

Thermodynamics: An Engineering Approach  
Seventh Edition in SI Units  
Yunus A. Cengel, Michael A. Boles  
McGraw-Hill, 2011

**Chapter 3**  
**PROPERTIES OF PURE SUBSTANCES**

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**CHAPTER 4 – THERMAL-FLUID SCIENCES TEXTBOOK**

- Properties of Pure Substances

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**Objectives**

- Introduce the concept of a pure substance.
- Discuss the physics of phase-change processes.
- Illustrate the  $P$ - $v$ ,  $T$ - $v$ , and  $P$ - $T$  property diagrams and  $P$ - $v$ - $T$  surfaces of pure substances.
- Demonstrate the procedures for determining thermodynamic properties of pure substances from tables of property data.
- 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.

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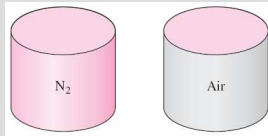
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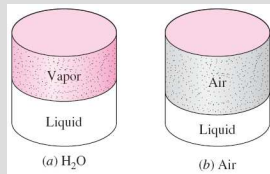
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## PURE SUBSTANCE

- **Pure substance:** A substance that has a fixed chemical composition throughout.
- Air is a mixture of several gases, but it is considered to be a pure substance.

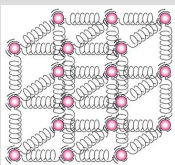


**FIGURE 3-1**  
Nitrogen and gaseous air are pure substances.

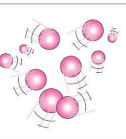
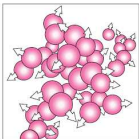
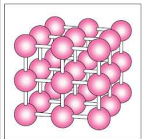


**FIGURE 3-2**  
A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

## PHASES OF A PURE SUBSTANCE



The molecules in a solid are kept at their positions by the large springlike inter-molecular forces.



In a solid, the attractive and repulsive forces between the molecules tend to maintain them at relatively constant distances from each other.

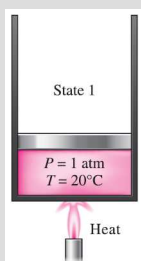
**FIGURE 3-5**

The arrangement of atoms in different phases: (a) molecules are at relatively fixed positions in a solid, (b) groups of molecules move about each other in the liquid phase, and (c) molecules move about at random in the gas phase.

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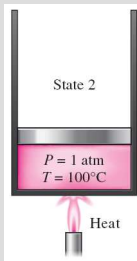
## PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

- **Compressed liquid (subcooled liquid):** A substance that it is *not* about to vaporize.
- **Saturated liquid:** A liquid that is *about* to vaporize.



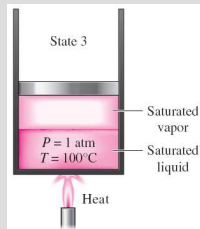
At 1 atm and 20°C, water exists in the liquid phase (**compressed liquid**).

At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (**saturated liquid**).



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- **Saturated vapor:** A vapor that is *about to condense*.
- **Saturated liquid–vapor mixture:** The state at which the *liquid and vapor phases coexist* in equilibrium.
- **Superheated vapor:** A vapor that is *not about to condense* (i.e., not a saturated vapor).



As more heat is transferred, part of the saturated liquid vaporizes (*saturated liquid–vapor mixture*).



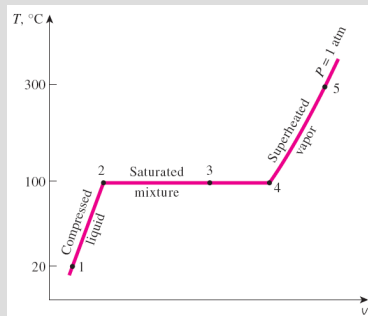
At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (*saturated vapor*).



As more heat is transferred, the temperature of the vapor starts to rise (*superheated vapor*).

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If the entire process between state 1 and 5 described in the figure is reversed by cooling the water while maintaining the pressure at the same value, the water will go back to state 1, retracing the same path, and in so doing, the amount of heat released will exactly match the amount of heat added during the heating process.

