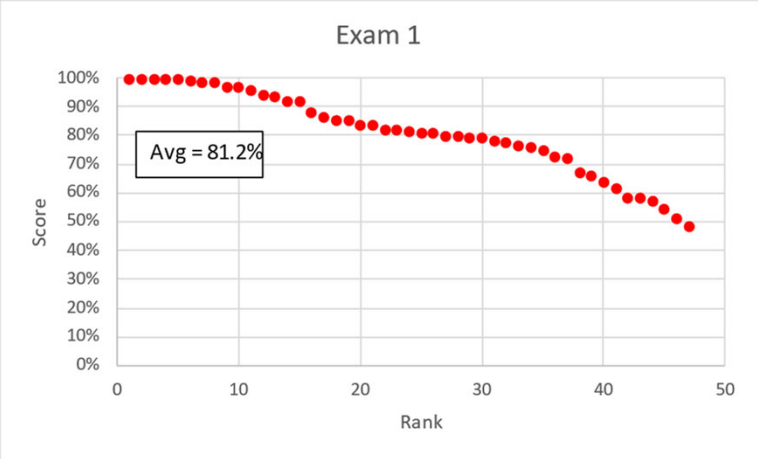
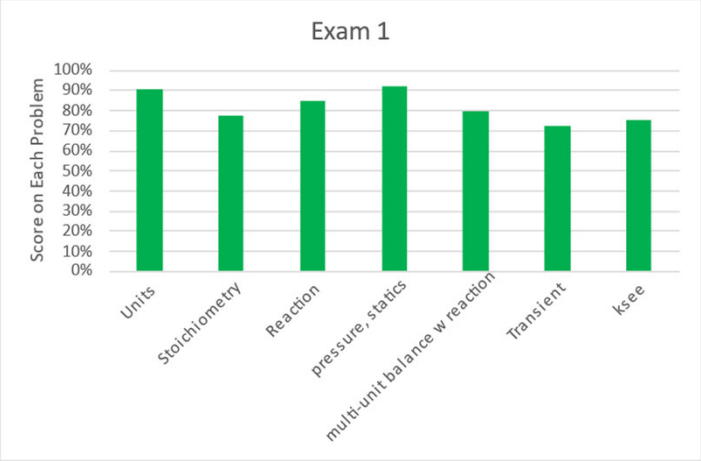
Exam 1 Results



1

Score on Each Problem



2

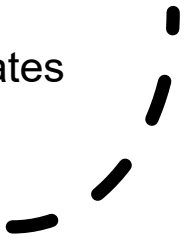
Sanity for Dr. Fletcher

- Please look at the answer key for Exam 1
- Rework what you missed
  - Find your mistake
  - I wrote “rework for more pts” on many exams, since if you made a mistake early in the problem everything snowballed
- Contact me if you think you deserve more than 2-3 points

3

Class 16 Non-Ideal Gases

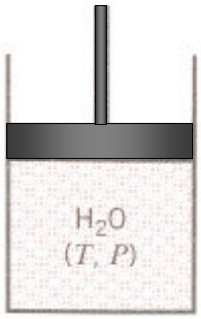
- Definitions
  - Critical Temperature, Pressure
  - Vapor
  - Gas
- Van der Waals EOS
- Other Equations of State
- Compressibility Factor
- Principle of Corresponding States
- Kay’s Rule



4

Water Phase Change

(change T, increase P until condensation occurs)



Run	T(°C)	P_{cond}(atm)	ρ_v(kg/m^3)	ρ_l(kg/m^3)
1	25.0	0.0329	0.0234	997.0
2	100.0	1.00	0.5977	957.9
3	201.4	15.8	8.084	862.8
4	349.8	163	113.3	575.0
5	373.7	217.1	268.1	374.5
6	374.15	218.3	315.5	315.5
7	>374.15	*No condensation occurs!*		

This point defines the critical temperature (T_c) and pressure (P_c) of H_2O!
- No condensation occurs as pressure increases

H_2O above T_c and P_c is called a supercritical fluid, not a gas or a liquid.

