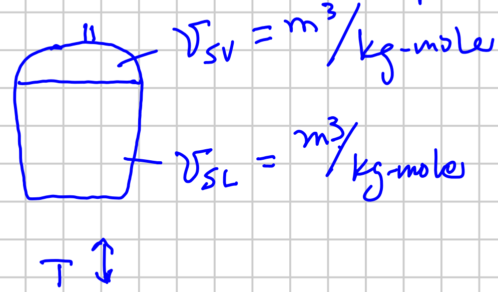
Propane Tank

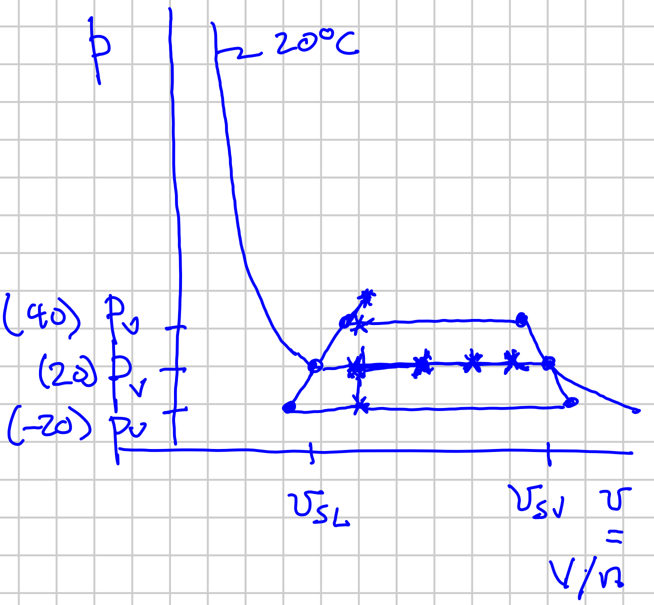
$\underbrace{-20°C}$ < T < $\underbrace{+40\,C}$

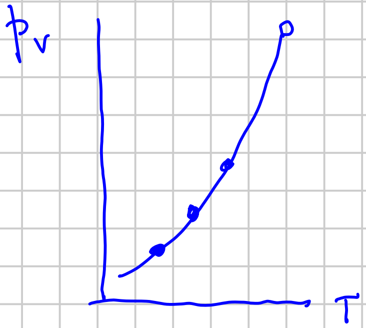
P_{min}

P_{max}

5 L = const







20°C P change as we empty the tank?

kg C_3 to fill the tank (5L) with 80% Liquid?
@ 20°C

ρ_L @ 20°C / p_v

ρ_v — " —

$$V = 5L = V_L + V_v = \frac{m_L}{\rho_L} + \frac{m_v}{\rho_v}$$

4 1

$$\frac{m_L}{\rho_L} = 4 \ L \qquad \frac{m_v}{\rho_v} = 1 \ L$$

$$m = m_L + m_v$$

$\rho_L = 501.18$ kg/m^3

$\rho_v = 18.029$ kg/m^3

$$= \rho_L \cdot V_L + \rho_v V_v$$

$$= (501.18)(0.004) + (18.029)(0.001) = \qquad \text{kg}$$

Part B of C_{7+} Characterization

$\{ i \quad M_i \}$ Part A $\qquad \{ T_{ci} \quad p_{ci} \quad \omega_i \quad s_i \}$ Part B

$\uparrow$

Lab | KF | Γ

C_7

C_8

$\vdots$

C_{N+}

Every PVT program does Part B differently.

