ABE 201
Biological Thermodynamics 1

Module 7:

Ideal and Non-Ideal Gas "Laws"

Outline

- Equations of State
- Ideal Gas Law
  - Review
  - Applications of Gas Mixtures
  - Limitations and deviations from ideality
- Critical Point and Supercritical Fluids
- Non Ideal Gas Laws
  - Virial Equation
  - Compressibility Factor

State Properties and Equations of State

- State properties are properties of a system that depend upon its <u>state</u> but are unaffected by the way the system got to that state (path)
  - Mass, Volume, Temperature, Pressure, Internal Energy, etc.

- Equations of State are mathematical expressions describing the relationships between state properties.

- Ideal Gas Law is simplest equation of state

Universal Gas Constant

- R = in units of (pressure * volume)/(mole * temperature)
- Pressure * Volume = Energy
  - Pa * m^3 = (N/m^2) * m^3 = N-m = force * distance
  - R = energy/(mole*temperature)
- Inside Back Cover of Text
  - 8.314 Pa-m^3/(mol-K)
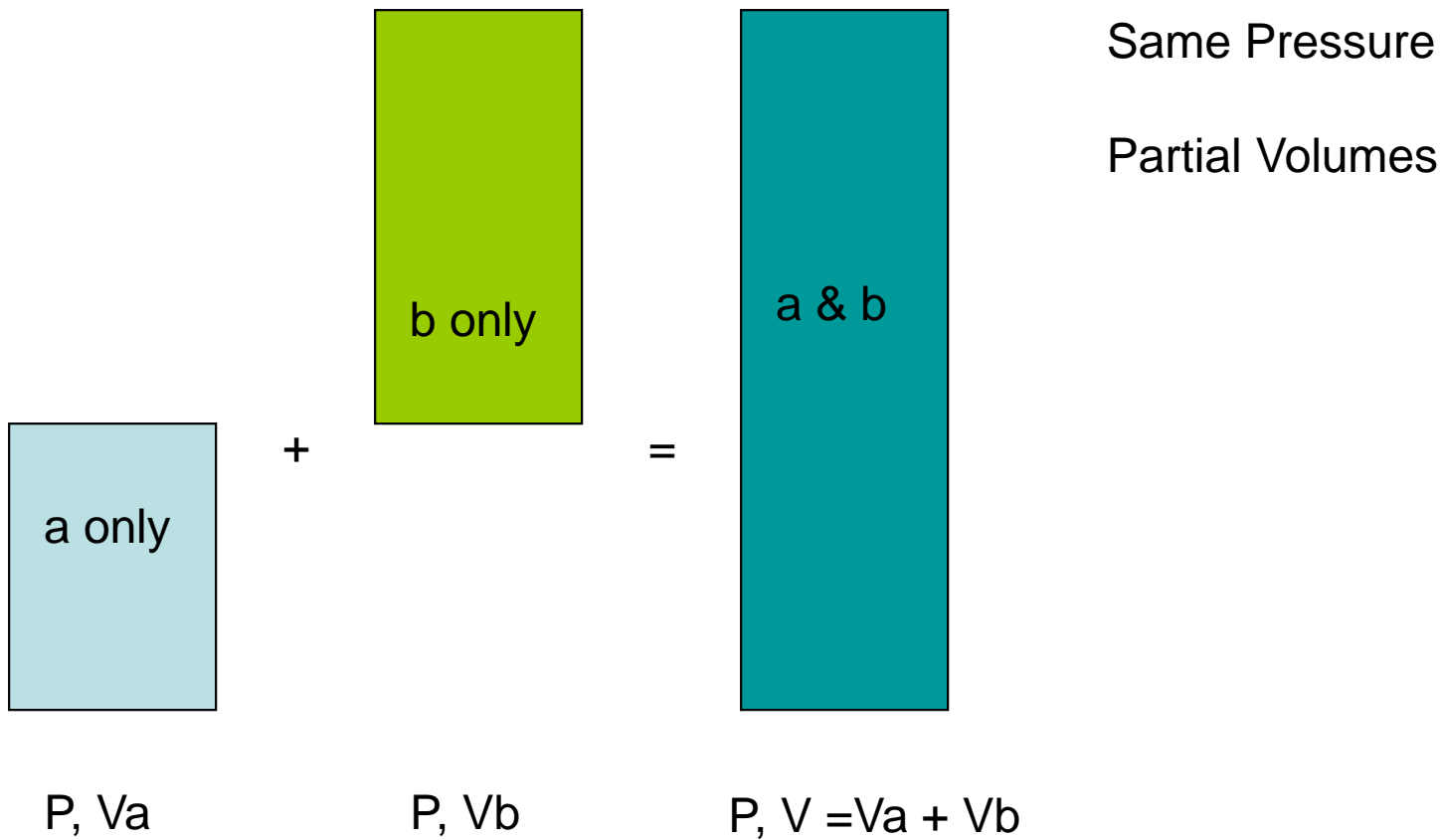 - 10.73 psia-ft^3/(lb-mol-R)
  - 8.314 J/(mol-K)