5

Definitions

- **Critical Temperature (T_c)**:
  - Highest temperature at which a species can coexist in two phases (liquid and vapor)
- **Critical Pressure (P_c)**:
  - Pressure that corresponds to critical temperature
- **Vapor**:
  - Gas phase
  - Usually used in the 2-phase region where liquid is present
- **Gas**:
  - Gas phase
  - Usually used when no liquid is present

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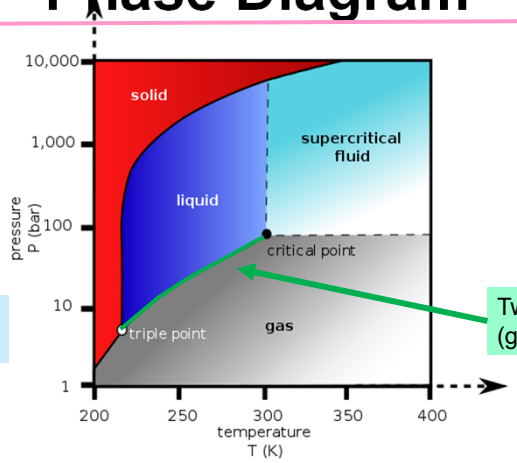
Pure Component Phase Diagram



Are there other 2-phase regions?

Two-phase region (gas-liquid)

Pressure-temperature phase diagram for CO_2

7

Why Do We Care About Critical T & P?

- Help determine the supercritical region
  - Fluid behavior in this region is very different
- Most thermodynamic behavior for different species is similar depending on how close you are to T_c and P_c for that species
- Non-ideal behavior occurs close to the critical point (T_c and P_c)

8

Definitions (cont.)

- **Reduced Temperature (T_r):**
  $T_r = T / T_c$
- **Reduced Pressure (P_r):**
  $P_r = P / P_c$
- **Supercritical fluid:**
  $T > T_c$ and $P > P_c$ (i.e., T_r and $P_r > 1$)

Remember to use absolute P's and T's in K or °R

Values of T_c and P_c are in Table B.1 in Appendix B in the book (also online or in the DIPPR website)

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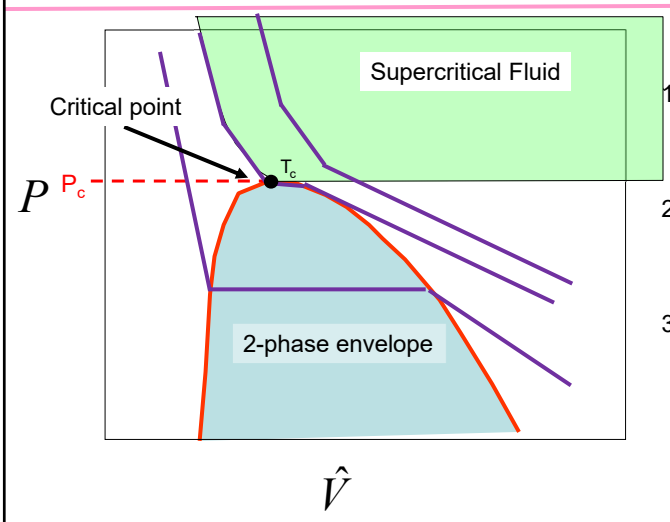
Phase Diagram for H_2O (Thought Quiz)



1. Label the following:
   a. 2-phase envelope
   b. Critical point
   c. P_c
2. Draw 3 isotherms
   a. Through 2-phase
   b. Through P_c
   c. Supercritical
3. Label T_c

10

Non-Ideal Gases

- High Density
  - Molecular interactions
  - Volume of molecule becomes important
  - Occurs near the critical points
- Methods
  - Equations of State
    - More terms than ideal gas law
    - Still relate P, T, and $\hat{V}$
  - Generalized compressibility chart

$$z = \frac{P\hat{V}}{RT}$$

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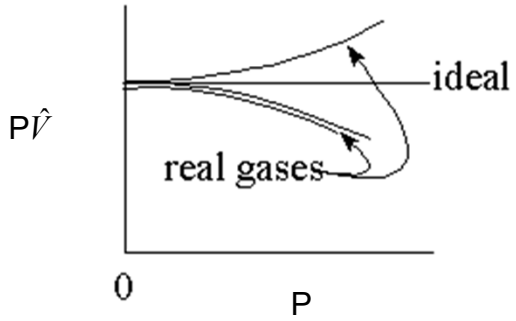
Ideal vs. Real Gases