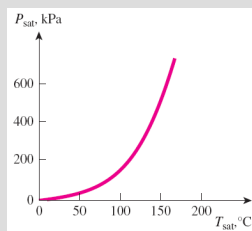


*T-v diagram for the heating process of water at constant pressure.*

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## Saturation Temperature and Saturation Pressure

- The temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.
- Water boils at 100°C at 1 atm pressure.
- **Saturation temperature  $T_{sat}$ :** The temperature at which a pure substance changes phase at a given pressure.
- **Saturation pressure  $P_{sat}$ :** The pressure at which a pure substance changes phase at a given temperature.



*The liquid–vapor saturation curve of a pure substance (numerical values are for water).*

TABLE 3-1

Saturation (boiling) pressure of water at various temperatures

Temperature, $T$ , °C	Saturation pressure, $P_{sat}$ , kPa
-10	0.26
-5	0.40
0	0.61
5	0.87
10	1.23
15	1.71
20	2.34
25	3.17
30	4.25
40	7.39
50	12.35
100	101.4
150	476.2
200	1555
250	3976
300	8588

- **Latent heat:** The amount of energy absorbed or released during a phase-change process.
- **Latent heat of fusion:** The amount of energy absorbed during melting. It is equivalent to the amount of energy released during freezing.
- **Latent heat of vaporization:** The amount of energy absorbed during vaporization and it is equivalent to the energy released during condensation.
- The magnitudes of the latent heats depend on the temperature or pressure at which the phase change occurs.
- At 1 atm pressure, the latent heat of fusion of water is 333.7 kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.
- The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation.

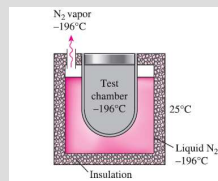
TABLE 3-2

Variation of the standard atmospheric pressure and the boiling (saturation) temperature of water with altitude

Elevation m	Atmospheric pressure, kPa	Boiling tempera- ture, °C
0	101.33	100.0
1,000	89.55	96.5
2,000	79.50	93.3
5,000	54.05	83.3
10,000	26.50	66.3
20,000	5.53	34.7

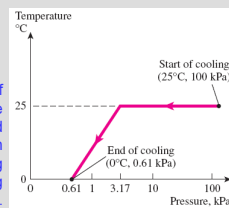
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### Some Consequences of $T_{\text{sat}}$ and $P_{\text{sat}}$ Dependence

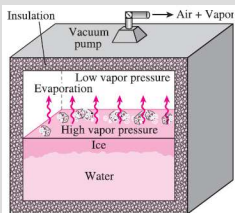


**FIGURE 3-13**  
The temperature of liquid nitrogen exposed to the atmosphere remains constant at  $-196^\circ\text{C}$ , and thus it maintains the test chamber at  $-196^\circ\text{C}$ .

The variation of the temperature of fruits and vegetables with pressure during vacuum cooling from  $25^\circ\text{C}$  to  $0^\circ\text{C}$ .

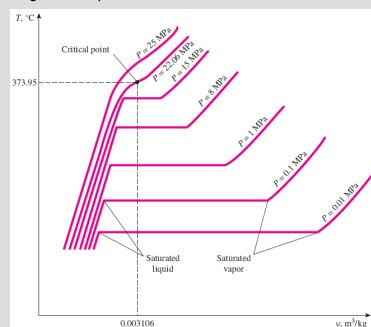


In 1775, ice was made by evacuating the air space in a water tank.



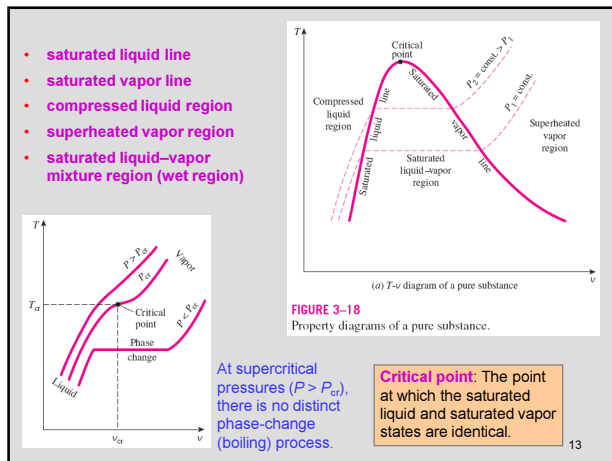
### PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

The variations of properties during phase-change processes are best studied and understood with the help of property diagrams such as the  $T$ - $v$ ,  $P$ - $v$ , and  $P$ - $T$  diagrams for pure substances.



