

# Thermodynamics: An Engineering Approach

8th Edition

Yunus A. Çengel, Michael A. Boles

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## Topic 2

# Thermodynamic States

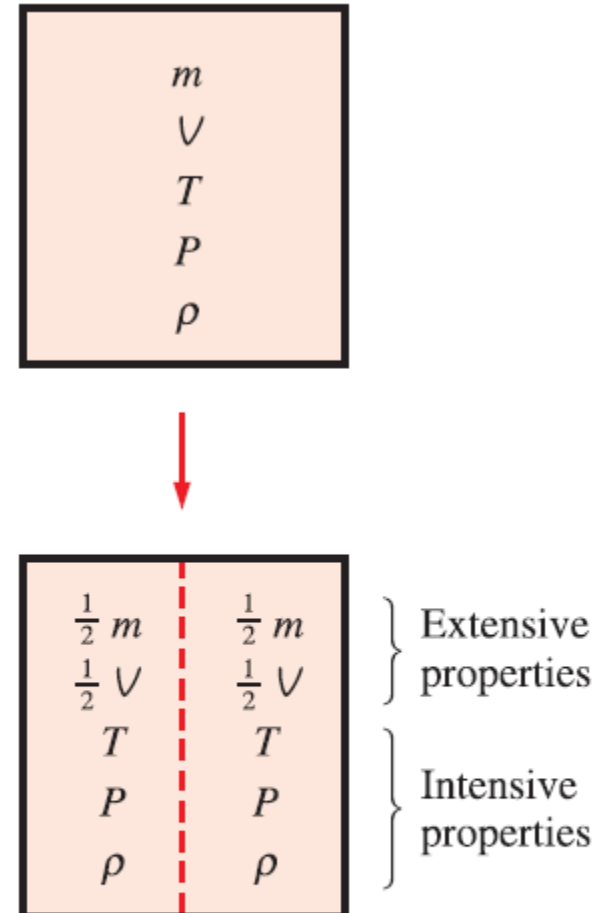
# Objectives

- Explain the basic concepts of thermodynamics such as system, state, state postulate, equilibrium, process, and cycle.
- Describe the hypothetical substance “ideal gas” and the ideal-gas equation of state.
- Apply the ideal-gas equation of state in the solution of typical problems.
- Introduce the compressibility factor, which accounts for the deviation of real gases from ideal-gas behavior.
- Present some of the best-known equations of state.
- Discuss the concepts of vapor pressure and humidity.

# PROPERTIES OF A SYSTEM

- **Property:** Any characteristic of a system.
- Some familiar properties are pressure  $P$ , temperature  $T$ , volume  $V$ , and mass  $m$ .
- Properties are considered to be either *intensive* or *extensive*.
- **Intensive properties:** Those that are independent of the mass of a system, such as temperature, pressure, and density.
- **Extensive properties:** Those whose values depend on the size—or extent—of the system.
- **Specific properties:** Extensive properties per unit mass.

$$(v = V/m) \quad (e = E/m).$$

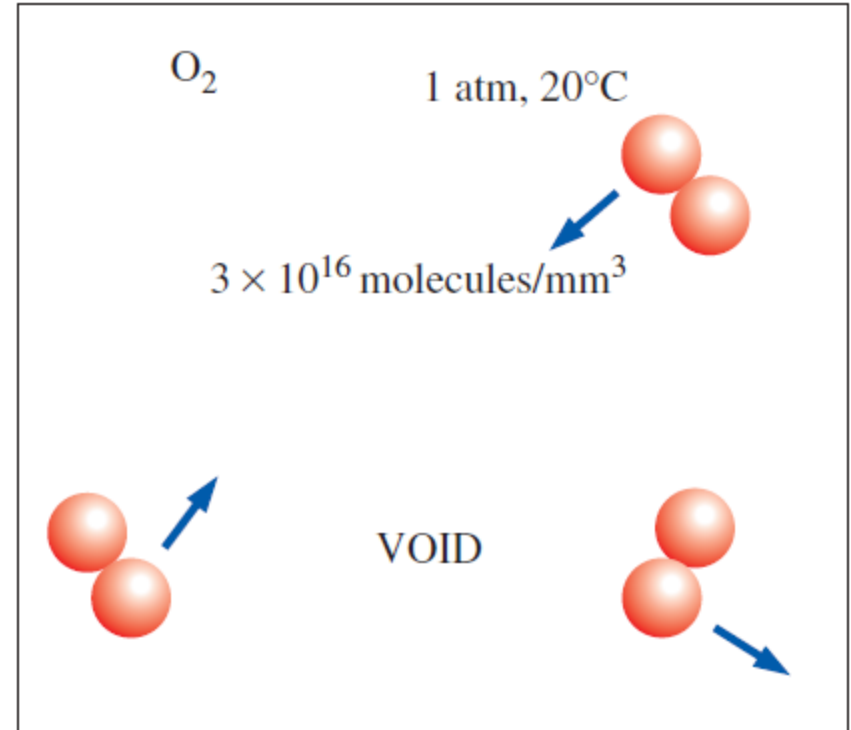


**FIGURE 1–23**

Criterion to differentiate intensive and extensive properties.

# Continuum

- Matter is made up of atoms that are widely spaced in the gas phase. Yet it is very convenient to disregard the atomic nature of a substance and view it as a continuous, homogeneous matter with no holes, that is, a **continuum**.
- The continuum idealization allows us to treat properties as point functions and to assume the properties vary continually in space with no jump discontinuities.
- This idealization is valid as long as the size of the system we deal with is large relative to the space between the molecules.
- This is the case in practically all problems.
- In this text we will limit our consideration to substances that can be modeled as a continuum.

