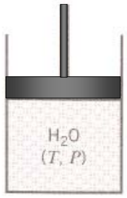
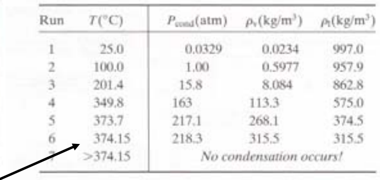
Class 17
Non-Ideal Gases

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

Water Phase Change

(set T, increase P until condensation occurs)





Run	T(°C)	P_{cond}(atm)	ρ_v(kg/m³)	ρ_l(kg/m³)
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!*		

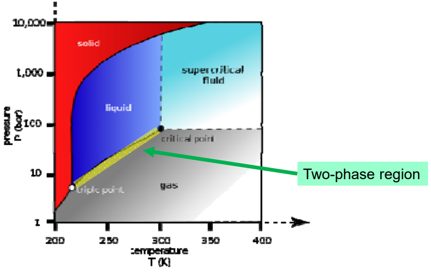
This point defines the critical temperature (T_c) and pressure (P_c) of H_2O!
- No condensation occurs as pressure increases

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

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

Pure Component Phase Diagram



Pressure-temperature phase diagram for CO_2

Definitions (cont.)

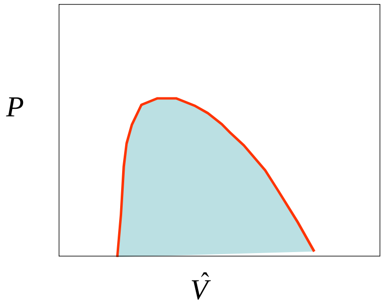
- **Reduced Temperature (T_r)**:

  $T_r = T / T_c$
- **Reduced Pressure (P_r)**:

  $P_r = P / P_c$
- **Supercritical fluid:**

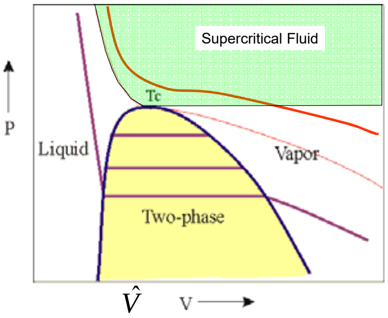
  $T > T_c$ and $P > P_c$

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

Phase Diagram for H_2O (Quiz Answers)



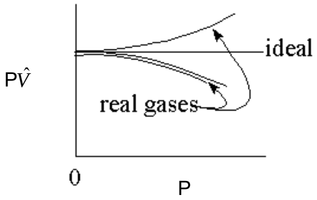
1. Please draw
2. Label the following:
   a. 2-phase envelope
   b. Critical point
   c. P_c
3. Draw 3 isotherms
   a. Through 2-phase
   b. Through P_c
   c. Supercritical
4. Label T_c

Non-Ideal Gases

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

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

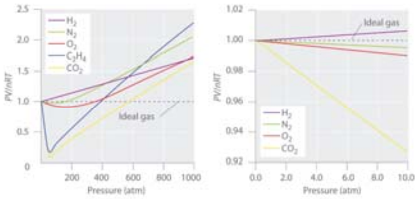
Ideal vs. Real Gases



From p. 192, ideal when:

$$\hat{V}_{ideal} > 5L/mol \quad (diatomic\ \ gases)$$
$$\hat{V}_{ideal} > 20L/mol \quad (other\ \ gases)$$

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:

$$\left(\frac{V}{n}\right)_{\text{ideal}} \quad \frac{RT}{P} > 5\,\frac{L}{mol}$$ 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

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)

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**

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

$$B_0 = 0.083 - \frac{0.42}{T_r^{1.6}}$$
$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$
$$B = \frac{RT_c}{P_c}(B_0 + \omega B_1)$$

- 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)

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

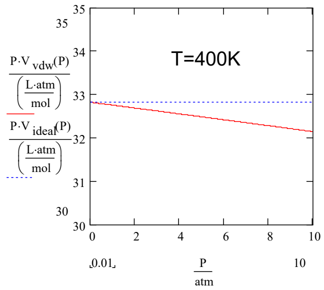
$a = 0.42747\ (RT_c)^2/P_c$
$b = 0.08664\ (RT_c)/P_c$
$m = 0.48508 + 1.55171\ \omega - 0.1561\ \omega^2$
$\alpha = [1 + m(1 - T_r^{0.5})]^2$

See Excel Example

See Mathcad Example

(A copy of this Mathcad file is on the ChEn 273 web page under Class Notes)

Van der Waals Results: CO_2



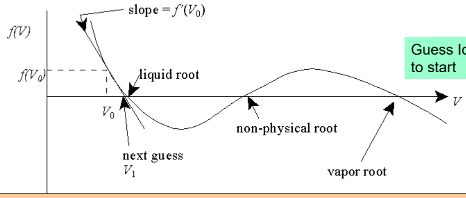
Does this increase in non-ideal behavior with increasing pressure make sense?

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

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%!