$T$ - $v$  diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

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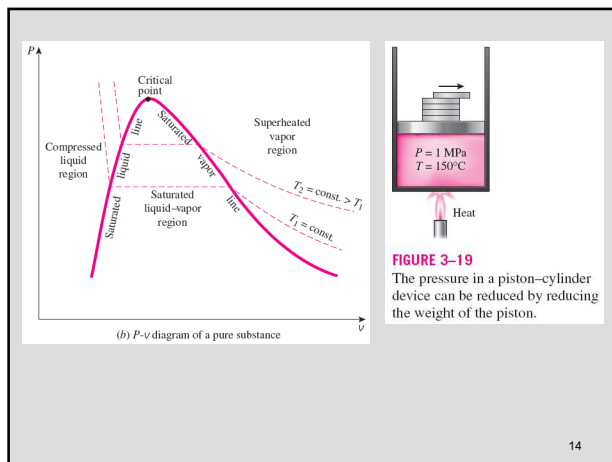
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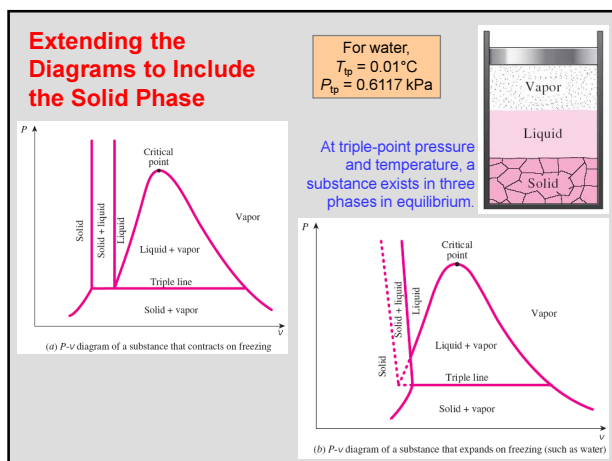
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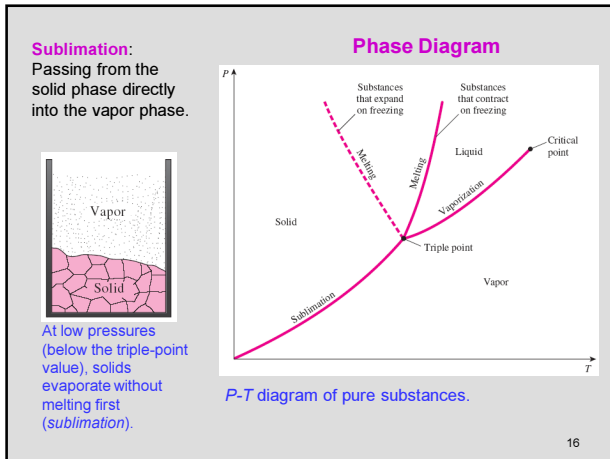
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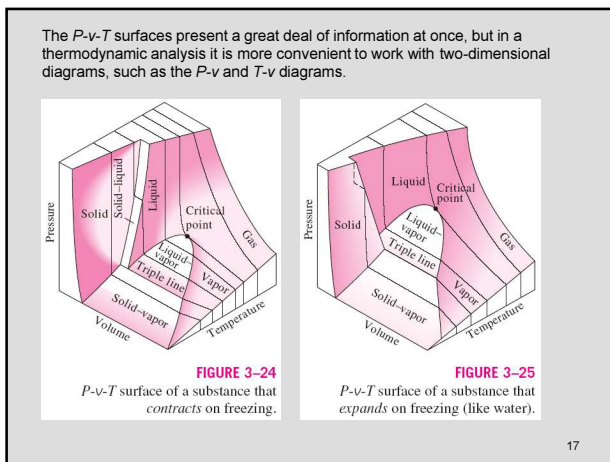
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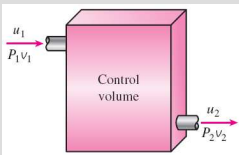
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**PROPERTY TABLES**

- For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations.
- Therefore, properties are frequently presented in the form of tables.
- Some thermodynamic properties can be measured easily, but others cannot and are calculated by using the relations between them and measurable properties.
- The results of these measurements and calculations are presented in tables in a convenient format.