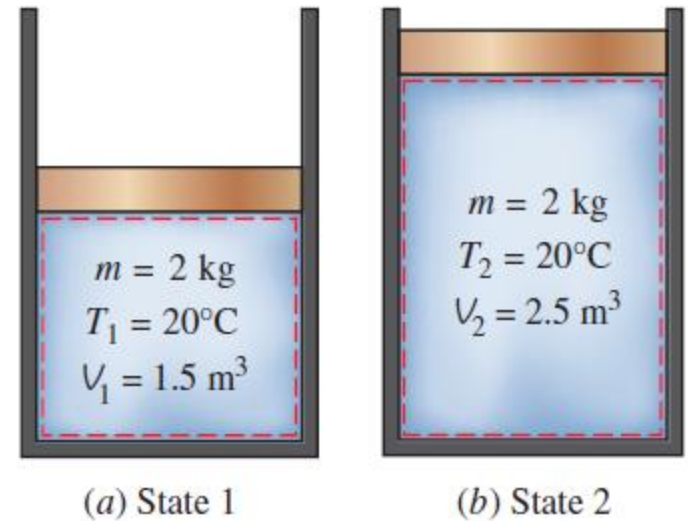


**FIGURE 1–24**

Despite the relatively large gaps between molecules, a gas can usually be treated as a continuum because of the very large number of molecules even in an extremely small volume.

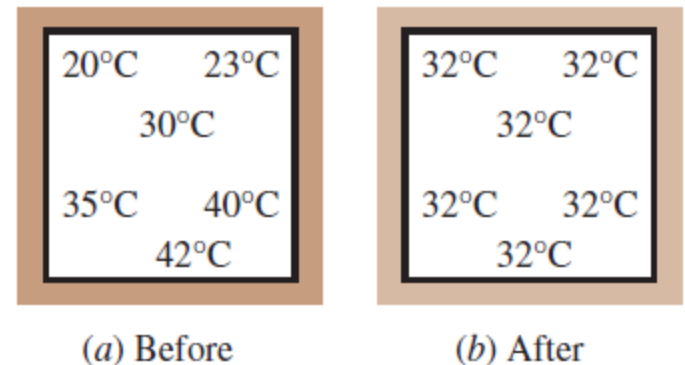
# STATE AND EQUILIBRIUM

- Thermodynamics deals with *equilibrium* states.
- **Equilibrium:** A state of balance.
- In an equilibrium state there are no unbalanced potentials (or driving forces) within the system.
- **Thermal equilibrium:** If the temperature is the same throughout the entire system.
- **Mechanical equilibrium:** If there is no change in pressure at any point of the system with time.
- **Phase equilibrium:** If a system involves two phases and when the mass of each phase reaches an equilibrium level and stays there.
- **Chemical equilibrium:** If the chemical composition of a system does not change with time, that is, no chemical reactions occur.



**FIGURE 1–26**

A system at two different states.



**FIGURE 1–27**

A closed system reaching thermal equilibrium.

# The State Postulate

- The number of properties required to fix the state of a system is given by the **state postulate**:
  - *The state of a simple compressible system is completely specified by two independent, intensive properties.*
- **Simple compressible system**: If a system involves no electrical, magnetic, gravitational, motion, and surface tension effects.



**FIGURE 1–28**

The state of nitrogen is fixed by two independent, intensive properties.

# THE IDEAL-GAS EQUATION OF STATE

- **Equation of state:** Any equation that relates the pressure, temperature, and specific volume of a substance.
- The simplest and best-known equation of state for substances in the gas phase is the **ideal-gas equation** of state. This equation predicts the  $P$ - $v$ - $T$  behavior of a gas quite accurately within some properly selected region.

$$P = R \left( \frac{T}{v} \right) \quad P v = R T \quad \text{Ideal gas equation of state}$$

$$R = \frac{R_u}{M} \quad (\text{kJ/kg} \cdot \text{K} \text{ or } \text{kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})$$

$R$ : gas constant

$M$ : molar mass (kg/kmol)

$R_u$ : universal gas constant

$$R_u = \begin{cases} 8.31447 \text{ kJ/kmol} \cdot \text{K} \\ 8.31447 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\ 0.0831447 \text{ bar} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\ 1.98588 \text{ Btu/lbmol} \cdot \text{R} \\ 10.7316 \text{ psia} \cdot \text{ft}^3/\text{lbmol} \cdot \text{R} \\ 1545.37 \text{ ft} \cdot \text{lbf/lbmol} \cdot \text{R} \end{cases}$$

Substance	$R$ , kJ/kg·K
Air	0.2870
Helium	2.0769
Argon	0.2081
Nitrogen	0.2968

Different substances have different gas constants.

Mass = Molar mass  $\times$  Mole number

$$m = MN \quad (\text{kg})$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \begin{array}{l} \text{Ideal gas} \\ \text{equation at two} \\ \text{states for a fixed} \\ \text{mass} \end{array}$$