Step 1. Estimate $\gamma_i = f(M_i, \underline{C_f})$ $\qquad \gamma_{7+}$ $\qquad$ All others

Most reliable if TBP data or Crude Assay data

$\gamma_i = A_0 + A_1 \ln(i)$ $\qquad \boxed{\rho_{C_6} \mid \rho_{C_{7+}}}$ KF $\qquad$ PVTsim

Very important to get ρ_o accurate,

$s_i \Leftrightarrow \gamma_i$

Input: $\underline{\gamma_{7+}} \stackrel{\checkmark}{=} \dfrac{\sum z_i M_i}{\sum \dfrac{z_i M_i}{\gamma_i(C_f)}}$

Step 2. $T_{ci} \qquad p_{ci}$

(a) All except PVTsim :

Est. $\underline{T_{bi}} = f(M_i, \gamma_i)$ $\qquad$ many correlations Twu

T_{ci}, p_{ci} $= f(T_{bi}, \gamma_i)$ $\qquad$ — " — Twu

* $\omega_i = f(T_{bi}, T_{ci}, p_{ci})$ $\qquad$ Correlations

or

$\underline{\omega_i}$ so that $T_{bi}^{EOS} = T_{bi}$ $\qquad$ PVTx PhazeComp

(b) PVTsim

$$\left.\begin{array}{l} T_{ci} \\ P_{ci} \\ m_i \end{array}\right\} f(M_i, \gamma_i) \quad \Rightarrow \text{EOS } (\omega_i) \Leftrightarrow m_i$$

Step 3. Volume Shift

Find s_i so that $\gamma_i^{EOS} = \gamma_i$ (step 1)

$$= \frac{\rho_{Li}^{EOS}(s0)}{\rho_w}$$

$$i \quad M_i \quad \{\gamma_i \quad T_{bi}\} \quad \underbrace{T_{ci} \quad p_{ci} \quad \omega_i \quad s_i}$$