**Enthalpy—A Combination Property**

$$h = u + Pv \quad (\text{kJ/kg})$$

$$H = U + PV \quad (\text{kJ})$$


The combination  $u + Pv$  is frequently encountered in the analysis of control volumes.

The product *pressure × volume* has energy units.

$\text{kPa} \cdot \text{m}^3 = \text{kJ}$   
 $\text{kPa} \cdot \text{m}^3/\text{kg} = \text{kJ/kg}$   
 $\text{bar} \cdot \text{m}^3 = 100 \text{ kJ}$   
 $\text{MPa} \cdot \text{m}^3 = 1000 \text{ kJ}$   
 $\text{psi} \cdot \text{ft}^3 = 0.18505 \text{ Btu}$

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## Saturated Liquid and Saturated Vapor States

- **Table A-4:** Saturation properties of water under temperature.
- **Table A-5:** Saturation properties of water under pressure.

A partial list of Table A-4.

Temp. °C $T$	Sat. press. kPa $P_{\text{sat}}$	Specific volume m <sup>3</sup> /kg	
		Sat. liquid $v_f$	Sat. vapor $v_g$
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

Specific temperature

Corresponding saturation pressure

Specific volume of saturated liquid

Specific volume of saturated vapor

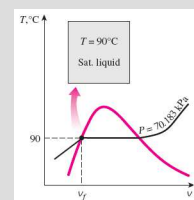
$v_f$  = specific volume of saturated liquid

$v_g$  = specific volume of saturated vapor

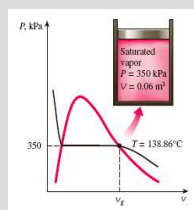
$v_{fg}$  = difference between  $v_g$  and  $v_f$  (that is,  $v_{fg} = v_g - v_f$ )

**Enthalpy of vaporization,  $h_{fg}$  (Latent heat of vaporization):** The amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure.

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**Examples:** Saturated liquid and saturated vapor states of water on T-v and P-v diagrams.



[Example 3-1](#)

[Example 3-2](#)

[Example 3-3](#)

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## Saturated Liquid–Vapor Mixture

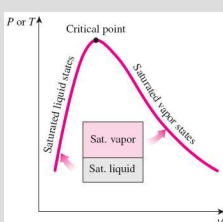
**Quality,  $x$ :** The ratio of the mass of vapor to the total mass of the mixture.

**Quality is between 0 and 1  $\rightarrow$  0: sat. liquid, 1: sat. vapor.**

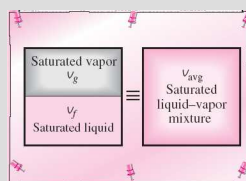
The properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapor.

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}} \quad m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$

Temperature and pressure are dependent properties for a mixture.

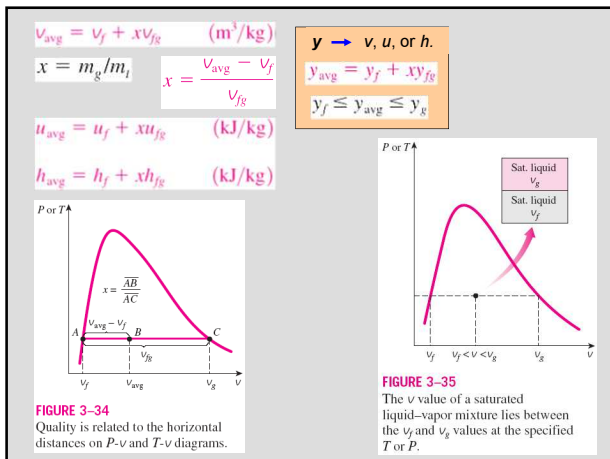


The relative amounts of liquid and vapor phases in a saturated mixture are specified by the **quality  $x$** .



