CH365 Chemical Engineering Thermodynamics

Lesson 13

Cubic Equations of State

Corresponding States

Reduced T: $T_r \equiv \frac{T}{T_C}$ Reduced P: $P_r \equiv \frac{P}{P_C}$

All fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree.

Two-parameter models in terms of T_C and P_C works for simple fluids (Ar, Kr, Xe)

Three-parameter models are greatly improved: use T_C and P_C, and "ω"

ω is the "acentric factor"

$$\omega \equiv -1.0 - \log\left(P_r^{sat}\right)_{T_r=0.7}$$

Eq. 3.52

Tables in App. B.1

- Introduced by Pitzer and coworkers, 1958
- Related to molecular structure, "centricity"
- Defined with respect to vapor pressure
- Difference between log of reduced vapor pressure of "simple" fluid and more complex fluids at T_r of 0.7

Measure of molecular asymmetry or deviation from molecules.

Used as a property correction.

Example: n-Octane

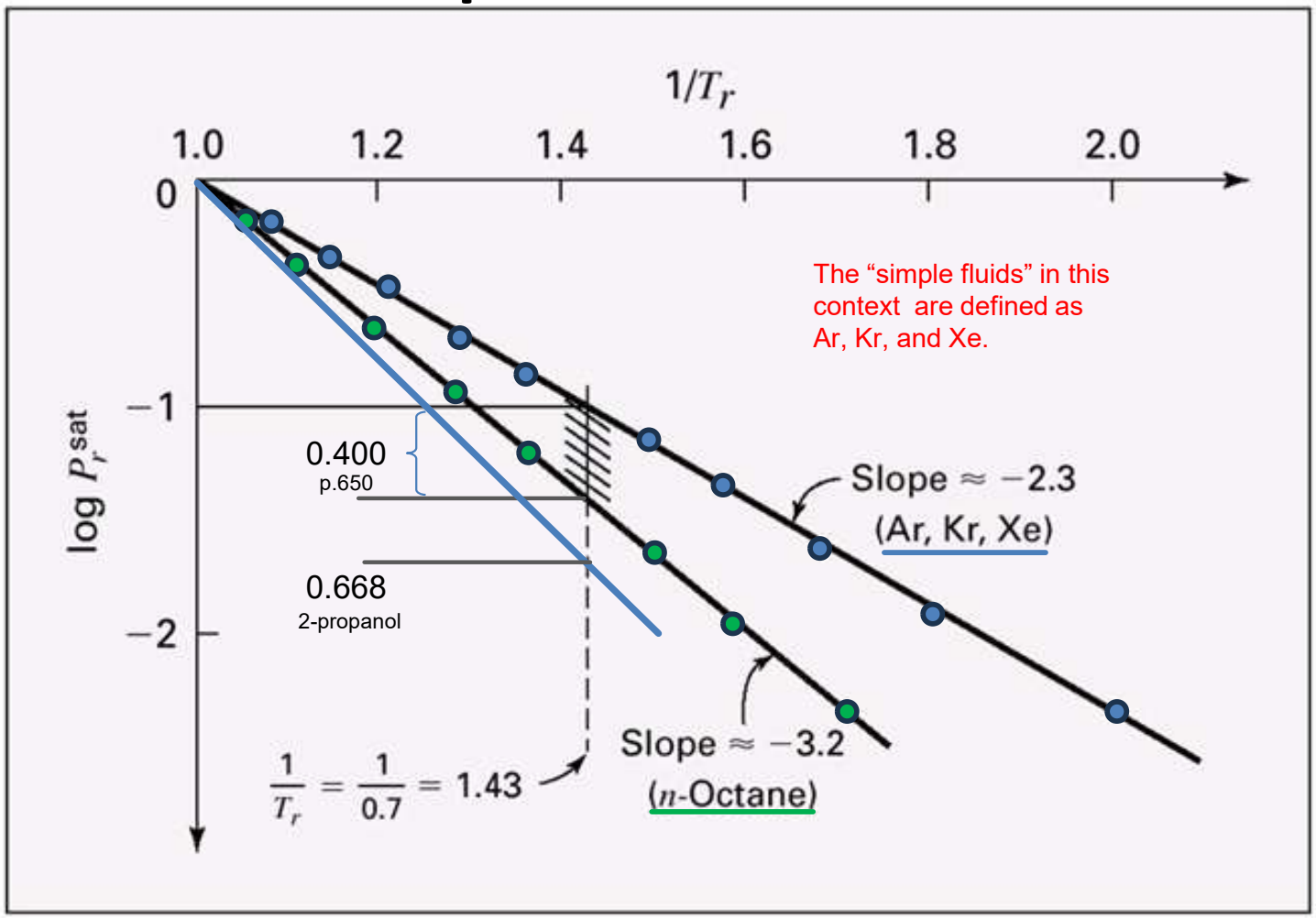


Figure 3.10: Approximate temperature dependence of the reduced vapor pressure.

3-Parameter Theorem of Corresponding States

Characteristic Properties of Pure Species, Table B.1, pages 663-665

	Molar Mass	ω	T_C K	P_C bar	Z_C	V_C cm^3mol^{-1}	T_n K
Methane	16.043	0.012	190.6	45.99	0.286	98.6	111.4
Ethane	30.070	0.100	305.3	48.72	0.279	145.5	184.6
Propane	44.097	0.152	369.8	42.48	0.276	200.0	231.1
n-Butane	58.123	0.200	425.1	37.96	0.274	255.	272.7
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
n-Octane	114.231	0.400	568.7	24.90	0.256	486.	398.8
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