From p. 192, ideal when:

$\hat{V}_{ideal} > 5L/mol \quad (diatomic\ \ gases)$

$\hat{V}_{ideal} > 20L/mol \quad (other\ \ gases)$

$$\hat{V}_{ideal} = \frac{RT}{P}$$

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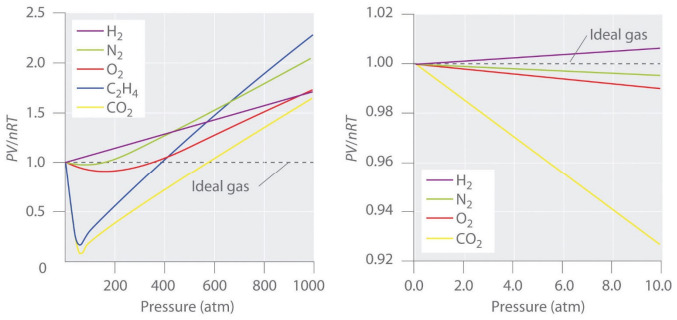
Ideal vs. Real Gases



(a) *PV/nRT* at high pressures **(b) *PV/nRT* at low pressures**

From p. 221, less than 1% error with Ideal Gas Assumption when:

$\left(\frac{V}{n}\right)_{\text{ideal}}$

$\frac{RT}{P} > 5\frac{L}{mol}$ for diatomic gases (H_2, N_2, O_2, etc.)

$\frac{RT}{P} > 20\frac{L}{mol}$ for other gases

https://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s14-08-the-behavior-of-real-gases.html

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J. D. van der Waals Idea

1. Real pressure gas = Ideal gas pressure minus the contracting forces per unit area due to the intermolecular attractions
   $P = P_{ideal} - a/V^2$, or $P_{ideal} = P + a/V^2$

2. Actual molar volume = volume occupied by the ideal gas (with the molecules occupying no space) + volume of the molecules themselves
   $V = V_{ideal} + b$, or $V_{ideal} = V - b$

Plug P_{ideal} and V_{ideal} into the ideal gas equation:

$P_{ideal}V_{ideal} = RT = (P + a/V^2)(V - b)$

Now solve for P:

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

Cubic form:

$$P\hat{V}^3 - (Pb + RT)\hat{V}^2 + a\hat{V} - ab = 0$$

This is one of the "virial" equations of state (meaning that it relates to molecular interactions)

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Non-Ideal Eqns. of State
(that are in the text)

- Virial
  - 1 constant
  - B = f(T_c,P_c, ω)
  - **Table 5.3.1 for ω**
    (ω is the acentric factor)

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} \qquad (5.3.2)$$

$$B_0 = 0.083 - \frac{0.42}{T_r^{1.6}}$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$B = \frac{RT_c}{P_c}(B_0 + \omega B_1)$$

- Van der Waals
  - 2 constants
  - a & b = f(T_c,P_c)

$$P = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}^2} \qquad (5.3.6)$$

$$a = \frac{27R^2T_c^2}{64P_c}$$

$$b = \frac{RT_c}{8P_c}$$

- Soave-Redlich-Kwong (SRK)
  - 3 constants
  - a & b = f(T_c,P_c)
  - α = f(T_c,P_c, ω)

$$P = \frac{RT}{\hat{V} - b} - \frac{a\alpha}{\hat{V}(\hat{V} + b)} \qquad (5.3.7)$$

$a = 0.42747\,(RT_c)^2/P_c$
$b = 0.08664\,(RT_c)/P_c$
$m = 0.48508 + 1.55171\,\omega - 0.1561\,\omega^2$
$\alpha = [1 + m(1 - T_r^{0.5})]^2$

Units must be in atm and Kelvin for all of these equations

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The SRK equation uses ω

- Pitzer acentric factor
- Accounts for geometry and polarity of the molecule
- Table in the book

Table 5.3-1 Pitzer Acentric Factors

Compound	Acentric Factor, ω
Ammonia	0.250
Argon	−0.004
Carbon dioxide	0.225
Carbon monoxide	0.049
Chlorine	0.073
Ethane	0.098
Hydrogen sulfide	0.100
Methane	0.008
Methanol	0.559
Nitrogen	0.040
Oxygen	0.021
Propane	0.152
Sulfur dioxide	0.251
Water	0.344

SOURCE: R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th Edition, McGraw-Hill, New York, 1986.