C_6

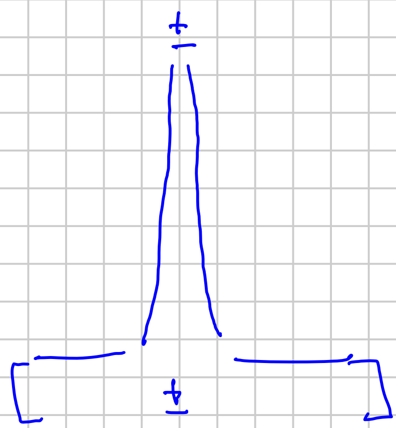
C_7

C_8

$\vdots$

$\boxed{C_{N+}}$

C_{25+} C_{35+}

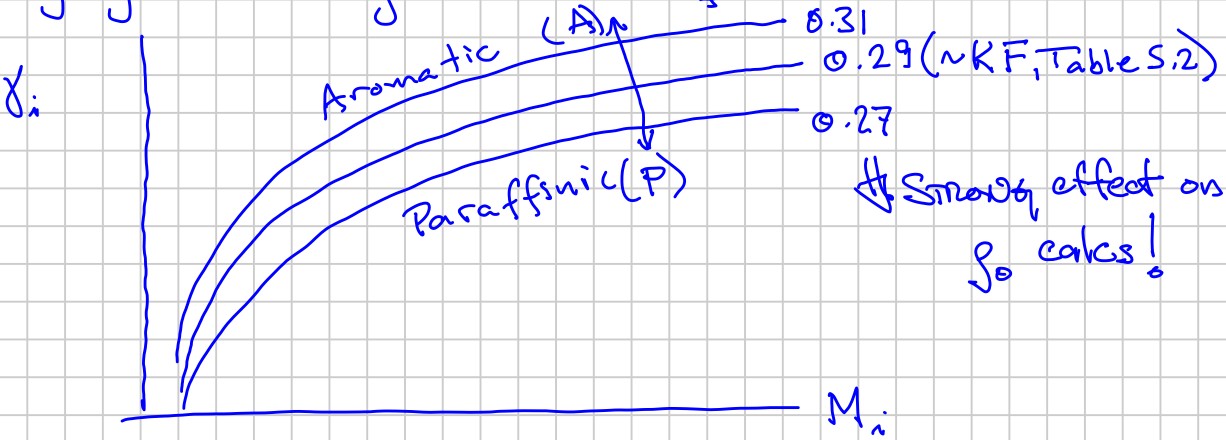


Run and study out files of c, d, e, f data sets that finally builds the complete C_{7+} characterization

```
TITLE "Core Laboratories Good Oil Well No. 4"
TITLE "(a) Input BHS mass (weight) composition."
TITLE "(b) Split C7+ using Gamma distribution model."
TITLE "(c) Determine C7+ SG-MW relationship (Soreide correlation)."
TITLE "(d) EOS calculations, no BIPS, no VT (volume translation)."
TITLE "(e) EOS with BIPs, no VT."
TITLE "(f) EOS with BIPs, with VT."
```

vs PVT Data

(c) Try changing mannually Soreide C_f value:

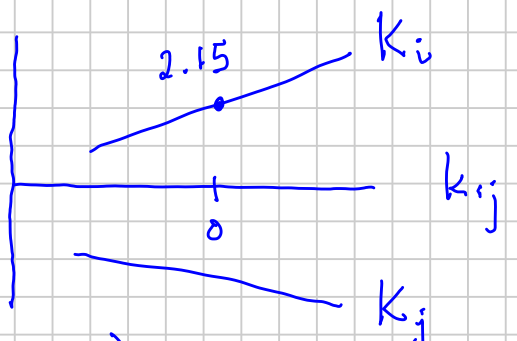


Strong effect on ρ_o calcs!

Søreide[35] ***Correlations.*** Søreide developed an accurate specific-gravity correlation based on the analysis of 843 TBP fractions from 68 reservoir C_{7+} samples.

$$\gamma_i = 0.2855 + C_f(M_i - 66)^{0.13}. \quad \ldots\ldots\ldots\ldots\ldots \quad (5.44)$$

(e) Compare K_{C_1} with and w/out C_1-C_{7+} BIPs @ p_b



BIPs k_{ij} : K_i K_j

K_{C_1} (e w/ BIPs) = 2.417 @ 2224 psig | K_{C_1} (d w/out BIPs) = 2.15 @ 2224 psig

