Note Title 10/27/2016

Fitting Storeide Eq. to $\gamma(M)$ "data"

- Selecting of "Data"
  - Flashed oils (average ~ C_{7+}) only real data
  - TBP (seldom available) - individual cuts
    SCN | Assay Cuts

"KF" SCN

- Data weighing
  - C_{7+} (°) highest
  - DLE | CVD C_{7+} not very reliable — low w_i
  - Sep Gases w/ extended analysis: C_{7+} - $w_i = 1$

$$K_W = 4.5579\, M^{0.15178}\, \gamma^{-0.84573}$$

NS : 11.8-12

< 11.5 Aromatic

> 12 Paraffinic (Wax)

K_{W7+} ~ 10.8

Cubic Equations of State (EOS)

$p-V-T-n$ $\qquad v \equiv \frac{V}{n}$

$p-v-T$ Equation

State : Phases (Vapor | Liquid (s)

Gas $\qquad$ Oil, Water

Normal | Heavier | Solid-like

Oil

Ideal Gas Law: $pv = RT$ $\qquad$ Limited to Ideal Gas

Real Gas Law : $pv = RTZ_{(p,T)}$

"Virial" EOS (BWR)

1940s

U. Michigan (Katz)

Standing-Katz Z-factor Chart

1980s : Equations that specifically "Fit" SK Chart

Yarborough and others

$$Z \equiv \frac{pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \cdots$$

$$\rho_m \equiv \frac{1}{v}$$

Liquids : $\quad c = -\frac{1}{V}\left(\frac{dV}{dp}\right)_T = \text{constant } (T)$

State

~1870 van der Waal : States (Vapor & Liquid)
Critical
Any Fluid State
(1 or 2 or ..)
phases

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$Z \equiv \frac{pv}{RT} \Rightarrow v = \frac{RT}{p} \cdot Z$$

vdW $\Rightarrow$

$$p(v-b)v^2 = RTv^2 - a(v-b)$$

$$pv^3 - pbv^2 - RTv^2 + av - ab = 0$$

$$\frac{p}{RT} v^3 - \frac{p}{RT} bv^2 - v^2 + \frac{a}{RT} v - \frac{ab}{RT} = 0$$

Cubic in volume $\Rightarrow$ thus Cubic EOS

$$\frac{p}{RT} \cdot \left(\frac{RT}{p}\right)^3 Z^3 + \left(-\frac{p}{RT} b - 1\right)\left(\frac{RT}{p}\right)^2 Z^2 + \frac{a}{RT} \cdot \left(\frac{RT}{p}\right) Z - \frac{ab}{RT} = 0$$

$$\left(\frac{RT}{p}\right)^2 Z^3 + \left(-\frac{p}{RT} b - 1\right)\left(\frac{RT}{p}\right)^2 Z^2 + \frac{a}{p} Z - \frac{ab}{RT} = 0$$

$$Z^3 + \left(-\frac{pb}{RT} - 1\right) Z^2 + \frac{a}{p} \cdot \left(\frac{p}{RT}\right)^2 Z - ab \frac{1}{RT}\left(\frac{p}{RT}\right)^2 = 0$$

$$Z^3 + C_2 Z^2 + C_1 Z + C_0 = 0$$

Cubic in Z also

$C_2 =$

$C_1 =$

$C_0 =$

where

$B' = \frac{bp}{RT}$

$A' = \frac{ap}{R^2T^2}$

We computationally solve for "volume" given p, T, compound most efficiently by solving the cubic eq. for Z

The van der Waals equation also can be written in terms of the Z factor ($Z = pv/RT$).

$$Z^3 - (B + 1)Z^2 + AZ - AB = 0, \quad \ldots\ldots\ldots\ldots\ldots \quad (4.8)$$

where $A = a\dfrac{p}{(RT)^2} = \dfrac{27}{64}\dfrac{p_r}{T_r^2}$

and $B = b\dfrac{p}{RT} = \dfrac{1}{8}\dfrac{p_r}{T_r}$. $\quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.9)$

Abbott[22] gives an interesting historical review of the van der Waals EOS, its strengths and weaknesses, and its analogy to other cubic EOS's.