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CO_2 at 50 atm and 400K

See Excel Example

See Python Example

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Python Example
SRK Equation of State

This is an example of CO2 using the SRK Equation of State

```
Tc = 304.2                                          # Critical Temperature in K
Pc = 72.9                                           # Critical Pressure in atm
R = 0.08206                                         # Universal Gas Constant in liter-atm/(K-gmole)
a = 0.42747*(R*Tc)**2/Pc                            # The "a" parameter in the SRK equation
b = 0.08664*(R*Tc)/Pc                               # The "b" parameter in the SRK equation
omega = 0.225                                       # Pitzer acentric factor from Table 5.3-1
m = 0.48508 + 1.55171*omega - 0.1561*omega**2       # The "m" parameter in the SRK equation

T = 400                                             # The system temperature in K
P = 50                                              # The system pressure in atm

Tr = T/Tc                                           # The reduced temperature
alpha = (1 + m*(1-Tr**0.5))**2                      # The alpha in the SRK

print ('a=',a,'b=',b,'m=',m,'Tr=',Tr,'alpha=',alpha)                          # Print the values of a,b,m,Tr,alpha

Videal = R*T/P                                      # Calculate the volume in liters from the ideal gas equation

print('V ideal =',Videal)                                   # Print the volume from the ideal gas equation

def g(x) :
    return P - R*T/(x - b) + a*alpha/(x*(x+b))      # This is the function evaluation, LHS - RHS of SRK equation
V = fsolve(g,Videal)                                # Fsolve finds the zero of the function g(V) with current T & P

print('V SRK =',V,'residual =',g(V))                                       # Print the value of V in liters
```

```
a= 3.6539244003896534 b= 0.0296675469037037 m= 0.8263121875 Tr= 1.314924391847469 alpha= 0.7722520745415591
V ideal = 0.65648
V SRK = [0.60109199] residual = [5.82645043e-13]
```

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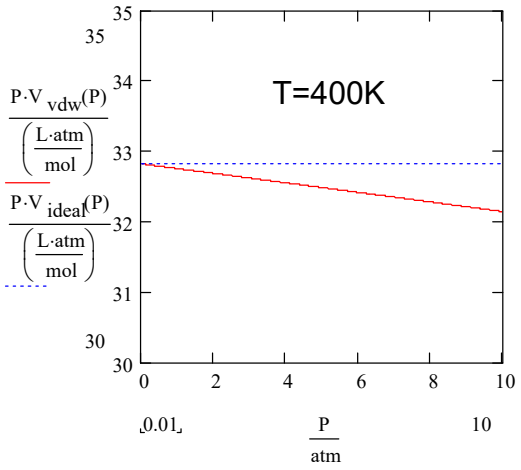
Van der Waals Results: CO_2



Does this increase in non-ideal behavior with increasing pressure make sense?

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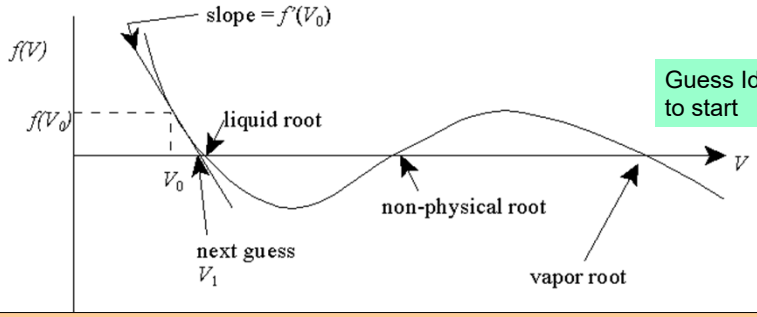
Van der Waals below T_c
(3 roots)

$$P\hat{V}^3 - (Pb + RT)\hat{V}^2 + a\hat{V} - ab = 0$$

Cubic EOS



Guess Ideal Gas to start

Bottom line: EOS can be used to try to calculate liquid densities

20

How accurate are these non-ideal equations of state?