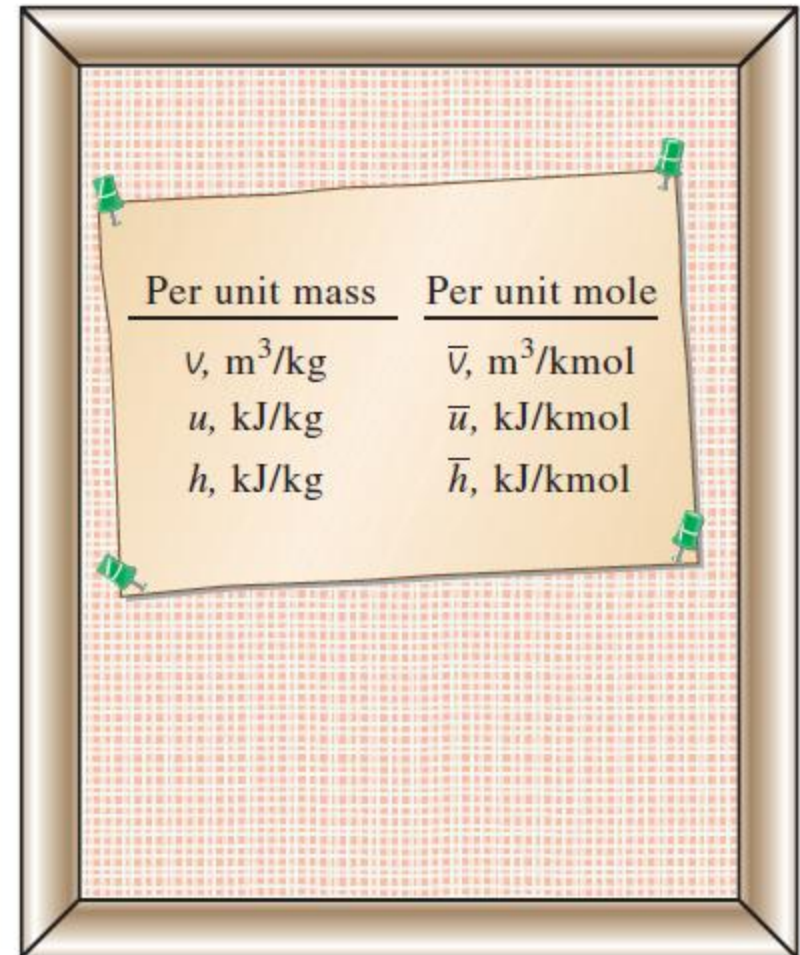
Various expressions  
of ideal gas equation

$$V = m\upsilon \longrightarrow PV = mRT$$

$$mR = (MN)R = NR_u \longrightarrow PV = NR_u T$$

$$V = N\bar{V} \longrightarrow P\bar{V} = R_u T$$

**Real gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).**



Per unit mass	Per unit mole
$\upsilon, \text{m}^3/\text{kg}$	$\bar{\upsilon}, \text{m}^3/\text{kmol}$
$u, \text{kJ/kg}$	$\bar{u}, \text{kJ/kmol}$
$h, \text{kJ/kg}$	$\bar{h}, \text{kJ/kmol}$

**FIGURE 3–43**

Properties per unit mole are denoted with a bar on the top.



## Example

Before going on a long trip you should measure your tire pressure. Before you drive off you measure the (gauge) pressure in your tires and find it to be 210 kPa. The temperature of the air both outside and inside your tire is 25°C. After traveling for a few hours, you measure the tire pressure and get a reading of 220 kPa. Assuming the tire volume does not change, what is the new temperature? Does this make sense?