Ideal Gas Mixtures

- ***Suppose we have a mixture of gases A, B and C with specified volume and temp…..***

- ***Partial Pressure:*** pressure that would be exerted by n_A moles of A alone in the same total volume V at the same temperature T.

- ***Partial Volume:*** the volume that would be occupied by n_A moles of A alone at the total pressure P and temperature T of the mixture.

Partial Pressure (noninteracting)

a only

+

b only

=

a & b

Same Volume

Partial Pressures

Pa, V   Pb, V   P= Pa+Pb, V
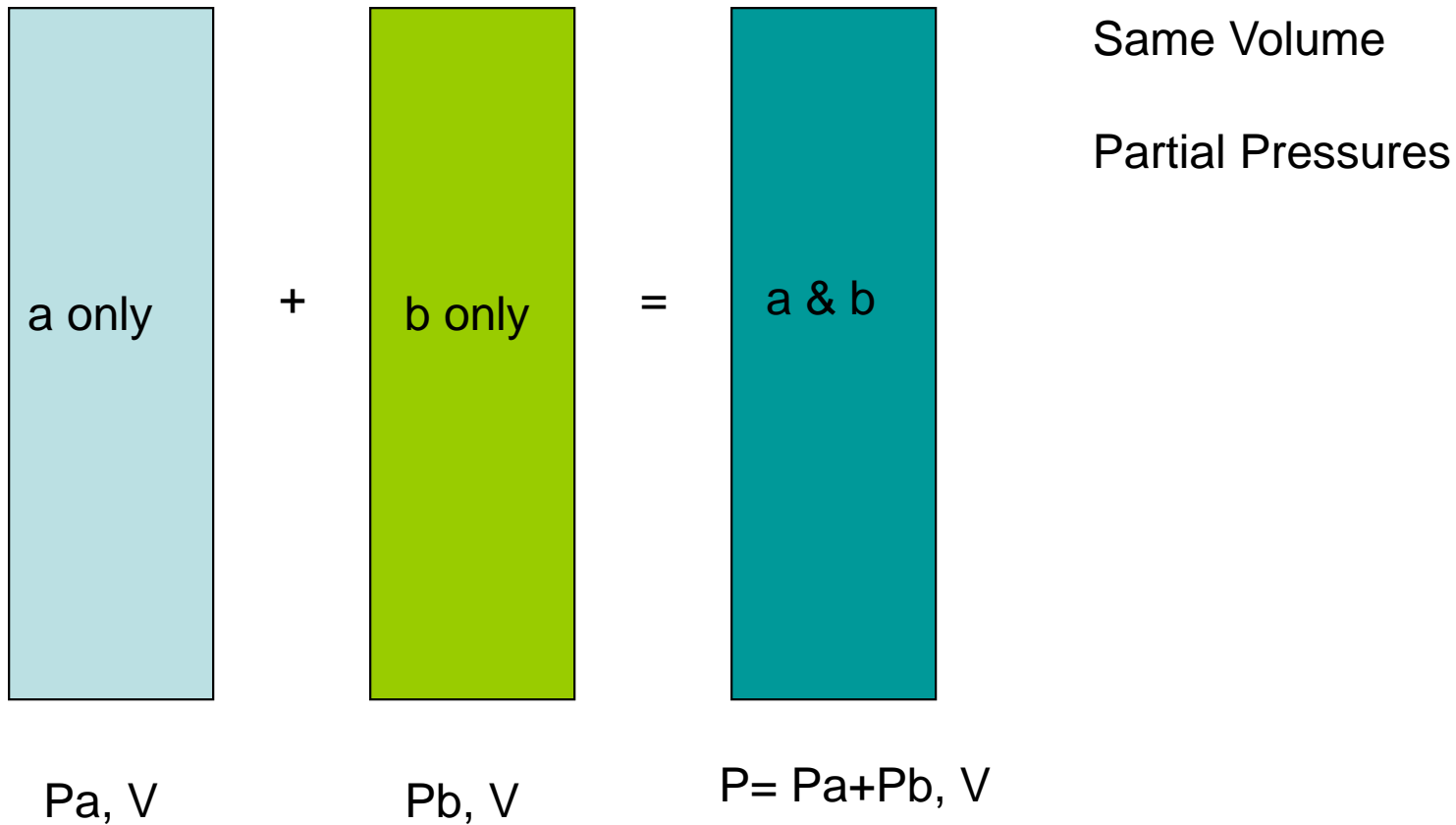
Partial Volume (noninteracting)