Nitric Acid	63.013	0.714	520.0	68.90	0.231	145.	356.2
Sulfuric Acid	98.080	…	924.0	64.00	0.147	177.0	610.0

All fluids having the same value of ω, when compared at the same T_r and P_r, have about the same value of Z, and all deviate from ideal-gas behavior to about the same degree.

Pitzer Correlations

For next lesson; needed for Problem 3.44(b)

2nd Virial Coefficient

$$Z = 1 + \frac{BP}{RT} = 1 + \hat{B}\frac{P_r}{T_r} \quad \text{(Eq. 3.57 and 3.36)} \qquad \text{where} \quad \hat{B} = \frac{BP_C}{RT_C} \quad \text{(Eq. 3.58)}$$

Pitzer and coworkers

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad \text{(Eq. 3.61)}$$

$$\hat{B} = B^0 + \omega B^1 \quad \text{(Eq. 3.59)}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad \text{(Eq. 3.62)}$$

3rd Virial Coefficient

$$Z = 1 + B\rho + C\rho^2 = 1 + \hat{B}\frac{P_r}{T_r Z} + \hat{C}\left(\frac{P_r}{T_r Z}\right)^2 \quad \text{(Eq. 3.63 and 3.38)} \qquad \text{where} \quad \hat{C} \equiv \frac{CP_C^2}{R^2T_C^2} \quad \text{(Eq. 3.64)}$$

$$\hat{C} = C^0 + \omega C^1 \quad \text{(Eq. 3.65)}$$

$$C^0 = 0.01407 + \frac{0.02432}{T_r} - \frac{0.00313}{T_r^{10.5}} \quad \text{(Eq. 3.66)}$$

$$C^1 = -0.02676 + \frac{0.05539}{T_r^{2.7}} - \frac{0.00242}{T_r^{10.5}} \quad \text{(Eq. 3.67)}$$

General Cubic Equations of State

$$P = \frac{RT}{V-b} - \frac{a}{(V+\varepsilon b)(V+\sigma b)}$$

(Page 97 Eq. 3.41)

Problem 3.44

$$a = \Psi \frac{\alpha R^2 T_C^2}{P_C} \quad \text{(Eq. 3.45)}$$

$$\alpha = \alpha(T, T_C, \omega)$$ ω comes in through α.