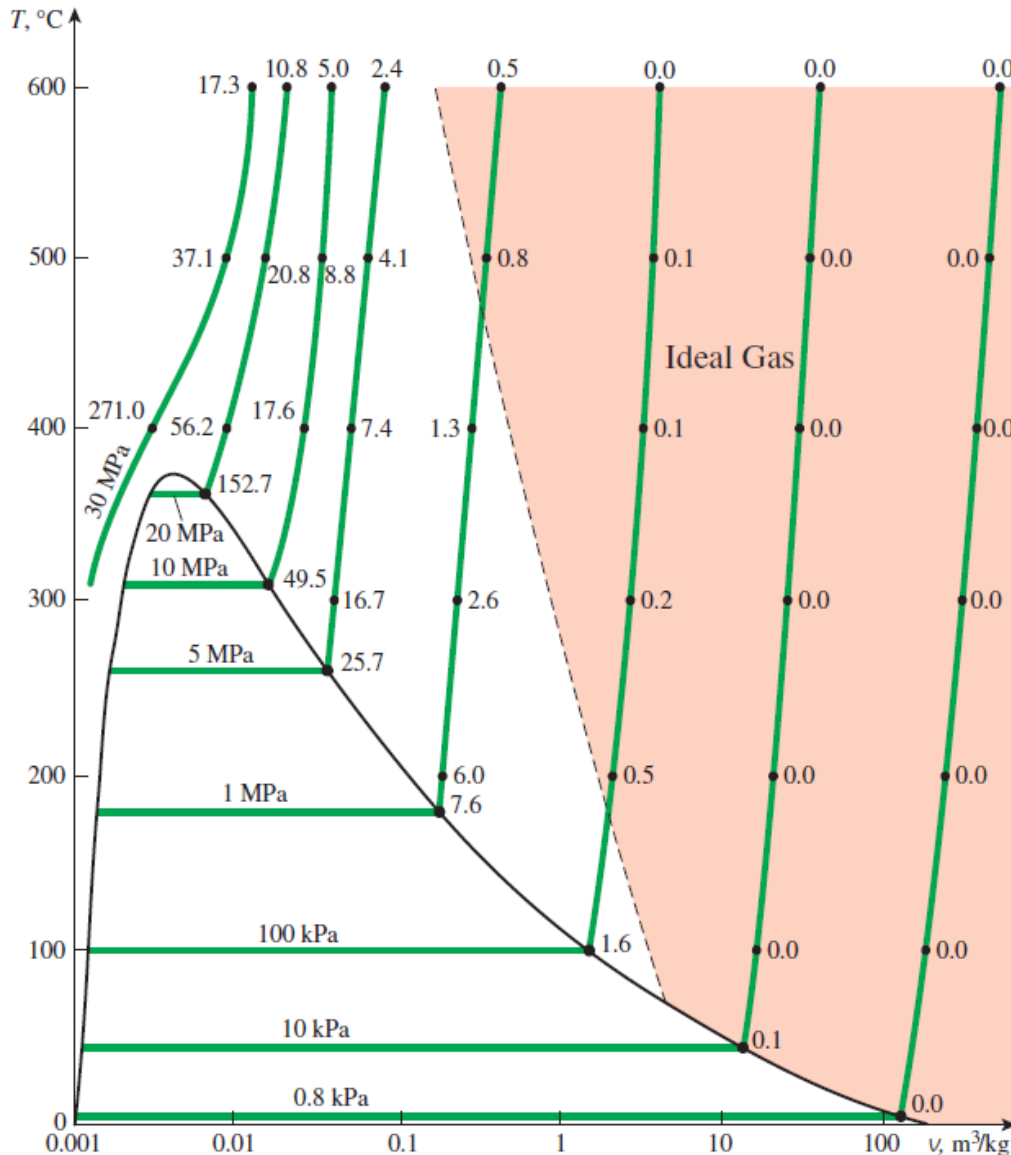
Solution

# Example

An equipment manager for a football team fills a football with 12 psig of air in a room with a temperature of 70°F. He also fills up another ball with 14 psig of air in the same room with the same temperature. Both balls are then taken outside where the outside temperature is 50°F. Assuming the volume does not change, what is the new pressure in each football?

Solution

# Is Water Vapor an Ideal Gas?



- At pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent).

At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line.

In air-conditioning applications, the water vapor in the air can be treated as an ideal gas. Why?

In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.

Percentage of error  

$$\left( \frac{|v_{\text{table}} - v_{\text{ideal}}|}{v_{\text{table}}} \times 100 \right)$$
 involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with less than 1 percent error.

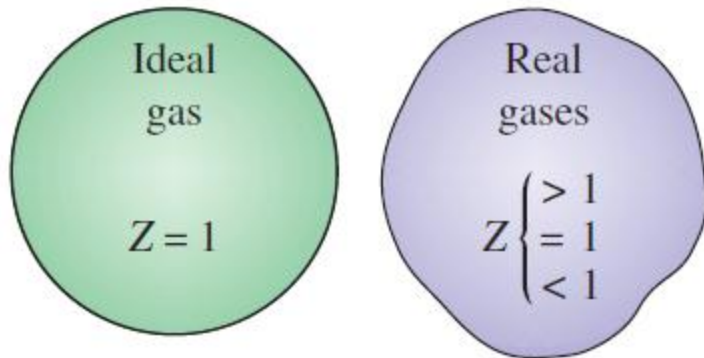
# COMPRESSIBILITY FACTOR—A MEASURE OF DEVIATION FROM IDEAL-GAS BEHAVIOR

## Compressibility factor $Z$

A factor that accounts for the deviation of real gases from ideal-gas behavior at a given temperature and pressure.

$$PV = ZRT$$

$$Z = \frac{PV}{RT} \quad Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}$$



**FIGURE 3–46**

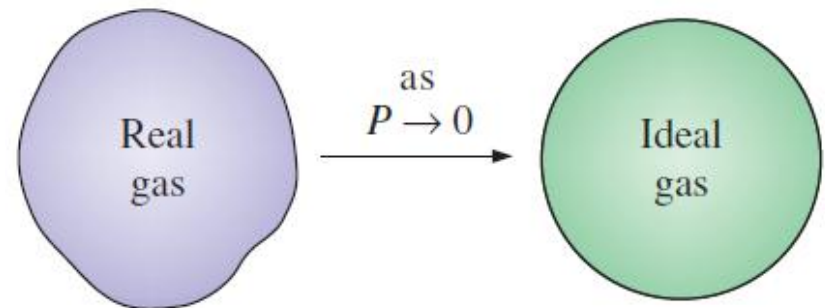
The compressibility factor is unity for ideal gases.

The farther away  $Z$  is from unity, the more the gas deviates from ideal-gas behavior.

*Gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).*

**Question:** What is the criteria for low pressure and high temperature?

**Answer:** The pressure or temperature of a gas is high or low relative to its critical temperature or pressure.



**FIGURE 3–48**

At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).

$$P_R = \frac{P}{P_{cr}} \quad T_R = \frac{T}{T_{cr}}$$

Reduced  
pressure

Reduced  
temperature

$$v_R = \frac{v_{actual}}{RT_{cr}/P_{cr}} \quad \text{Pseudo-reduced specific volume}$$

$$\left. \begin{aligned} P_R &= \frac{P}{P_{cr}} \\ v_R &= \frac{v}{RT_{cr}/P_{cr}} \end{aligned} \right\} Z = \dots \quad (\text{Fig. A-15})$$

$Z$  can also be determined from a knowledge of  $P_R$  and  $v_R$ .