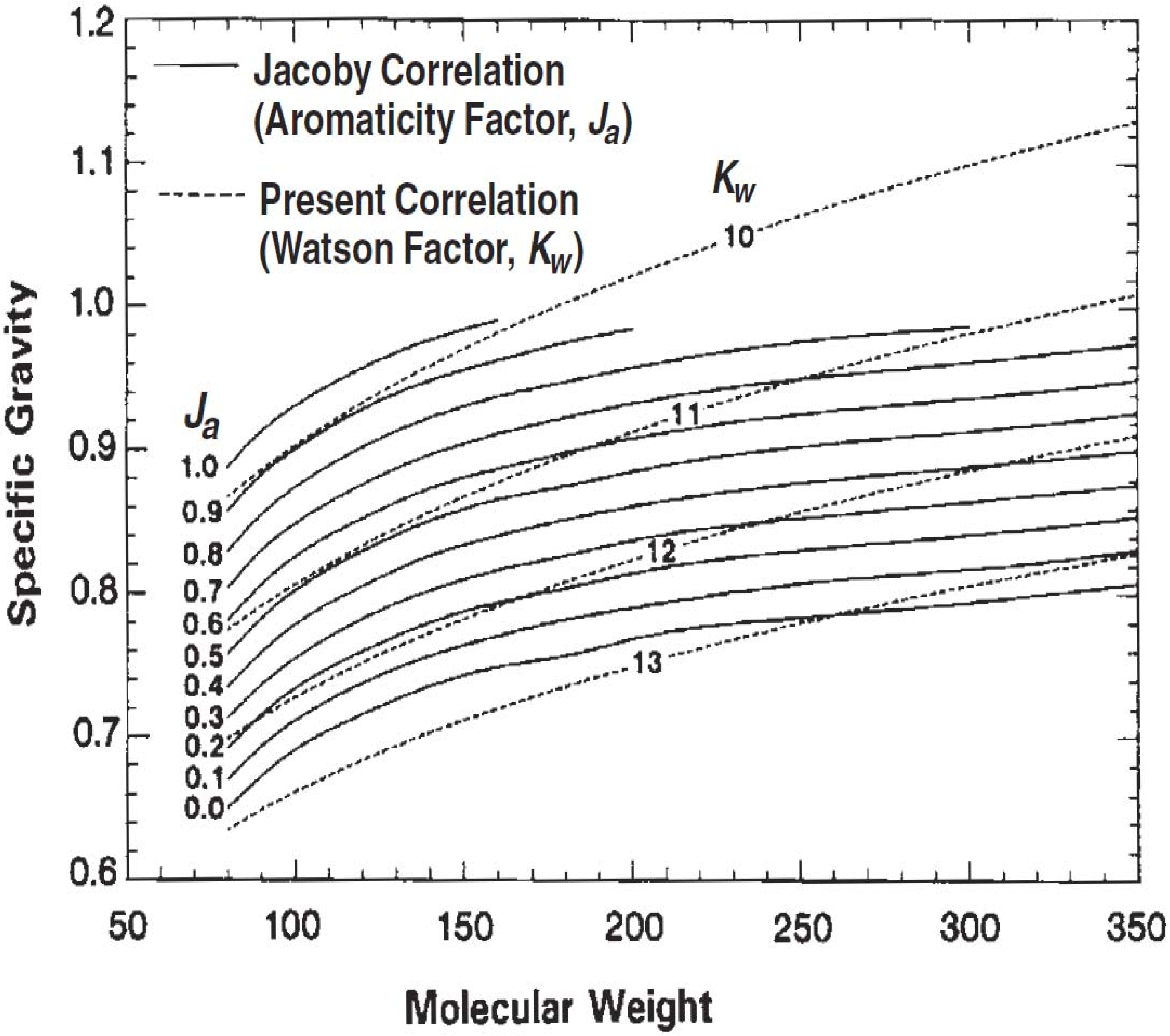


Fig. 5.14—Specific gravity vs. molecular weight for constant values of the Jacoby aromaticity factor (solid lines) and the Watson characterization factor (dashed lines). After Whitson.[25]

$$\gamma_i = 6.0108\, M_i^{0.17947} K_w^{-1.18241} \qquad (5.36)$$

$$\gamma = 0.8468 - \frac{15.8}{M} + J_a\left(0.2456 - \frac{1.77}{M}\right) \qquad (5.42)$$

$$\boxed{\frac{\gamma}{M} = A_0 + A_1 M}$$

not published, used by some labs (~ KF)

Add an experiment to the final f run

C_{31+} : $z_{30+} = 1$

ρ @ STC $= \gamma_{30+}$?

$p_v = p_{sat}$ @ $T = T_b$

```
Note: "Check C30+ TB and AF | SG and VS are consistent"

MIX FEED C30+ 1 MOLE
TEMP = 1444.39 R PSAT
TEMP 60 F PRES 1 ATM FLASH

EOF
```

```
Saturation Pressure Calculation 2
=================================

One Phase at Temperature = 1444.39 R, Pressure = -0.000647378 psig:
```

✓ 1 atm

```
Flash Calculation 1
===================

One Phase at Temperature = 60 F, Pressure = 1 atm:
```

Rel. Moles:	1.0000e+00	1.0000e+00	0.0000e+00
Mol. Weight:	494.339	494.339	494.339
Z-Factor:	2.2628e-02	2.2628e-02	2.2628e-02
Density (g/cc):	9.2217e-01	$\boxed{9.2217e-01}$	9.2217e-01

✓

vs

$\gamma_{30+} = 0.9231$ CHAR Table

✓

"v" $\boxed{\left(\frac{M_i}{\gamma_i}\right) = A_0 + A_1 M_i}$ not published, used by some labs (~ KF)

$$\bar{\gamma} = \frac{\sum z_i M_i}{\sum \frac{z_i M_i}{\gamma_i}} \qquad \frac{\text{mass}}{\text{volume}}$$