* a, b different for each compound

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

Repulsive Forces — Attractive Forces

H_2O

Steam Table

T p v

T v p p^{eos}

min SSQ

$\hat{a}$ $\hat{b}$

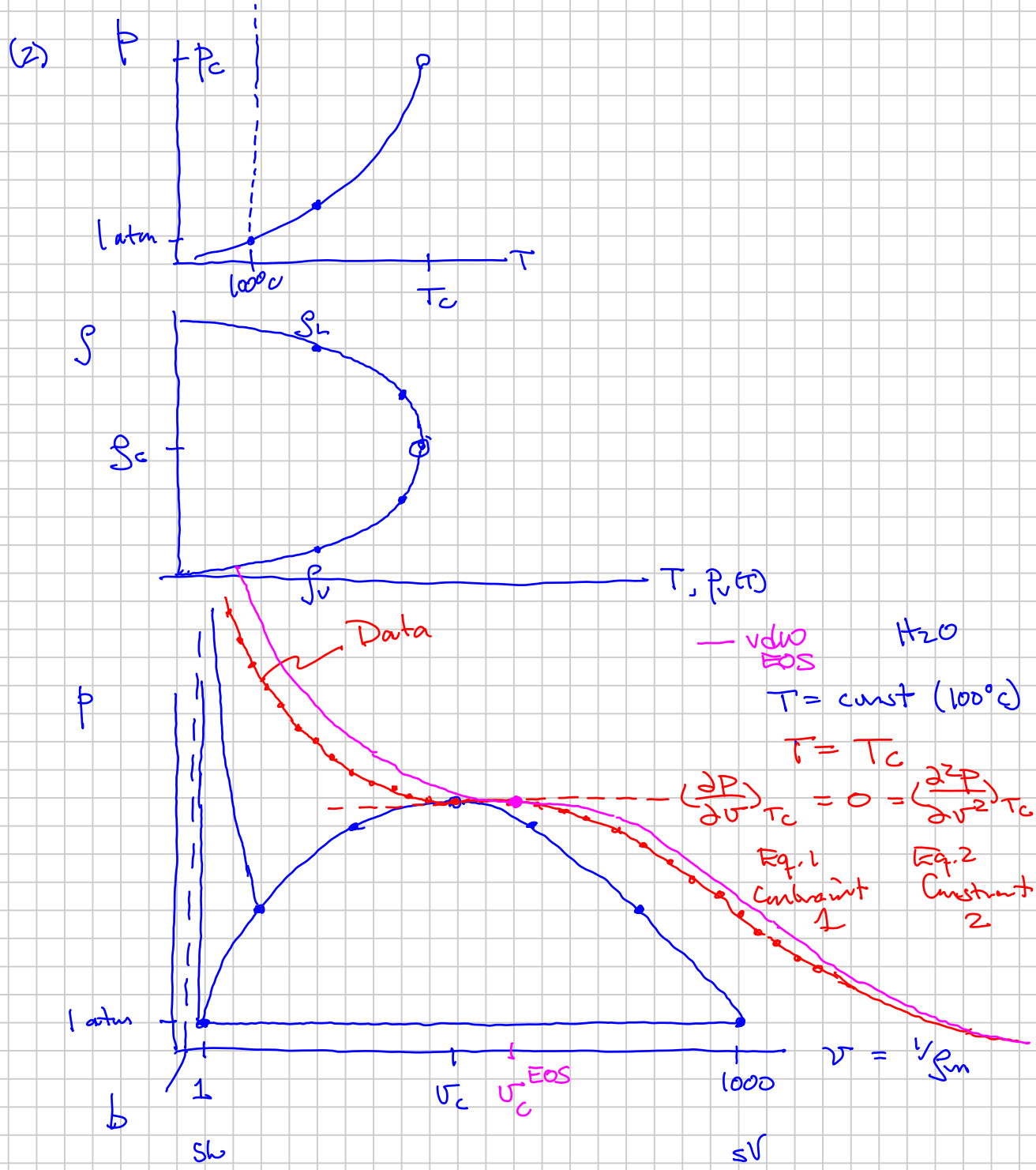
$\frac{m^3}{kg\text{-}mole}$ b = co-volume (min volume to contain 1 mole of the compound)

a =

How to establish a, b for a compound ?

(1) Best Fit to accurate measured data p-v-T

Many $(\hat{a}, \hat{b})$ depending on ...



vdW Critical Criterion to find (a, b)

$$\frac{dp}{dv} = 0 \qquad (1)$$

$$\frac{\partial^2 p}{\partial v^2} = 0 \qquad (2)$$

} at the Critical Point (T_c, P_c, v_c)

Find (a, b) : Need Two Eqs 1, 2

@ Specified (T_c, P_c) *

(T_c, v_c)

(P_c, v_c)

vdW CC

* Conditions are met @ (T_c, P_c) but at the wrong v_c & $b_{(T_c P_c)}$ will be wrong (too large) by 10-40%, & v_L (ρ_L) will be wrong (too large) 10-40%.

Problem using (a,b) Cubic with EOS PRO

$$\left.\begin{aligned} \frac{\partial P}{\partial v} &= 0 \\ \frac{\partial^2 P}{\partial v^2} &= 0 \\ v &= v_c \end{aligned}\right\} \text{ at } (T_c, P_c)$$

a, b, c

1982 Peneloux, Rauzy, Freze

Any two-constant Cubic EOS can "fix" (v_c, v_L, ρ_L) problem in a simple way

$$v' = v_{EOS2} - c$$

$$\uparrow$$

$$(a, b)_{T_c, P_c}$$

wrong $\quad v_{EOS2} = v' + c$

$\uparrow$

Correct

$$P = \frac{RT}{(v'+c)-b} - \frac{a}{(v'+c)}$$

$$\boxed{P = \frac{RT}{v+c-b} - \frac{a}{v+c}}$$

This allows one to get all vdW critical criteria right

vdW + Peneloux (Volume Translation)

Volume Shift

$c[\ ]$ $b[\ ]$ molar volume unit

1986: Jhaveri – Youngren (Arco)

Dimensionless V.S. $s \equiv c/b$

DVTsim: uses c w/ units

also s

Hysys: Input V.S. c or s with wrong sign

$$\left\{ \begin{matrix} c \\ s \end{matrix} \right\}_{\text{Input to Hysys}} = -\left\{ \begin{matrix} c \\ s \end{matrix} \right\}$$

Peneloux & ALL other programs on Earth

v_c varies for each compound

vdW: $Z_c = \frac{P_c v_c}{RT_c}$

= same constant = $\frac{3}{8}$ = 0.375 all compounds for vdW

$Z_c(C_1) \sim 0.3^+$ Heavy HCs $Z_c \to 0.25$-ish

Definition of (a, b) : vdW CC (T_c, p_c)

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

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

1949 : Redlich Kwong

$$p = \frac{RT}{v-b} - \frac{a \cdot \overset{②}{\alpha(T)}}{\underset{①}{[v(v+b)]}}$$

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

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

② $\alpha(T)$: Improve the $p_v(T)$ for Light HCs

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

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