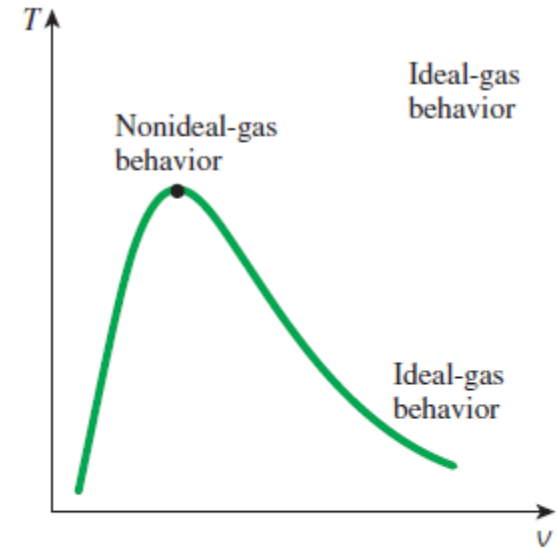
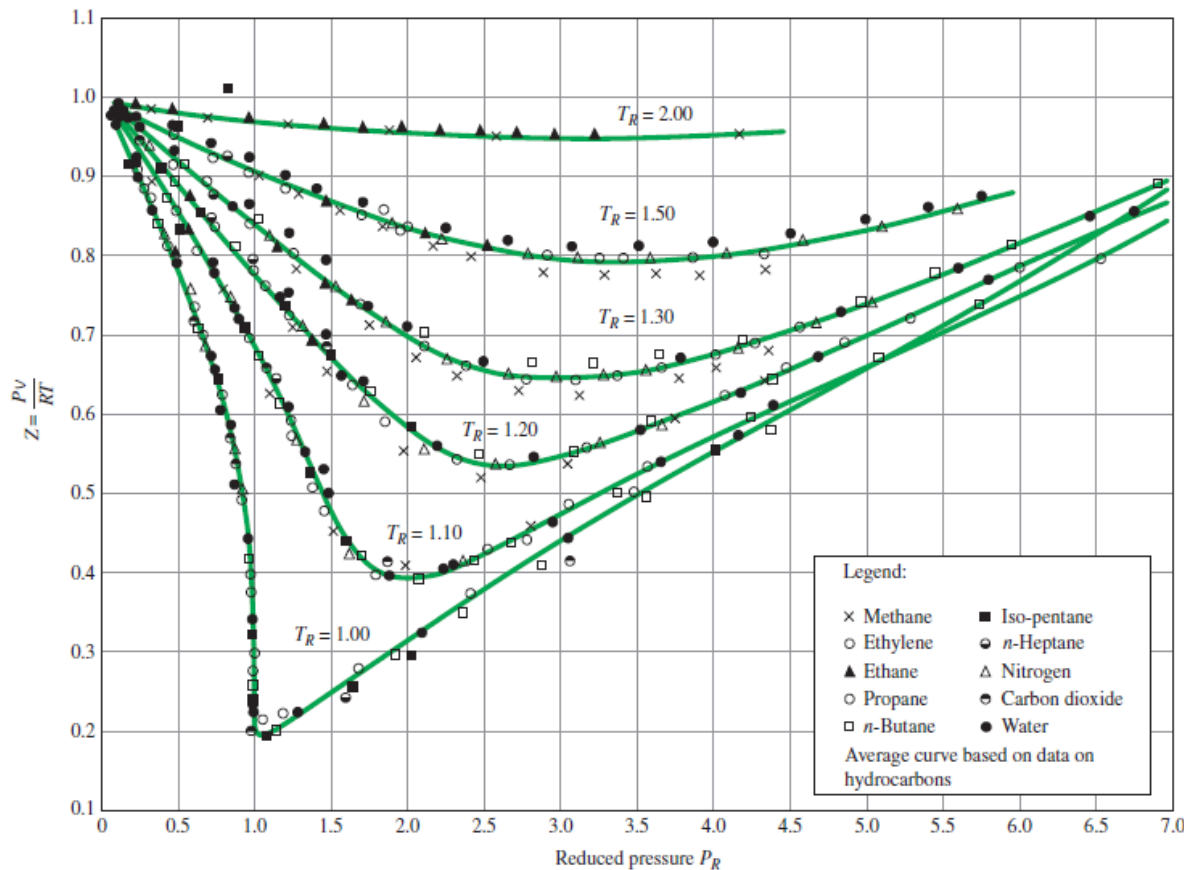


FIGURE 3-49

Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

Comparison of  $Z$  factors for various gases.