- Need to compare against reliable data
- Example in book for propane at 423 K and 70 atm
  - Ideal gas Volume error = 92%
  - SRK Volume error = 12%!

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Law of Corresponding States

- Physical properties of a gas depend on the proximity to its critical state
  - Basis for using T_r and P_r

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Compressibility Factor

$$z = \frac{P\hat{V}}{RT} = \frac{PV}{nRT}$$

$$P\hat{V} = zRT$$

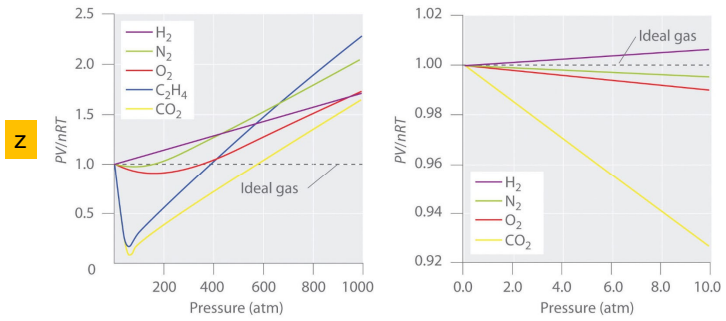
$$PV = znRT$$

- Simple equation, similar to ideal gas law
- z accounts for real gas behavior
  - z = 1 for ideal gas
  - z ≠ 1 for nonideal gas
- How do you get values for z?
  - Look up for particular compounds (e.g. Perry's Handbook)
  - Law of Corresponding States

23

Ideal vs. Real Gases

z



(a) *PV/nRT* at high pressures (b) *PV/nRT* at low pressures

From p. 221, less than 1% error with Ideal Gas Assumption when:

$\left(\frac{V}{n}\right)_{\text{ideal}}$

$\frac{RT}{P} > 5\frac{L}{mol}$ for diatomic gases (H_2, N_2, O_2, etc.)

$\frac{RT}{P} > 20\frac{L}{mol}$ for other gases

https://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s14-08-the-behavior-of-real-gases.html

24

Law of Corresponding States

- Physical properties of a gas depend on the proximity to its critical state
  - Basis for using T_r and P_r to get z
- Objective: Know two of T,P, and V, and want to find the third for a real gas
- Procedure
  - Calculate the reduced T, P, and/or V

$$T_r = \frac{T}{T_c},\ P_r = \frac{P}{P_c},\ and\ /\ or\ \ \hat{V}_r^{ideal} = \frac{\hat{V}P_c}{RT_c}$$

Note: the author uses V_r^{ideal} and $\hat{V}_r^{ideal}$ interchangeably

  - Use the reduced values to find z from Figs. 5.4-1 to 5.4-3
  - Use z to find the missing value from eq. 5.4-2

Adjustments for H_2 or He:

