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Lecture Notes 5

E134 – 2023-09-12

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Chapter 3 Real Fluids

Equations of State

All equations of state are of the form

$$f(P, V, T) = 0$$

which implies that

$$dV = \left.\frac{\partial V}{\partial T}\right|_P dT + \left.\frac{\partial V}{\partial P}\right|_T dP$$

or

$$dT = \left.\frac{\partial T}{\partial V}\right|_P dV + \left.\frac{\partial T}{\partial P}\right|_V dP$$

or …

Start with the 1st equation

Introduce

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$ The *volume expansivity* (like linear coeff. of therm. exp.)

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$ The *isothermal compressibility*

$$\frac{dV}{V} = \beta dT - \kappa dP$$

For liquids

Approximation #1

$\beta \approx 0$, $\kappa \approx 0$ Incompressible liquid. Useful but not precise.

Approximation #2

$\beta \approx$ constant , $\kappa \approx$ constant

$$\Rightarrow \ln\frac{V_2}{V_1} = \beta\left(T_2 - T_1\right) - \kappa\left(P_2 - P_1\right)$$

Fairly accurate for reasonable changes in T , P .

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Equations of State

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Ideal gas

$PV^t = nRT$, $PV = RT$

$PV^t - nRT = 0$, $PV - RT = 0$

Compressibility

$$Z \equiv \frac{PV}{RT}$$

What sort of expressions should we use for Z ?

The virial equation, which has a theoretical stat-mech basis.

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$$Z = 1 + B'P + C'P^2 + D'P^3 + \ldots$$

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots$$

For 1 term use $Z = 1 + B'P$, $B' = \frac{B}{RT}$

For 2 term use $Z = 1 + \frac{B}{V} + \frac{C}{V^2}$

Fairly useless as given but see the Benedict-Webb-Rubin equation

$$P = \frac{RT}{V} + \frac{B_0 RT - A_0 - C_0/T^2}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{V^3 T^2}\left(1 + \frac{\gamma}{V^2}\right)\exp\left(-\frac{\gamma}{V^2}\right)$$

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For BWR

$A_0,\ B_0,\ C_0,\ a,\ b,\ c,\ \alpha,$ and γ

are all constants specific to a given fluid (See BWRConstants.xlsx).

Generic Cubic Equations of State

$$P = \frac{RT}{V-b} - \frac{\theta(V-\eta)}{(V-b)(V^2+\kappa V+\lambda)}$$

For the problem sets

$\eta = b,\ \theta = a(T),\ \kappa = (\epsilon+\sigma)b,\ \lambda = \epsilon\sigma b^2$ or

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

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For

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

$$a(T) = \psi\frac{\alpha(T_r)R^2T_c^2}{P_c}$$

$$b = \Omega\frac{RT_c}{P_c}$$

Table 3.1 on p. 97 of SVN has $\alpha(T_R)$, σ, ϵ, Ω, and ψ for four e.o.s.

TABLE 3.1 Parameter Assignments for Equations of State

Eqn. of State	$\alpha(T_r)$	σ	ε	Ω	Ψ	Z_c
vdW (1873)	1	0	0	1/8	27/64	3/8
RK (1949)	$T_r^{-1/2}$	1	0	0.08664	0.42748	1/3
SRK (1972)	$\alpha_{SRK}(T_r;\omega)^\dagger$	1	0	0.08664	0.42748	1/3
PR (1976)	$\alpha_{PR}(T_r;\omega)^\ddagger$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724	0.30740

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

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

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Law of Corresponding States

Plot $Z \equiv \dfrac{PV}{RT}$ vs. $P_r \equiv \dfrac{P}{P_c}$ with $T_r \equiv \dfrac{T}{T_c}$ as a parameter.

For almost all gases and vapors, the plots are very similar. You then use two parameters, T_c, and P_c to determine the corresponding states.

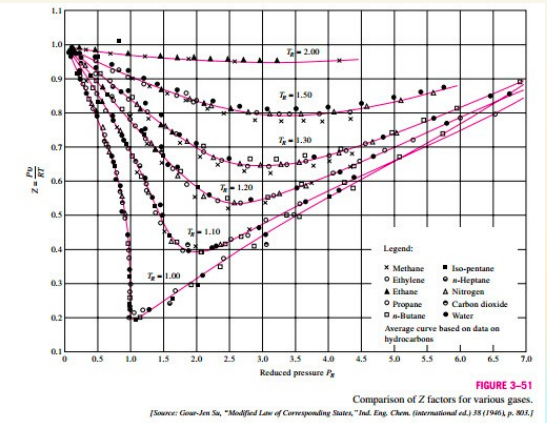


FIGURE 3–51
Comparison of Z factors for various gases.
[Source: Gour-Jen Su, "Modified Law of Corresponding States," Ind. Eng. Chem. (international ed.) 38 (1946), p. 803.]