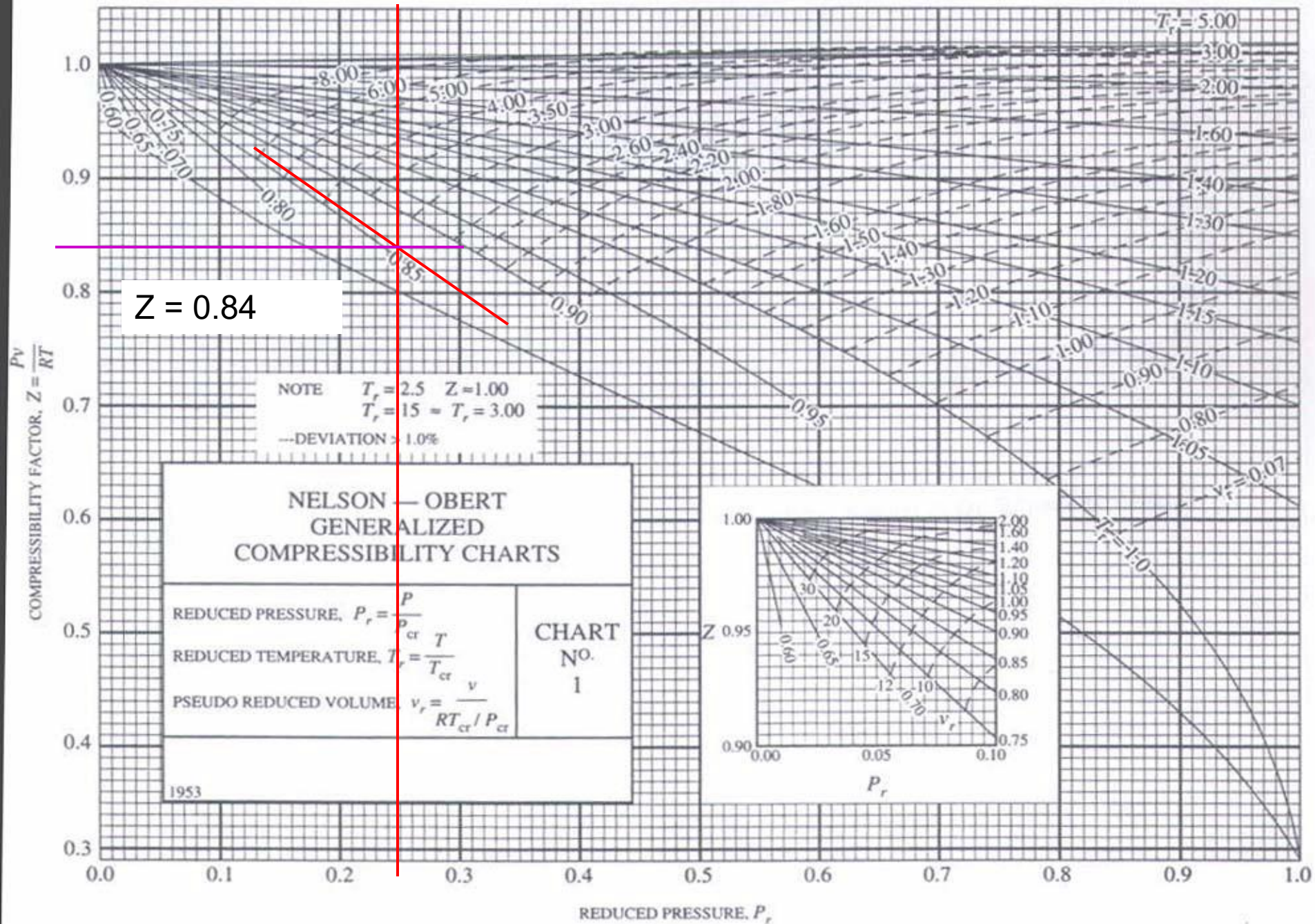
## Example

Determine the specific volume of R-134a at 1 MPa and 50°C. Use the ideal gas equation and also use the compressibility chart. What is it listed as in the tables in the back of your textbook?

Solution



(a)  $0 < P_i < 1.0$



# OTHER EQUATIONS OF STATE

Several equations have been proposed to represent the  $P$ - $v$ - $T$  behavior of substances accurately over a larger region with no limitations.

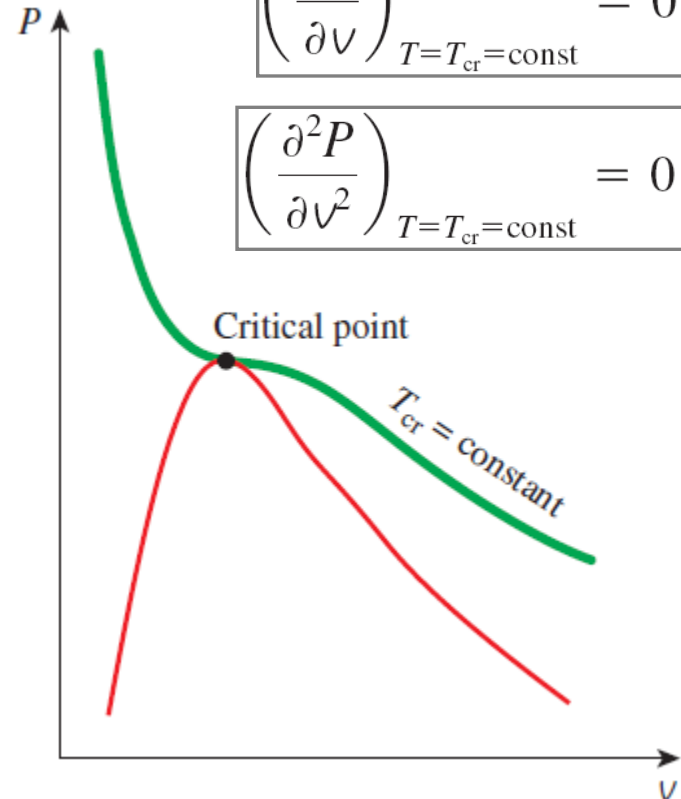
## Van der Waals Equation of State

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

$$a = \frac{27R^2T_{\text{cr}}^2}{64P_{\text{cr}}} \quad b = \frac{RT_{\text{cr}}}{8P_{\text{cr}}}$$

This model includes two effects not considered in the ideal-gas model: *the intermolecular attraction forces and the volume occupied by the molecules themselves*. The accuracy of the van der Waals equation of state is often inadequate.

Critical isotherm of a pure substance has an inflection point at the critical state.



van der Waals  
Berthelet  
Redlich-Kwang  
Beattie-Bridgeman  
Benedict-Webb-Rubin  
Strobridge  
Virial



## Beattie-Bridgeman Equation of State

$$P = \frac{R_u T}{\bar{V}^2} \left( 1 - \frac{c}{\bar{V} T^3} \right) (\bar{V} + B) - \frac{A}{\bar{V}^2}$$
$$A = A_0 \left( 1 - \frac{a}{\bar{V}} \right) \quad B = B_0 \left( 1 - \frac{b}{\bar{V}} \right)$$

The constants are given in Table 3–4 for various substances. It is known to be reasonably accurate for densities up to about  $0.8\rho_{\text{cr}}$ .

## Benedict-Webb-Rubin Equation of State

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

The constants are given in Table 3–4. This equation can handle substances at densities up to about  $2.5 \rho_{\text{cr}}$ .

## Virial Equation of State

$$P = \frac{RT}{V} + \frac{a(T)}{V^2} + \frac{b(T)}{V^3} + \frac{c(T)}{V^4} + \frac{d(T)}{V^5} + \dots$$

The coefficients  $a(T)$ ,  $b(T)$ ,  $c(T)$ , and so on, that are functions of temperature alone are called **virial coefficients**.