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

Compressibility Factor

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

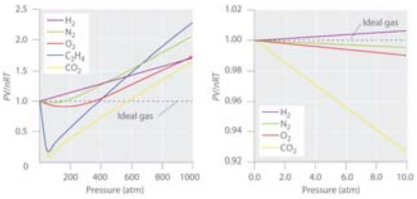
$$P\hat{V} = zRT$$

$$PV = znRT$$

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

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:

$$\left(\frac{V}{n}\right)_{\text{ideal}} \qquad \frac{RT}{P} > 5\frac{L}{mol} \quad \text{for diatomic gases } (H_2, N_2, O_2, \text{etc.})$$

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

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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 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

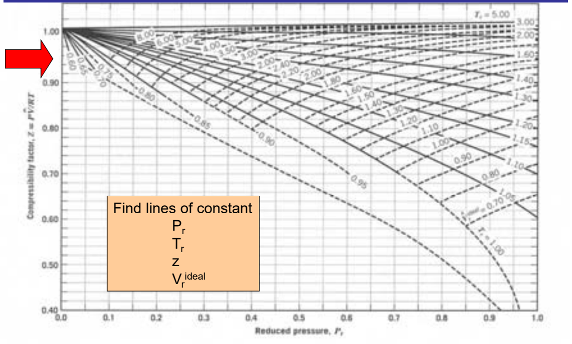
Adjustments for H_2 or He:

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

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

Use adjusted values on compressibility charts

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

This one is correct!

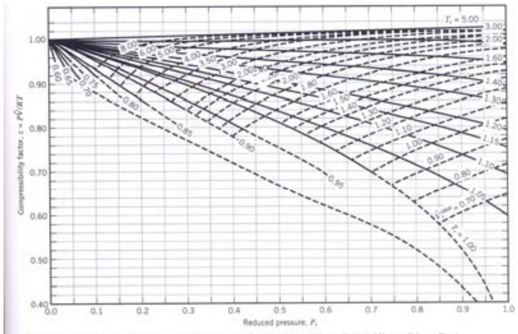
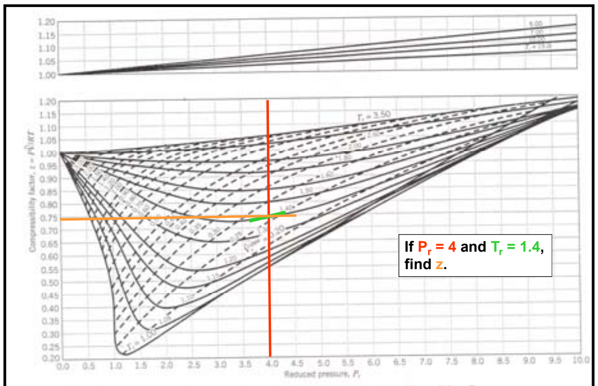


Figure 5.4-2 Generalized compressibility chart, low pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 175. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)



If P_r = 4 and T_r = 1.4, find z.

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.)

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

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

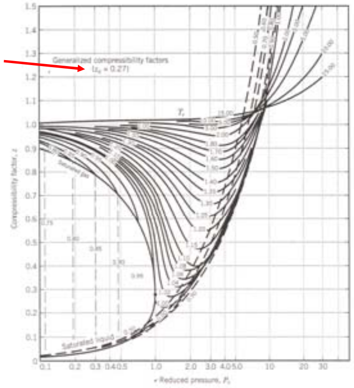


Figure 5.4-1 (Reprinted with permission from *Chemical Process Principles Charts*, 2nd Edition, by O. A. Hougen, K. M. Watson, and R. A. Ragatz, John Wiley & Sons, New York, 1960.)

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

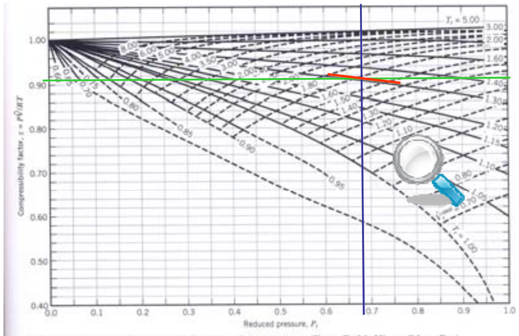


Figure 5.4-2 Generalized compressibility chart, low pressures. (From D. M. Himmelblau, *Basic Principles and Calculations* … by permission of Prentice …

z = 0.91 (Van der Waals = 0.89)

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 EOS in Thermo or on web

Corresponding States: Mixtures
(Kay's Rule)

Note that these are weighted by mole fraction

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

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

$$T_r' = T / T_c'$$

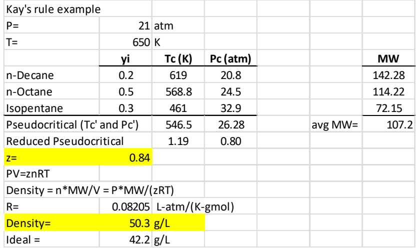
$$P_r' = P / P_c'$$

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

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 $z_{tot} = \sum y_i z_i$

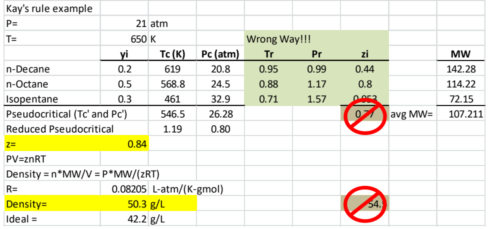
Corresponding States: Mixtures
(Kay's Rule Example)



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!

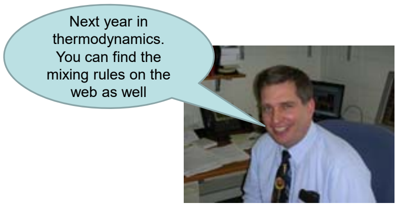
Corresponding States: Mixtures
(Kay's Rule Example)



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!

Mixing Rules for SRK EOS



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

Homework

(all workbook problems)

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