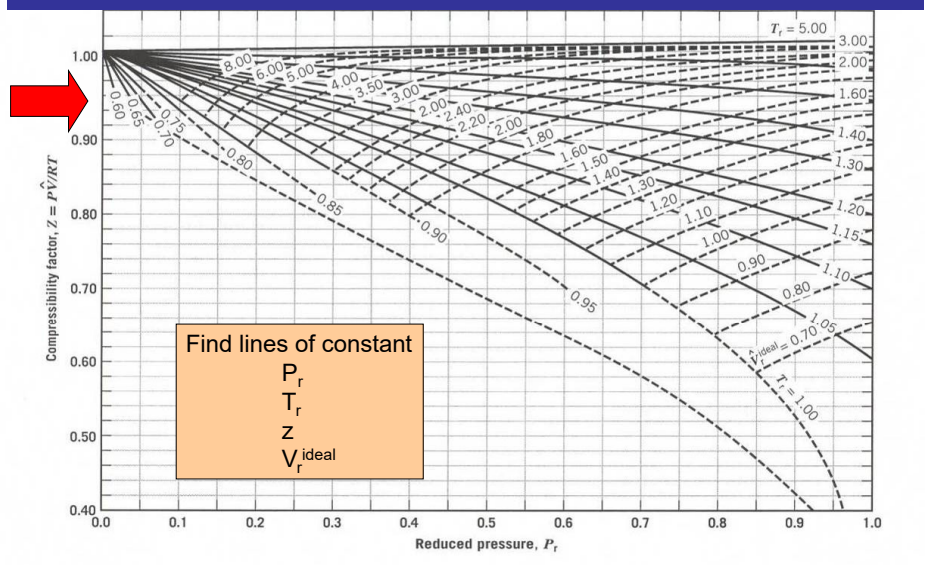
$$T_{c,adjusted} = T_c + 8\,K$$

$$P_{c,adjusted} = P_c + 8\,atm$$

Use adjusted values on compressibility charts

25

Note: This chart was taken from the blue & red version of the book. It has too many divisions between 0.9 and 1.0!! The version in the black & red book is correct.



Find lines of constant
P_r
T_r
z
V_r^{ideal}

FIGURE 5.4-2

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This one is correct!

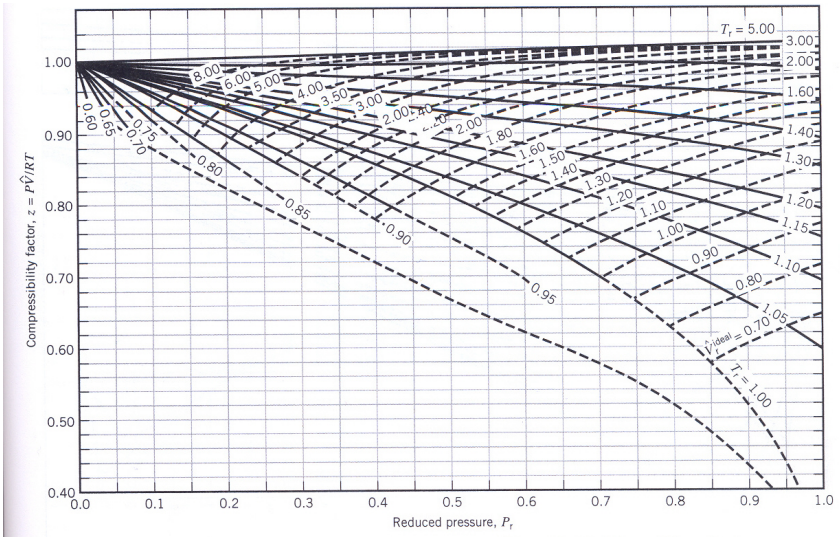

Figure 5.4-2 Generalized compressibility chart, low pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 175. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

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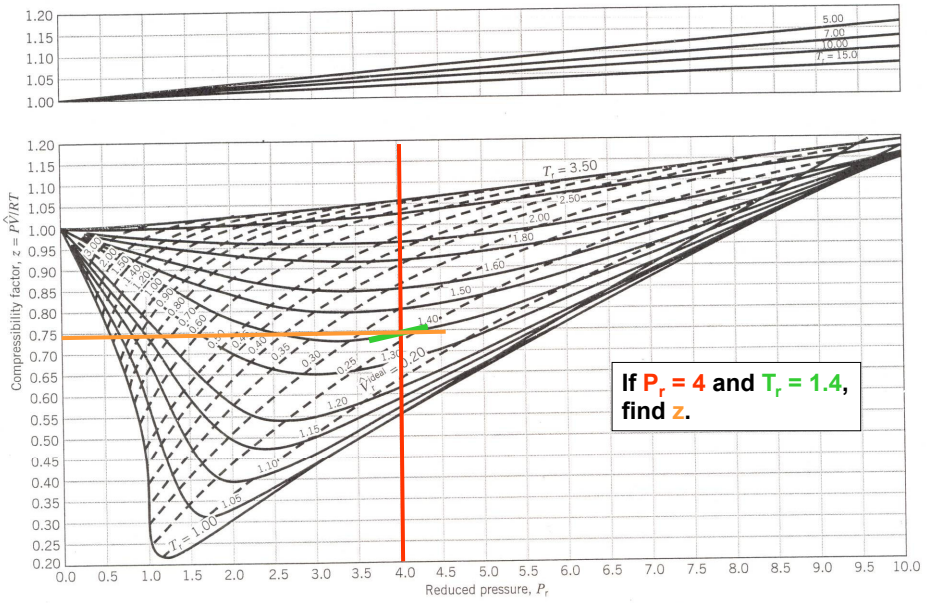