TABLE 3-4

Constants that appear in the Beattie-Bridgeman and the Benedict-Webb-Rubin equations of state

(a) When  $P$  is in kPa,  $\bar{v}$  is in  $\text{m}^3/\text{kmol}$ ,  $T$  is in K, and  $R_u = 8.314 \text{ kPa}\cdot\text{m}^3/\text{kmol}\cdot\text{K}$ , the five constants in the Beattie-Bridgeman equation are as follows:

Gas	$A_0$	$a$	$B_0$	$b$	$c$
Air	131.8441	0.01931	0.04611	-0.001101	$4.34 \times 10^4$
Argon, Ar	130.7802	0.02328	0.03931	0.0	$5.99 \times 10^4$
Carbon dioxide, $\text{CO}_2$	507.2836	0.07132	0.10476	0.07235	$6.60 \times 10^5$
Helium, He	2.1886	0.05984	0.01400	0.0	40
Hydrogen, $\text{H}_2$	20.0117	-0.00506	0.02096	-0.04359	504
Nitrogen, $\text{N}_2$	136.2315	0.02617	0.05046	-0.00691	$4.20 \times 10^4$
Oxygen, $\text{O}_2$	151.0857	0.02562	0.04624	0.004208	$4.80 \times 10^4$

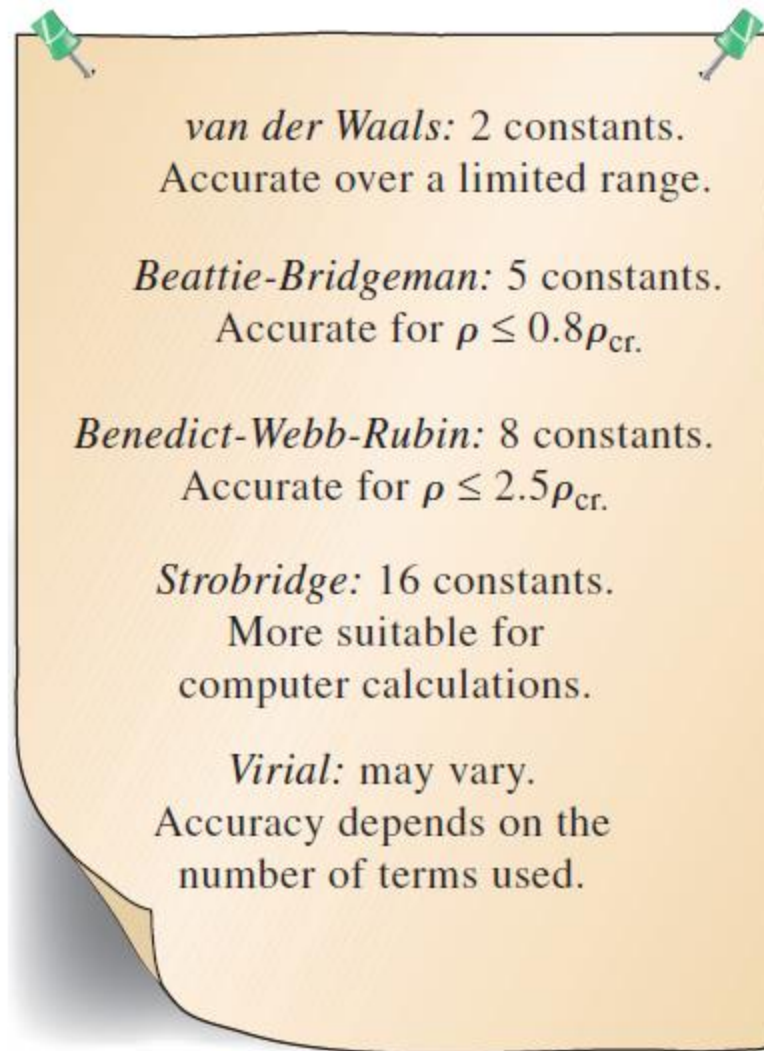
Source: Gordon J. Van Wylen and Richard E. Sonntag, *Fundamentals of Classical Thermodynamics*, English/SI Version, 3rd ed. (New York: John Wiley & Sons, 1986), p. 46, table 3.3.

(b) When  $P$  is in kPa,  $\bar{v}$  is in  $\text{m}^3/\text{kmol}$ ,  $T$  is in K, and  $R_u = 8.314 \text{ kPa}\cdot\text{m}^3/\text{kmol}\cdot\text{K}$ , the eight constants in the Benedict-Webb-Rubin equation are as follows:

Gas	$a$	$A_0$	$b$	$B_0$	$c$	$C_0$	$\alpha$	$\gamma$
n-Butane, $\text{C}_4\text{H}_{10}$	190.68	1021.6	0.039998	0.12436	$3.205 \times 10^7$	$1.006 \times 10^8$	$1.101 \times 10^{-3}$	0.0340
Carbon dioxide, $\text{CO}_2$	13.86	277.30	0.007210	0.04991	$1.511 \times 10^6$	$1.404 \times 10^7$	$8.470 \times 10^{-5}$	0.00539
Carbon monoxide, CO	3.71	135.87	0.002632	0.05454	$1.054 \times 10^5$	$8.673 \times 10^5$	$1.350 \times 10^{-4}$	0.0060
Methane, $\text{CH}_4$	5.00	187.91	0.003380	0.04260	$2.578 \times 10^5$	$2.286 \times 10^6$	$1.244 \times 10^{-4}$	0.0060
Nitrogen, $\text{N}_2$	2.54	106.73	0.002328	0.04074	$7.379 \times 10^4$	$8.164 \times 10^5$	$1.272 \times 10^{-4}$	0.0053