α, Ψ, ε, σ, and Ω are defined in Table 3.1

$$T_r = \frac{T}{T_C} \text{ (reduced temperature)}$$

T_C is the critical temperature, Table B.1

P_C is the critical pressure, Table B.1

R is the gas constant, Table A.2

$$b = \Omega \frac{RT_C}{P_C} \quad \text{(Eq. 3.44)}$$

van der Waals

$\alpha = 1$, $\varepsilon = 0$ and $\sigma = 0$, T3.1

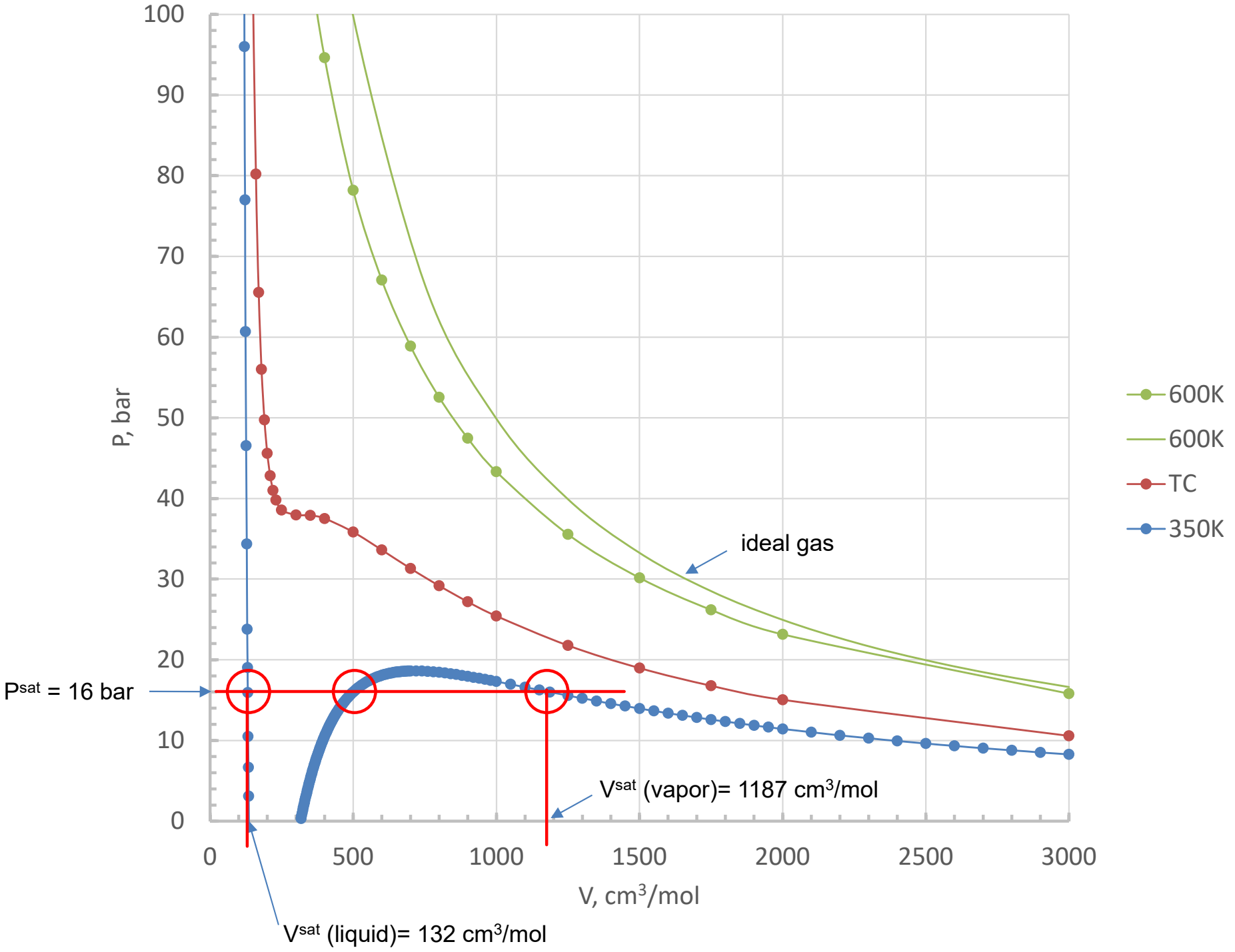
$\Psi = \frac{27}{64}$, $\Omega = \frac{1}{8}$, $\alpha = 1$, T3.1

