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

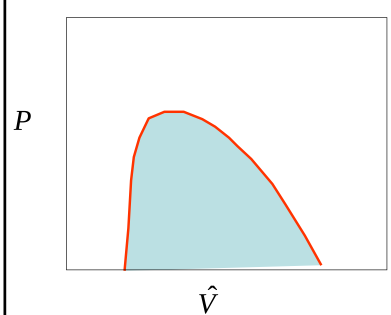
Definitions

- **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**: Gaseous species below T_c
  - Usually used in the 2-phase region
- **Gas**: Species above T_c at a pressure low enough to be more like vapor than liquid
  - Usually used when no liquid is present

Definitions (cont.)

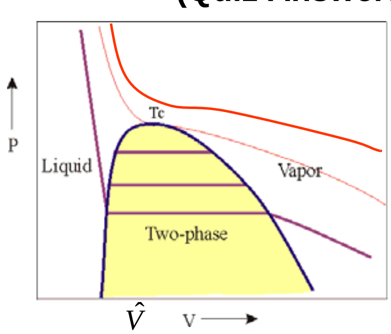
- **Reduced Temperature (T_r)**:
  $T_r = T / T_c$
- **Reduced Pressure (P_r)**:
  $P_r = P / P_c$

Phase Diagram for H_2O (Quiz)



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

Phase Diagram for H_2O (Quiz Answers)



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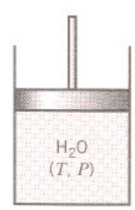
Water Phase Change
(set T, change P until condensation occurs)



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!*		

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

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

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

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

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

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

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

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

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

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

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

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

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

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

van der Waals: Cubic form

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

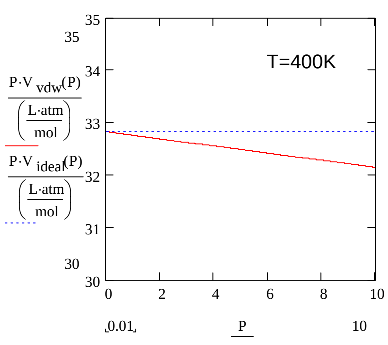
Transforms to:

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

See Mathcad Example

(This Mathcad file is on the web page)

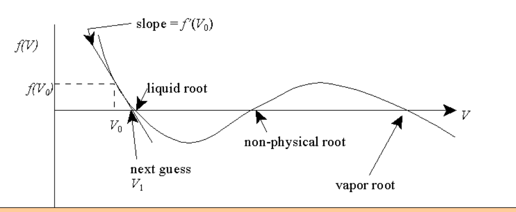
Van der Waals Results: CO_2



Van der Waals below T_c
(3 roots)

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

Cubic EOS



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

Compressibility Factor

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

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

- 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

Corresponding States

- 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

$$T_r = \frac{T}{T_c}, P_r = \frac{P}{P_c}, V_r^{ideal} = \frac{\hat{V}P_c}{RT_c}$$

  - 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

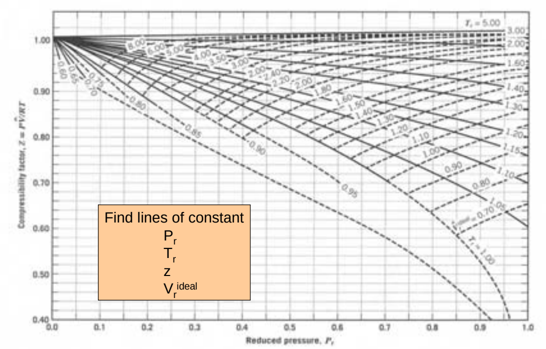


 FIGURE 5.4-2

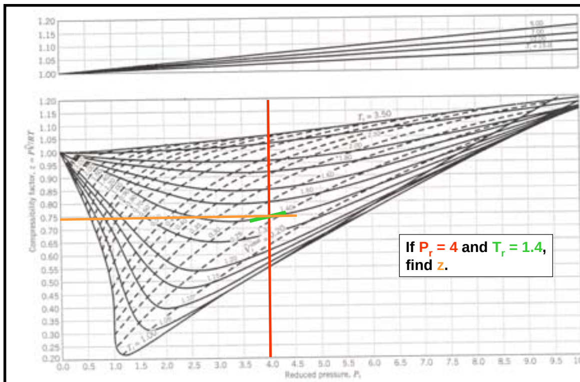


Figure 5.4-3 Generalized compressibility chart, medium pressures. (From D. M. Himmelblau, Basic Principles and Calculations in Chemical Engineering, 3rd Edition, copyright © 1974, p. 176. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

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

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

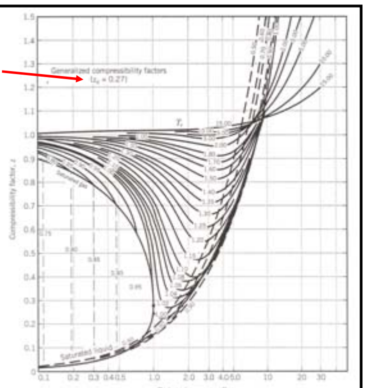
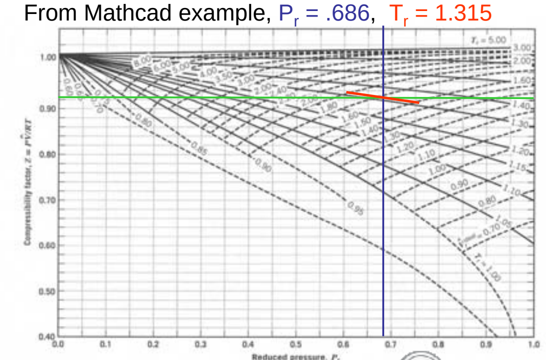


Figure 5.4-1 (Reprinted with permission from Chemical Process Principles Charts, 2nd Edition, by O. A. Hougen, K. M. Watson, and R. A. Ragatz, John Wiley & Sons, New York, 1960.)

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



z = 0.92

 FIGURE 5.4-2

Corresponding States: Mixtures

- 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

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!

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
- 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 z_{mix}
  - Other mixing rules available (not in our book) for equations of state