Figure 5.4-3 Generalized compressibility chart, medium pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 176. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

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Only good for this value of z_c, (i.e., most simple fluids)

$$z_c = \frac{P_c \hat{V}_c}{RT_c}$$

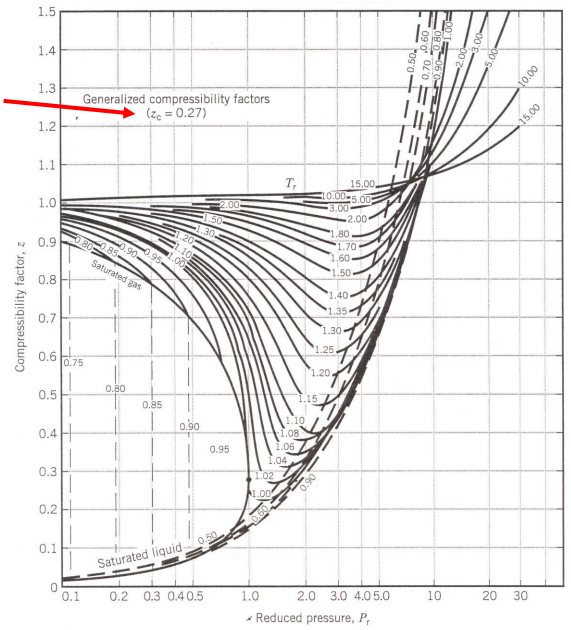

Figure 5.4-1 (Reprinted with permission from *Chemical Process Principles Charts*, 2nd Edition, by O. A. Hougen, K. M. Watson, and R. A. Ragatz, John Wiley & Sons, New York, 1960.)

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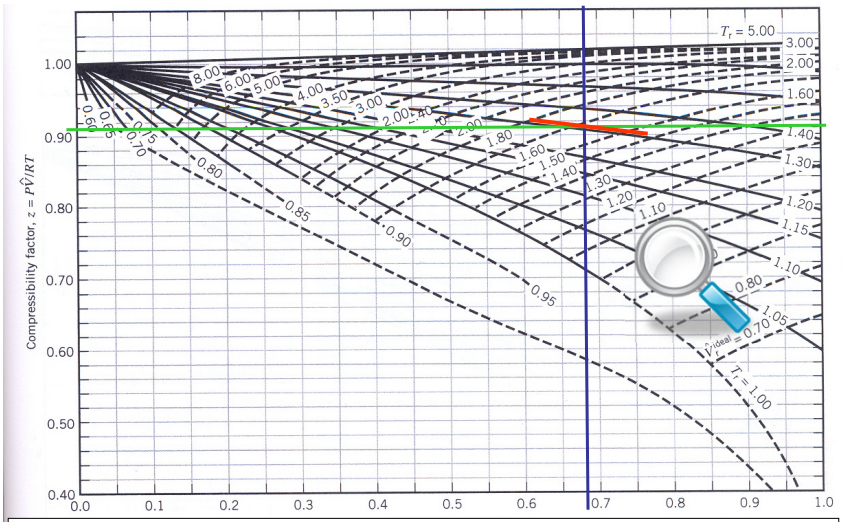
From Excel example, P_r = .686, T_r = 1.315



z = 0.91 (Van der Waals = 0.891, SRK = 0.916)

by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

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Nonideal Gas Mixtures

- Mixtures require “mixing rules”
  - These can get quite complicated
- Mixing rules for Law of Corresponding States (z)
  - Use Kay’s rule to calculate a “Pseudo-critical” Temperature and Pressure for the mixture
  - Determine the “Pseudo-reduced” Temperature and Pressure
  - Find z_m for the mixture from the compressibility chart as before
- This mixing rule **not** good for other EOS approaches
  - You will get mixing rules for other EOS in Thermo or on web

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Corresponding States: Mixtures (Kay's Rule)

Note that these are weighted by mole fraction

$$T_c' = y_A T_{cA} + y_B T_{cB} + y_C T_{cC} + \ldots.$$

$$P_c' = y_A P_{cA} + y_B P_{cB} + y_C P_{cC} + \ldots.$$

$$T_r' = T / T_c'$$

$$P_r' = P / P_c'$$

Hint: We will be using this a lot for mixtures!