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Would three parameters match better?

Suggest a third parameter.

How do you like $Z_c \equiv \dfrac{P_c V_c}{RT_c}$ (see Problem 3.80 in SVN for further info)

How do you like $\omega \equiv -1.00 - \log_{10}\left(P_r^{\text{sat}}\right)_{T_r=0.7}$?

It is called the acentric factor.

The generalized correlation then becomes

$$Z = Z^0(P_r, T_r) + \omega Z^1(P_r, T_r)$$

Z^0 is the two-parameter law of corresponding states.

ωZ^1 is the third-parameter correction.

There is no simple equation or form for Z^0 and Z^1.
To evaluate them use the tables in Appendix D or the charts on the website.
The values were calculated from the Lee-Kesler Equation of State.
There is a copy of a spreadsheet on the website with Lee-Kesler if you want to use it.
For $P_r < 2$ and $Z^0 > 0.8$ you can use

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad Z^0 = 1 + B^0 \frac{P_r}{T_r}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad Z^1 = B^1 \frac{P_r}{T_r}$$

Remember the restrictions on their use!

Example: Determine the molar volume of n-butane at 510 K and 25 bar by (see RealGasExample.xlsx on website):

(a) Ideal gas

(b) Generalized compressibility

(c) Linearized version of generalized compressibility

(d) SRK e.o.s.

(e) PR e.o.s.

(f) BWR e.o.s.

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(a) Ideal Gas

$$V = \frac{RT}{P} = \frac{(8.314)(510)}{25 \times 10^5} = 1.696 \times 10^{-3} \frac{\text{m}^3}{\text{mol}}$$

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(b) Generalized Compressibility

$$T_c = 425.1 \text{ K}, \; P_c = 38.0 \text{ bar}, \; \omega = 0.200$$

$$T_r = \frac{510}{425.1} = 1.200, \; P_r = \frac{25}{38} = 0.6579$$

From Tables D.1 & D.2

$$Z^0 = 0.865, \; Z^1 = 0.037$$

$$Z = Z^0 + \omega Z^1 = 0.865 + 0.2 \cdot 0.037 = 0.872$$

$$V = \frac{ZRT}{P} = 1.480 \times 10^{-3} \frac{\text{m}^3}{\text{mol}}$$

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(c) Linearized Generalized Compressibility

$$B^0 = 0.083 - \frac{0.422}{(1.200)^{1.6}} = -0.232$$

$$B^1 = 0.139 - \frac{0.172}{(1.200)^{4.2}} = 0.059$$

$$Z = 1 + B^0\frac{P_r}{T_r} + \omega B^1\frac{P_r}{T_r}$$

$$Z = 1 + (-0.232)\frac{0.658}{1.200} + 0.200(0.059)\frac{0.658}{1.200} = 0.879$$

$$V = \frac{ZRT}{P} = 1.491 \times 10^{-3}\frac{\text{m}^3}{\text{mol}}$$

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(d) & (e) SRK and PR

Plug in values from Table 3.1 into Equations 3.41, 3.44, and 3.45

Use P_c , T_c , and ω.

d) SRK e.o.s.				
a	b	m	α	
1405.31	0.080586	0.78918	0.85522	
P_{SRK}	2500.00	kPa		
error	0.00033212	kPa	<- Set to 0 with goal seek	
V	1.487E-03	m^3/mol		
	1.4866	m^3/kg-mol	<- Vary with goalseek	

e) PR				
a	b	κ	α	
1503.16	0.072360	0.67230	0.87595	
P_{PR}	2500	kPa		
error	3.9628E-06	kPa	<- Set to 0 with goal seek	
V	1.455E-03	m^3/mol		
	1.4549	m^3/kg-mol	<- Vary with goalseek	

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(f) BWR

See the spreadsheet for summary

f) BWR							
a	A_0	b	B_0	c	C_0	α	γ
190.68	1021.6	0.039998	0.12436	32050000	100600000	0.001101	0.034
P_{BWR}	2500	kPa					
error	9.0291E-07	kPa	<- Set to 0 with goal seek				
V	1.476E-03	m^3/mol					
	1.4762	m^3/kg-mol	<- Vary with goalseek				

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For cubic equations of state and the BWR equation when written as

$$f(P, V, T) = 0$$

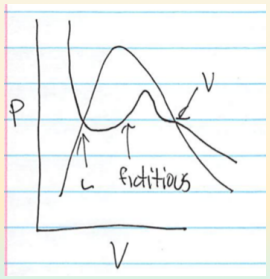
For a given P and T, there are three possible roots in V, 3 real or 1 real and 2 complex conjugates.