Ideal Volume Mixing

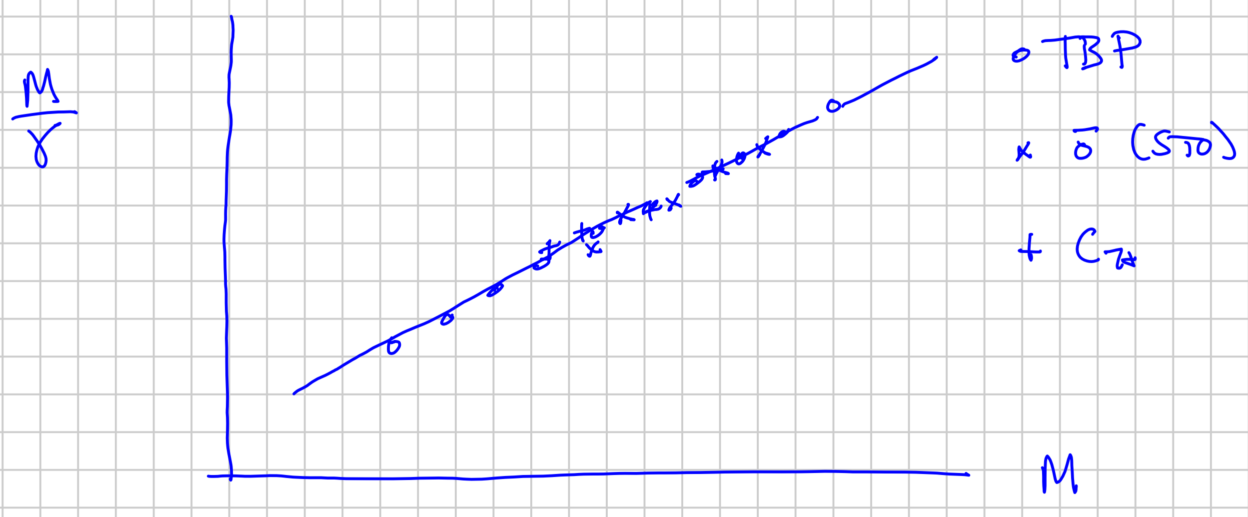
$$= \frac{\sum z_i M_i}{\sum z_i \cdot (A_0 + A_1 M_i)} = \frac{\sum z_i M_i}{A_0 + A_1 \sum z_i M_i}$$