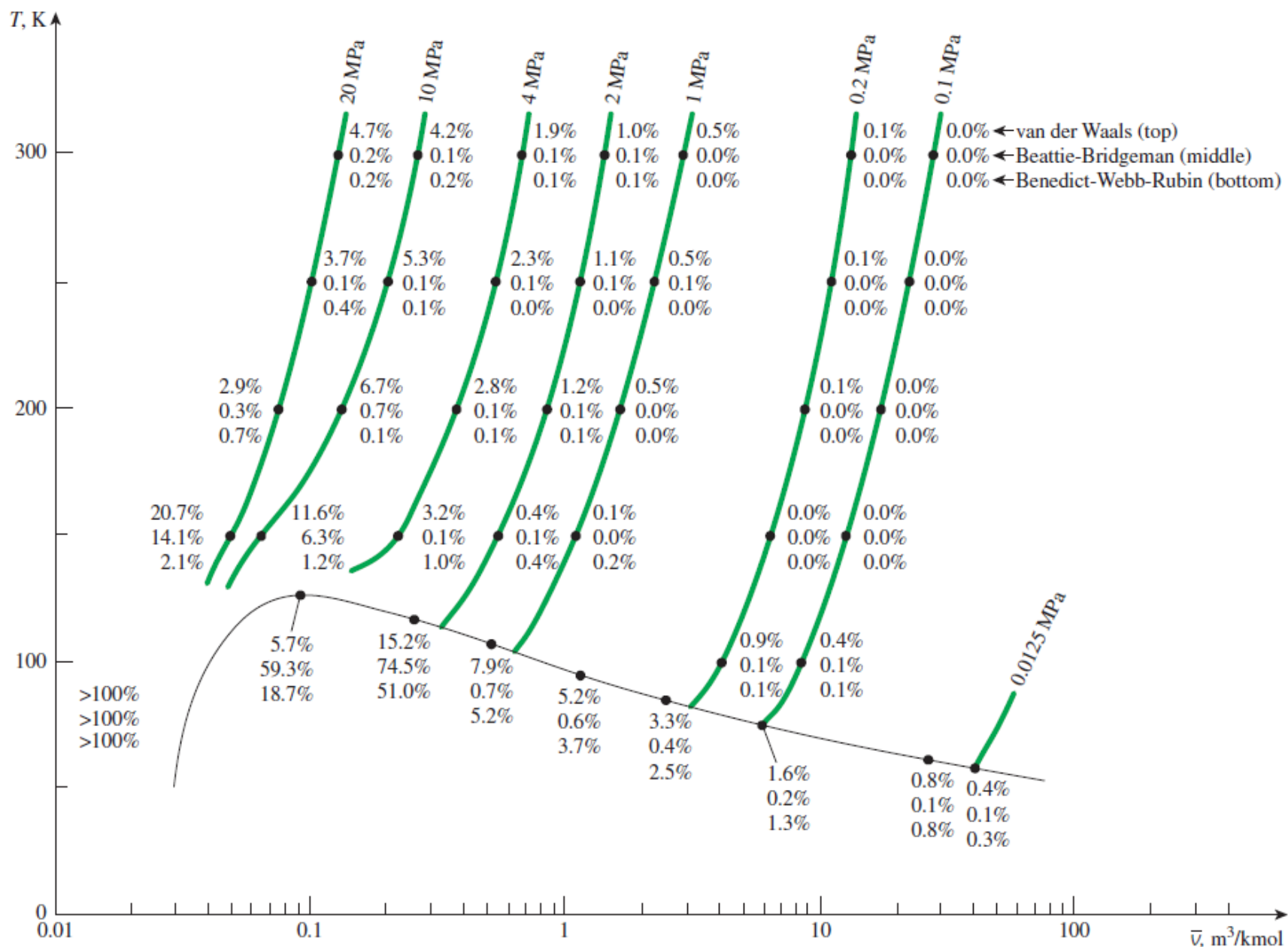
Pressure of N<sub>2</sub> at 175 K with  $v = 0.00375 \text{ m}^3/\text{kg}$

Method	Value (MPa)	% error
Experimental	10.000	----
Ideal Gas Eq.	13.851	38.5%
van der Waals	9.471	5.3%
Beattie-Bridgeman	10.110	1.1%
Benedict-Webb-Rubin	10.009	0.09%



**FIGURE 3–55**

Complex equations of state represent the  $P$ - $v$ - $T$  behavior of gases more accurately over a wider range.



**FIGURE 3-56**

Percentage of error involved in various equations of state for nitrogen (% error =  $[(v_{\text{table}} - v_{\text{equation}})/v_{\text{table}}] \times 100$ ).

# Boiling vs. Evaporation

- We use the terms interchangeably, but they are slightly different.
- Both terms refer to the phase change from liquid to vapor.
- **Evaporation** occurs at a liquid-vapor interface when the vapor pressure is less than the saturation pressure.
  - Evaporation of water from a pool or lake
  - Sweating
- **Boiling** occurs at a solid-liquid interface when the solid surface temperature is higher than  $T_{\text{sat}}$  for the liquid.
  - Boiling water on a stove top
- Note that in boiling there are vapor bubbles; there are no bubbles in evaporation.

# Summary

- Properties of a system
  - Continuum
- State and equilibrium
  - The state postulate
- The ideal gas equation of state
  - Is water vapor an ideal gas?
- Compressibility factor
- Other equations of state
  - van der Waals Equation of State, Beattie-Bridgeman Equation of State
  - Benedict-Webb-Rubin Equation of State, Virial Equation of State
- Vapor Pressure and Humidity
  - Difference of boiling and evaporation