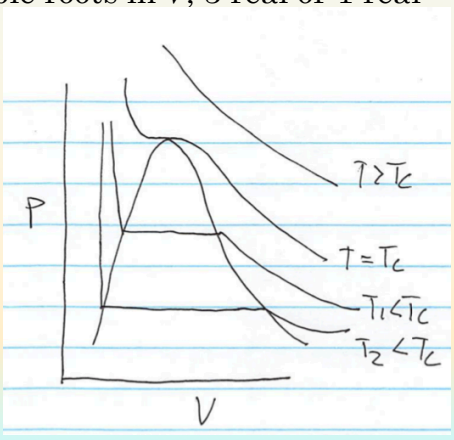
If there are three roots:

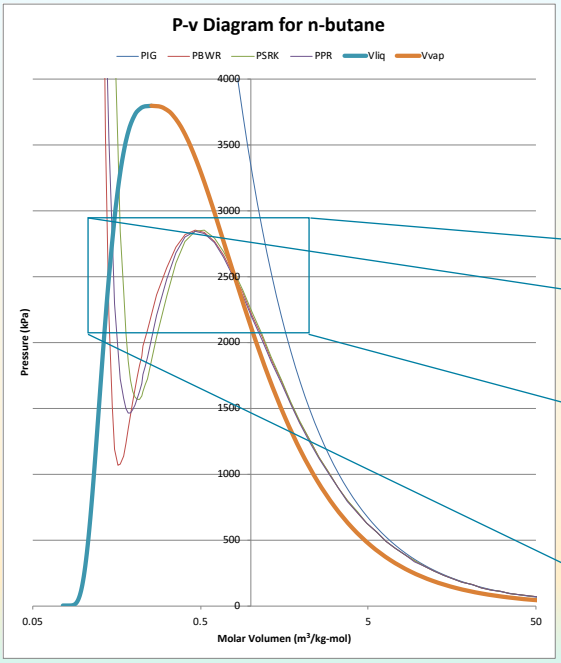
One is liquid volume

One is vapor volume

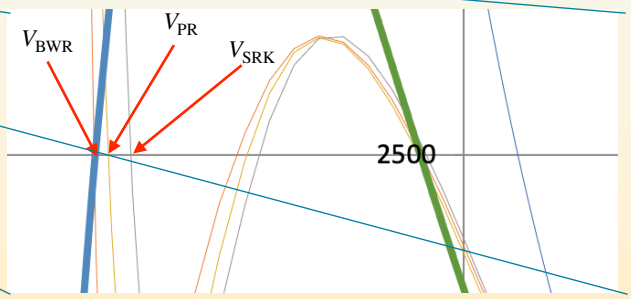
One is fictitious







Isotherms for $T = 400$ K
Looking for where the isotherm intersects the $P = 2500$ kPa



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The vapor values of all three are pretty close (V^{ig} is way off).
The liquid BWR is good for hydrocarbons.
The liquid PR is not bad, but not great.
The liquid SRK is not very good.

At the critical point

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

Can be used to calculate Z_c for an equation of state.
Table 3.1 has a column of Z_c values for several equations.

Other options for calculating V_{liquid}.

The Rackett correlation

$$V^{\text{sat}} = V_c Z_c^{(1-T_r)^{2/7}} \text{ or } Z^{\text{sat}} = \frac{P_r}{T_t} Z_c^{[1+(1-T_r)^{2/7}]}$$

A generalized chart such as Figure 3.15

Find $\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V}$ from P_r and T_r.

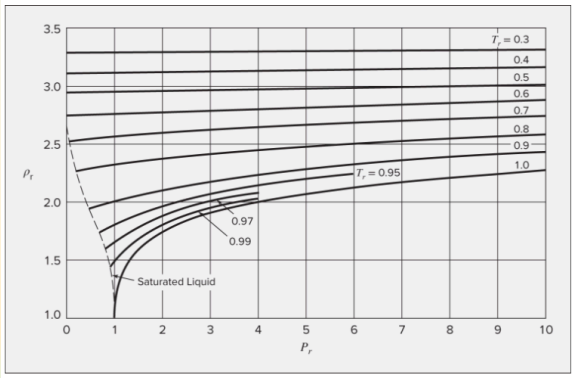


FIGURE 3.15 Generalized density correlation for liquids.