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$a = \frac{27}{64} \frac{R^2 T_C^2}{P_C}$$

$$b = \frac{RT_C}{8P_C}$$

n-Butane Isotherms from Redlich-Kwong EOS



Parameters for Cubic Equations

RK, SRK and PR equations of state were specifically developed for vapor-liquid calculations

Equation of State	α	σ	ε	Ω	Ψ	Z_c
vdW	1	0	0	0.12500	0.42188	0.37500
RK	α_{RK}	1	0	0.08664	0.42748	0.33333
SRK	α_{SRK}	1	0	0.08664	0.42748	0.33333
PR	α_{PR}	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724	0.30740

Smith, van Ness, Abbott, and Swihart, **Table 3.1, page 100**

$$\alpha_{RK} = 1/\sqrt{T_r} = T_r^{-1/2}$$

$$\alpha_{SRK} = \left[1+\left(0.480+1.574\,\omega-0.176\,\omega^2\right)\left(1-\sqrt{T_r}\right)\right]^2$$

$$\alpha_{PR} = \left[1+\left(0.37464+1.54226\,\omega-0.26992\,\omega^2\right)\left(1-\sqrt{T_r}\right)\right]^2$$

vdW – van der Walls – 1873
RK – Redlich-Kwong – 1949
SRK – Soave-Redlich-Kwong – 1972
PR – Peng-Robinson – 1976

Example 3.9

Given that the vapor pressure of n-butane at 350 K is 9.4573 bar, find the molar volumes of (a) saturated vapor and (b) saturated liquid n-butane at these conditions as given by the Redlich-Kwong equation.

Eq. 3.41 gives three roots. Largest is vapor. Smallest is liquid.

$$P = \frac{RT}{V-b} - \frac{a}{(V+\varepsilon b)(V+\sigma b)}$$

(Eq. 3.41)

Claimed to be better for vapor

(Eq. 3.48)

$$Z = 1 + \beta - q\beta\frac{Z-\beta}{(Z+\varepsilon\beta)(Z+\sigma\beta)}$$

$$\beta = \Omega\frac{P_r}{T_r} \qquad q = \frac{\Psi\alpha(T_r,\omega)}{\Omega T_r}$$

(Eq. 3.46 combined with 3.44) (Eq. 3.47 with 3.44)

Claimed to be better for liquid

$$Z = \beta + (Z+\varepsilon\beta)(Z+\sigma\beta)\frac{1+\beta-Z}{q\beta}$$

(Eq. 3.49)

Easy to demonstrate with “FindRoot” in Mathematica (numerical; requires initial guess)

Questions

Homework

Problem 3.44

Calculate Z and V for ethylene at 25 deg C and 12 bar by the following equations:

(a) The truncated virial equation (Eq. 3.38) with the following experimental values of virial coefficients:

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} \qquad (3.38)$$

$B = -140.\ \mathrm{cm^3\ mol^{-1}}$ and $C = 7,200\ \mathrm{cm^6\ mol^{-2}}$

(b) The truncated virial equation (Eq. 3.36), with a value of B from the generalized Pitzer correlation (Eqs. 3.58-3.62)

(c) The Redlich/Kwong equation.

(d) The Soave/Redlich/Kwong equation

(e) The Peng/Robinson equation.

CHEMCAD Thermodynamics

Which EOS is best?

- Selection of the appropriate thermodynamic method is key to producing accurate simulations
- PR is the most widely used thermodynamic package as it applies to all applications involving hydrocarbons
- Special packages should be used when simulation involves non-hydrocarbon components: TEG, amines, sour water, etc.
- Methanol for hydrate prevention has special fit of BIPs in PR equation of state
- In refinery models, review oil characterization before suspecting thermodynamics

Same comments for Aspen/HYSYS