A two-phase system can be treated as a homogeneous mixture for convenience.

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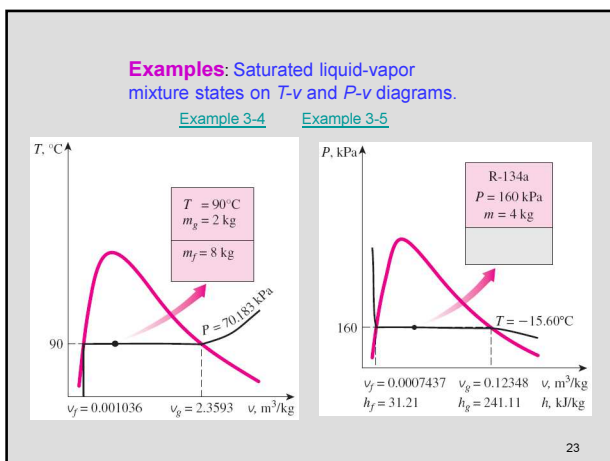
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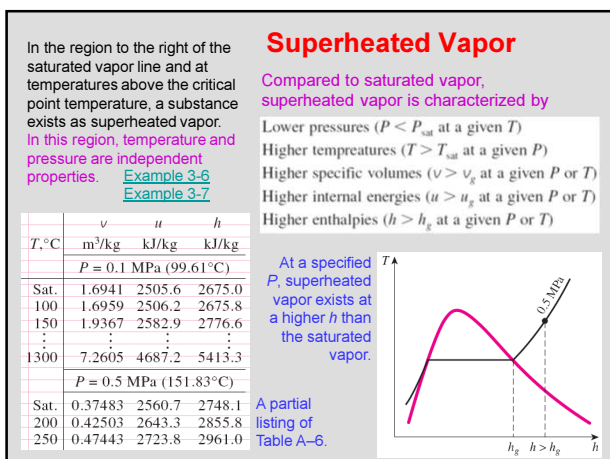
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The compressed liquid properties depend on temperature much more strongly than they do on pressure.

$$y \cong y_f @ T \quad y \rightarrow v, u, \text{ or } h$$

A more accurate relation for  $h$

$$h \cong h_f @ T + v_f @ T (P - P_{\text{sat}} @ T)$$

Given:  $P$  and  $T$

$$v \cong v_f @ T$$

$$u \cong u_f @ T$$

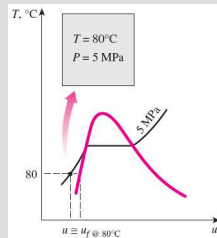
$$h \cong h_f @ T$$

A compressed liquid may be approximated as a saturated liquid at the given temperature.

## Compressed Liquid

Compressed liquid is characterized by

- Higher pressures ( $P > P_{\text{sat}}$  at a given  $T$ )
- Lower temperatures ( $T < T_{\text{sat}}$  at a given  $P$ )
- Lower specific volumes ( $v < v_f$  at a given  $P$  or  $T$ )
- Lower internal energies ( $u < u_f$  at a given  $P$  or  $T$ )
- Lower enthalpies ( $h < h_f$  at a given  $P$  or  $T$ )



Example 3-8

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## Reference State and Reference Values

- The values of  $u$ ,  $h$ , and  $s$  cannot be measured directly, and they are calculated from measurable properties using the relations between properties.
- However, those relations give the *changes* in properties, not the values of properties at specified states.
- Therefore, we need to choose a convenient *reference state* and assign a value of *zero* for a convenient property or properties at that state.
- The reference state for water is  $0.01^\circ\text{C}$  and for R-134a is  $-40^\circ\text{C}$  in tables.
- Some properties may have negative values as a result of the reference state chosen.
- Sometimes different tables list different values for some properties at the same state as a result of using a different reference state.
- However, in thermodynamics we are concerned with the *changes* in properties, and the reference state chosen is of no consequence in calculations.