$$\bar{\gamma} = \frac{\bar{M}}{A_0 + A_1 \bar{M}}$$

$$\boxed{\frac{\bar{M}}{\bar{\gamma}} = A_0 + A_1 \bar{M}}$$

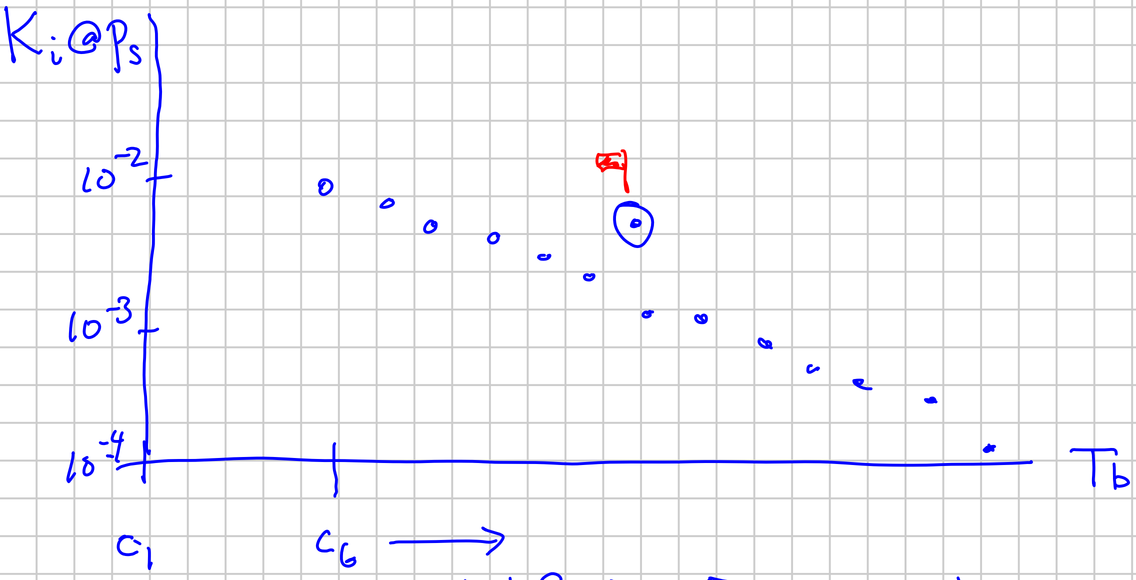
Data M, γ : C_{7+} C_{15} $\bar{o}$

TBP fractions



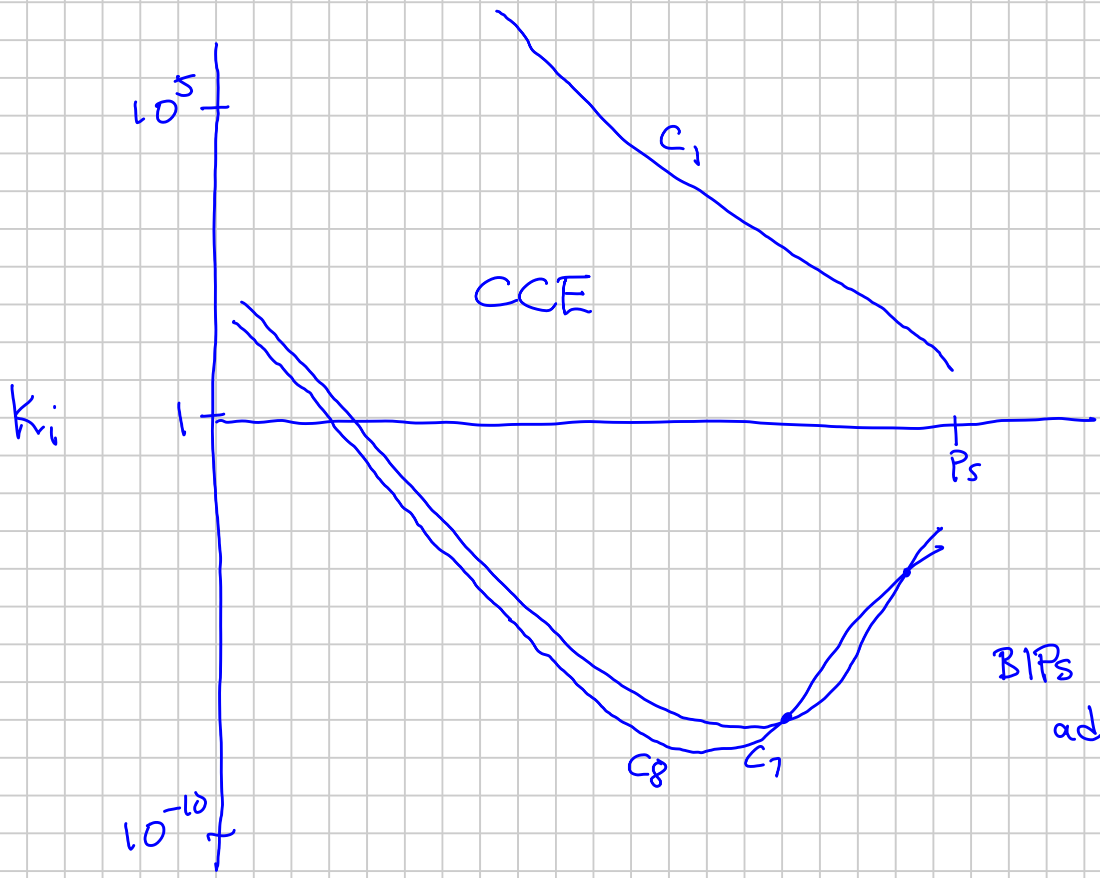
"QC on EOS"