a only

b only

a & b

Same Pressure

Partial Volumes

+

=

P, Va

P, Vb

P, V =Va + Vb

Ideal Gas Mixtures

If it is an ideal mixture each of the components does not interact with the others and therefore behaves ideally.

$$PV = nRT$$

$$\Sigma p_i V = \Sigma n_i RT$$

$$p_A V = n_A RT$$

$$p_B V = n_B RT$$

$$p_C V = n_C RT \quad \text{etc}....$$

Ideal Gas Mixtures

Dividing the partial ideal gas equation by the overall ideal gas expression we get:

$$\frac{p_A}{P} = \frac{n_A}{n} = y_A$$

Partial Pressures can be Used to find mole fractions!

And therefore:

$$p_A = y_A P$$

$$v_A = y_A V$$

Volume fraction: is the partial volume divided by the entire volume. This fraction multiplied by 100 gives the *percentage by volume* (% v/v) commonly referred to in problems.

STP

- Standard Temperature and Pressure
- Basis for comparison between different gasses and gas flows

System	T	P	V	N
SI	273 K	1 atm	0.0224 m^3	1 mol
CGS	273 K	1 atm	22.4 L	1 mol
US	491 R	1 atm	0.791 ft^3	1 mol

Standard vs. Actual

$$PV = nRT$$

$$P_s \hat{V}_s = RT_s \quad (\hat{V}_s = \text{specific molar volume})$$
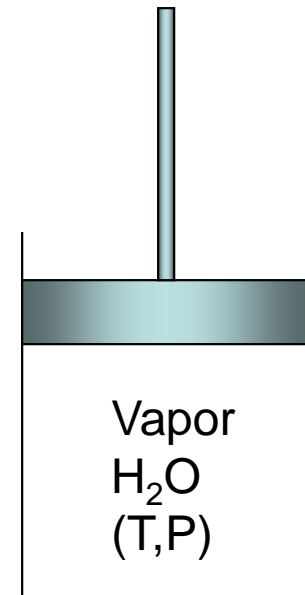
$$\frac{PV}{P_s \hat{V}_s} = n \frac{T}{T_s}$$
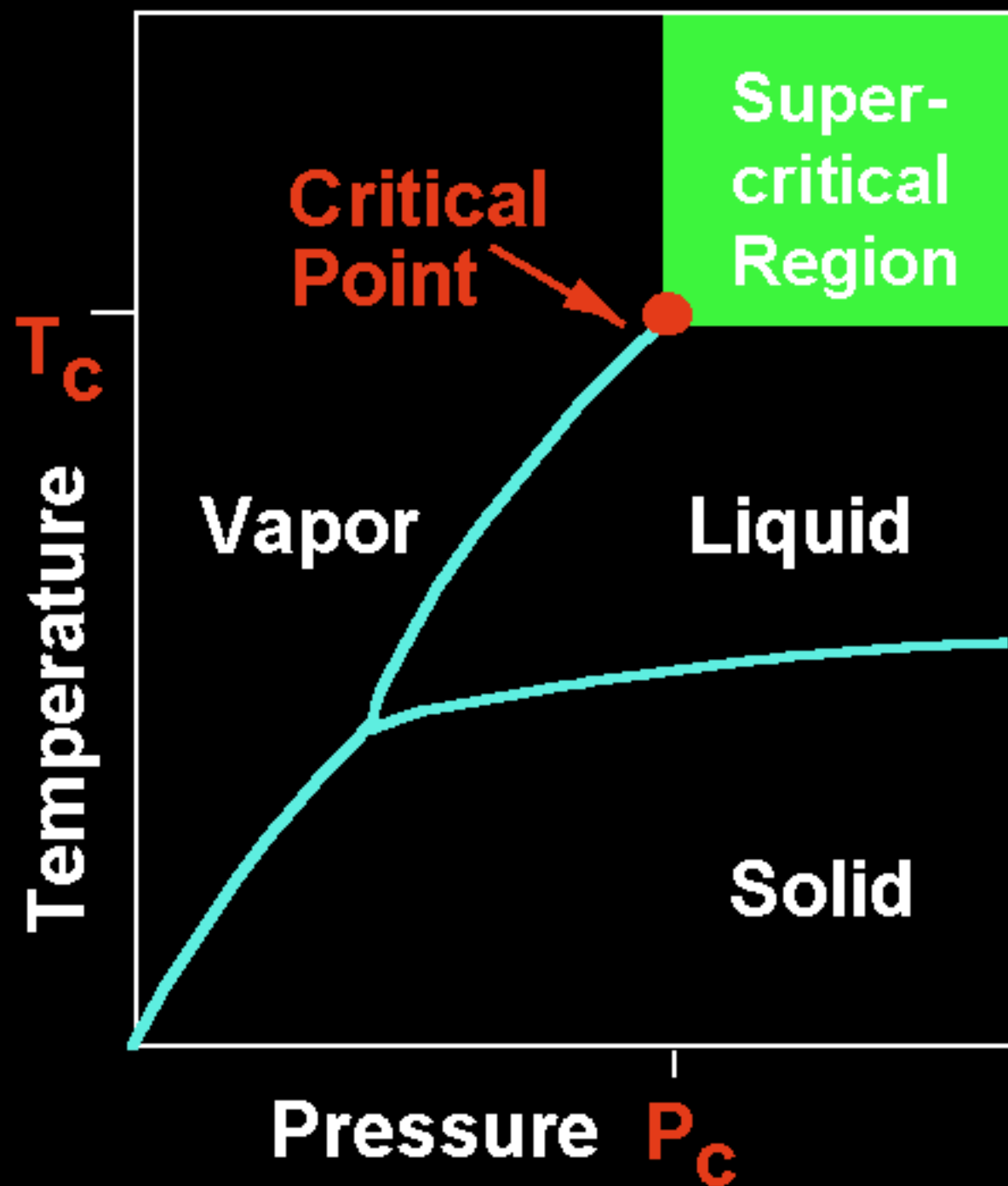
Non Ideal Gas Equations of State

Water Vapor in a closed piston

Run	T(C)	P$_{cond}$ (atm)	Vapor Density	Liquid Density
1	25	0.033	0.023	997
2	100	1.0	0.6	958
3	200	16	8.1	863
4	350	163	113	575
5	374	217	268	375
6	*374.15*	*218.3*	316	316
7	374	No condensation occurs		

Tc

Pc

Vapor
H$_2$O
(T,P)

Definitions:

Critical Temperature: highest temperature at which a species can coexist in two phases (liquid and vapor)

Critical Pressure: Corresponding pressure at the critical point defined above.

These critical values are reported in Table B.1

Substances that are above the critical point conditions are referred to as **supercritical fluids**.

Equations of State

Virial Equation

Cubic Equations:

    van der Waals   Beattie-Bridgeman

    Redlich-Kwong   Benedict-Webb-Rubin

    Soave-Redlich-Kwong (SRK)

    Peng Robinson   Berthelot

Compressibility Factor Equation

Virial Equation of State

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} \cdot$$

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

$$B_0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

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

$$T_r > 0.686 + 0.439 P_r$$

$$T_r = T / T_c$$

$$P_r = P / P_c$$

- The virial equation allows us to calculate P,V or T given two of these three. It is an empirical expression so more terms can be added, but usually it is truncated after the B term.
- Can be used at wide range of densities

Virial Equation Cont'd.

In the expressions for B, the following terms must be defined:

Pitzer Acentric Factor: ω = (Table 5.3-1)

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The acentric factor reflects the polarity as well as the shape of the molecules.

Smaller ω means more symmetrical and non-polar

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

Compressibility Factor
Equation of State

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

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

- What is the value of the compressibility factor for an ideal gas?