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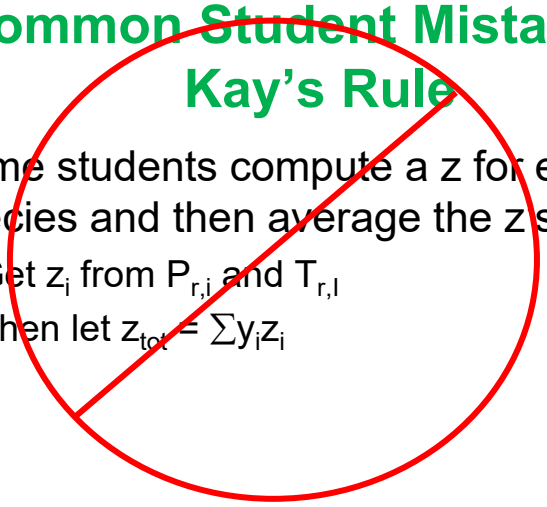
Common Student Mistake on Kay's Rule



- Some students compute a z for each species and then average the z's
  - Get z_i from $P_{r,i}$ and $T_{r,I}$
  - Then let $z_{tot} = \sum y_i z_i$

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Corresponding States: Mixtures
(Kay's Rule Example)

Kay's rule example						
P=	21	atm				
T=	650	K				
	yi	**Tc (K)**	**Pc (atm)**			**MW**
n-Decane	0.2	619	20.8			142.28
n-Octane	0.5	568.8	24.5			114.22
Isopentane	0.3	461	32.9			72.15
Pseudocritical (Tc' and Pc')		546.5	26.28		avg MW=	107.2
Reduced Pseudocritical		1.19	0.80			
z=	0.84					
PV=znRT						
Density = n*MW/V = P*MW/(zRT)						
R=	0.08205	L-atm/(K-gmol)				
Density=	50.3	g/L				
Ideal =	42.2	g/L				

Hint: We will be using this a lot for mixtures!

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Corresponding States: Mixtures
(Kay's Rule Example)

Kay's rule example								
P=	21	atm						
T=	650	K		Wrong Way!!!				
	yi	**Tc (K)**	**Pc (atm)**	**Tr**	**Pr**	**zi**		**MW**
n-Decane	0.2	619	20.8	0.95	0.99	0.44		142.28
n-Octane	0.5	568.8	24.5	0.88	1.17	0.8		114.22
Isopentane	0.3	461	32.9	0.71	1.57	0.953		72.15
Pseudocritical (Tc' and Pc')		546.5	26.28			0.77	avg MW=	107.211
Reduced Pseudocritical		1.19	0.80					
z=	0.84							
PV=znRT								
Density = n*MW/V = P*MW/(zRT)								
R=	0.08205	L-atm/(K-gmol)						
Density=	50.3	g/L				54.		
Ideal =	42.2	g/L						

Hint: We will be using this a lot for mixtures!

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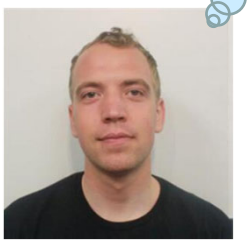
Mixing Rules for SRK EOS

Dr. Fletcher, what about mixing rules for the SRK EOS?



Next year in thermodynamics. You can find the mixing rules on the web as well

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Summary

- Non-ideal equations of state are iterative if you are calculating $\hat{V}$
  - Use ideal gas as first guess
  - Use T_c and P_c to get parameters
  - Alternate: Calculate P at a lot of different $\hat{V}$'s and interpolate
- Compressibility factors are alternate approach
  - Use T_c and P_c to get T_r and P_r
  - Use z in modified ideal gas equation
- Mixing rules required for mixtures
  - Kay's rule for compressibility factor calculations
    - Use $T_{c,\,mix}$ and $P_{c,\,mix}$ to get $P_{r,mix}$ and $T_{r,\,mix}$, then get z for mixture
  - Other mixing rules available (not in our book) for equations of state

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Homework

(all workbook problems)

1. SRK Eq. of State
2. Compressibility Chart
3. Kay's Rule

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