① K_i @ p_s (all other pressures) ~ monotonic vs $T_{bi}^{(EOS)}$
M_i



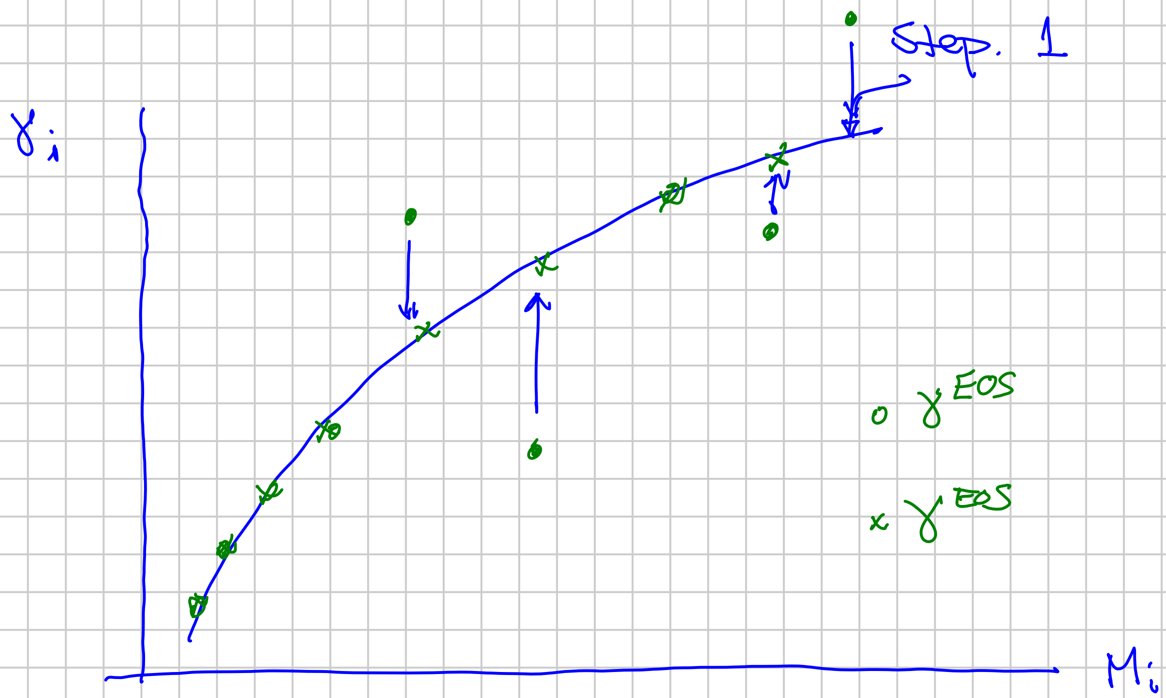
Modifying EOS parameters

② $K_i(p)$ for HCs, no crossing at higher pressures



BIPs need adjustment

③ $\rho_{L_i}^{EOS}$ $i \in G_{+}$ follow closely the $\gamma_i(M_i)$ trend



PVTsim (pre 2014)

other programs

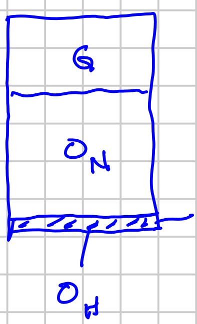
Start with $s_i \Leftrightarrow \gamma_i$

Change T_c, P_c, ω of a fraction w/out updating s_i to stay on trend.

Easy to fix

④ The EOS predicts 3-phases in certain (p, T, z) space

PhazeComp



Very Heavy C_{N+} dominated phase

EOS-based

Real problem in Reservoir Simulation