- Extent to which z varies from 1 measures its non-ideality.

- Determine z using charts $z = z(T_r, P_r)$ and then use the modified ideal gas equation above to solve for the unknown. (pp 208-211)
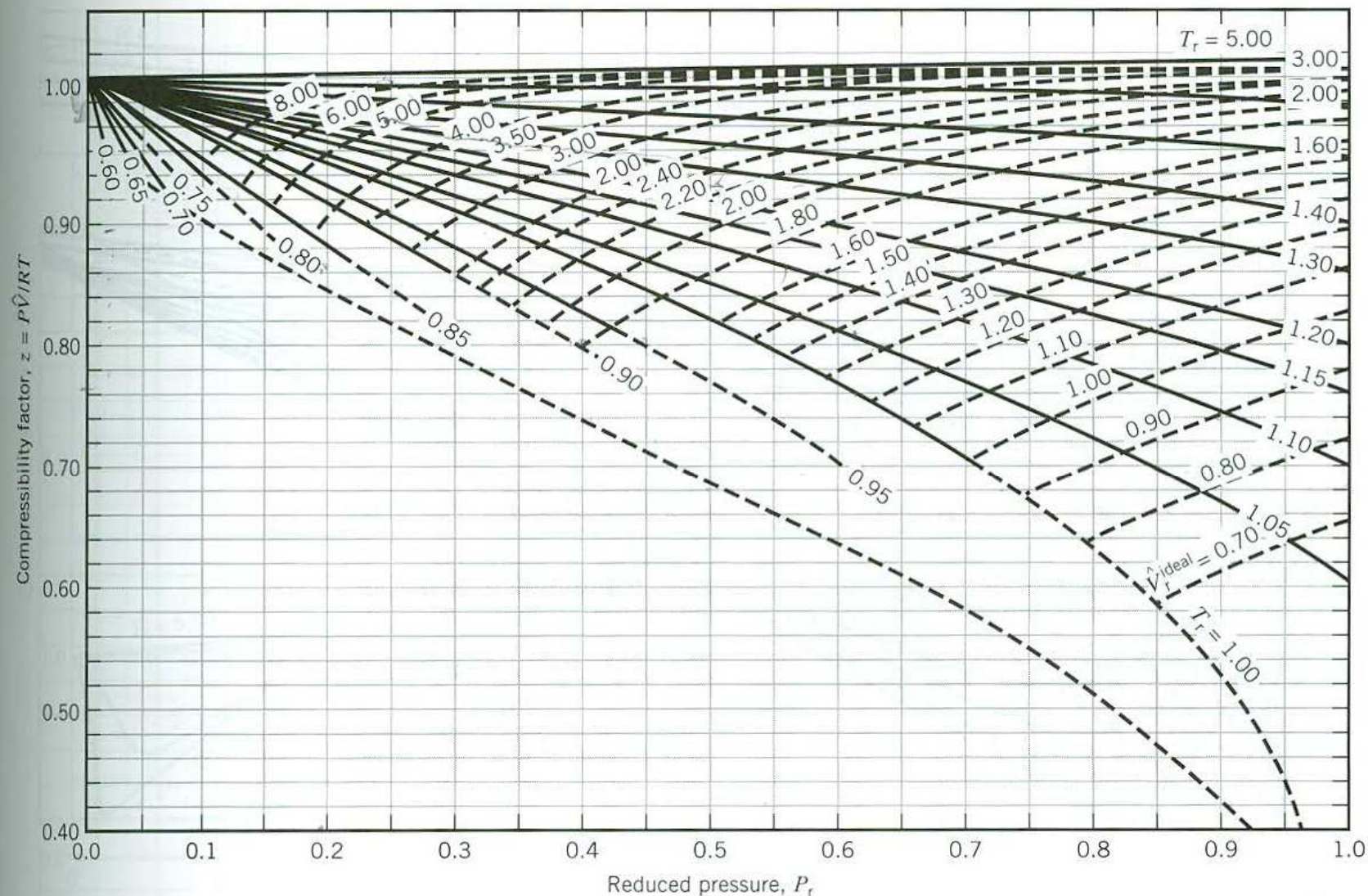
Figure 5.4-2 Generalized compressibility chart, low pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 175. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)
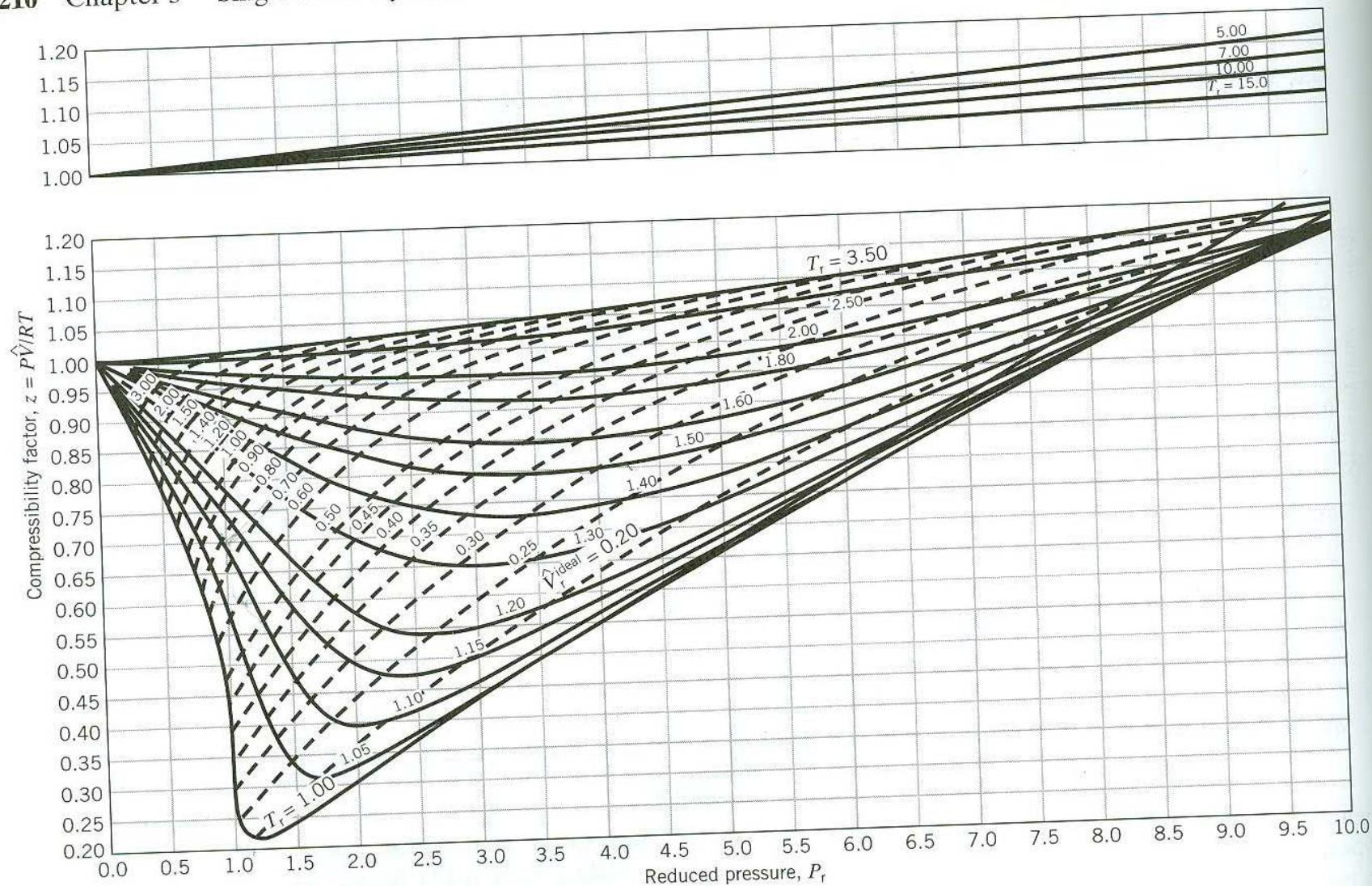
Figure 5.4-3 Generalized compressibility chart, medium pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 176. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

Procedure:

Look up the critical pressure and temperature using Table B.1

Calculate the reduced values

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

Look up the value of z as a function of two of the above reduced values.

Solve the compressibility equation

Summary

- Equations of state are mathematical expressions describing the relationship between state properties.

- Ideal gas law is simplest equation of state.

- Ideal gas law is a good approximation for dilute (low pressure) gasses far from the critical point.

- Non-ideal gas equations use various approaches to account for deviation from ideality.