Example 3-9

Saturated water—Temperature table

Temp., $T$ , $^\circ\text{C}$	Specific volume, $\text{m}^3/\text{kg}$		Internal energy, $\text{kJ/kg}$				Enthalpy, $\text{kJ/kg}$				Entropy, $\text{kJ/kg} \cdot \text{K}$	
	Sat. liquid, $v_f$	Sat. vapor, $v_g$	Sat. liquid, $u_f$	Evap., $u_{fg}$	Sat. vapor, $u_g$	Sat. liquid, $h_f$	Evap., $h_{fg}$	Sat. vapor, $h_g$	Sat. liquid, $s_f$	Evap., $s_{fg}$	Sat. vapor, $s_g$	
0.01	0.001000	206.00	0.000	2374.9	2374.9	0.001	2500.9	2500.9	0.0000	9.1556	9.1556	
5	0.001000	147.03	21.019	2360.8	2381.8	21.020	2489.1	2510.1	0.0763	8.9487	9.0249	

Saturated refrigerant-134a—Temperature table

Temp., $T$ , $^\circ\text{C}$	Specific volume, $\text{m}^3/\text{kg}$		Internal energy, $\text{kJ/kg}$				Enthalpy, $\text{kJ/kg}$				Entropy, $\text{kJ/kg} \cdot \text{K}$	
	Sat. liquid, $v_f$	Sat. vapor, $v_g$	Sat. liquid, $u_f$	Evap., $u_{fg}$	Sat. vapor, $u_g$	Sat. liquid, $h_f$	Evap., $h_{fg}$	Sat. vapor, $h_g$	Sat. liquid, $s_f$	Evap., $s_{fg}$	Sat. vapor, $s_g$	
-40	51.25	0.0007054	0.36081	-0.036	207.40	207.37	0.000	225.86	225.86	0.00000	0.96866	0.96866

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## 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.

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

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

$R$ : gas constant

$M$ : molar mass ( $\text{kg/kmol}$ )

$R_u$ : 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	$R$ , $\text{kJ/kg} \cdot \text{K}$
Air	0.2870
Helium	2.0769
Argon	0.2081
Nitrogen	0.2968

Different substances have different gas constants.

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Mass = Molar mass  $\times$  Mole number  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$  Ideal gas equation at two states for a fixed mass

$m = MN$  (kg)

$V = m\bar{v} \rightarrow P\bar{v} = mRT$

$mR = (MN)R = NR_u \rightarrow P\bar{v} = NR_u T$

$V = N\bar{v} \rightarrow P\bar{v} = R_u T$

Various expressions of ideal gas equation

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

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

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

Example 3-10

FIGURE 3-45 The ideal-gas relation often is not applicable to real gases; thus, care should be exercised when using it.

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### Is Water Vapor an Ideal Gas?

Percentage of error ( $|(v_{\text{table}} - v_{\text{ideal}})/v_{\text{table}}| \times 100$ ) 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.

- 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.

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### 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.

$P\bar{v} = ZRT$

$Z = \frac{P\bar{v}}{RT}$   $Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}}$

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 The compressibility factor is unity for ideal gases.

FIGURE 3-50 At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).

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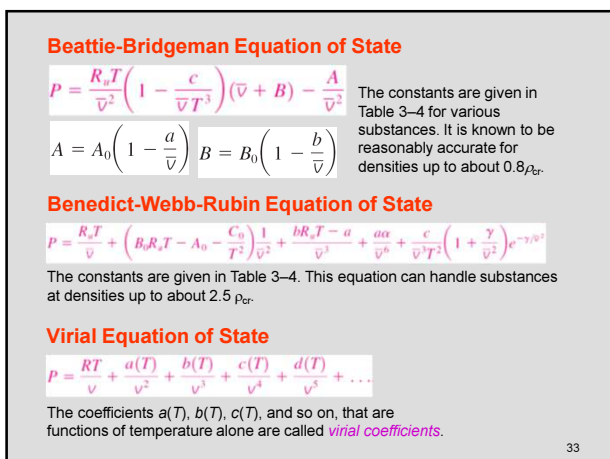
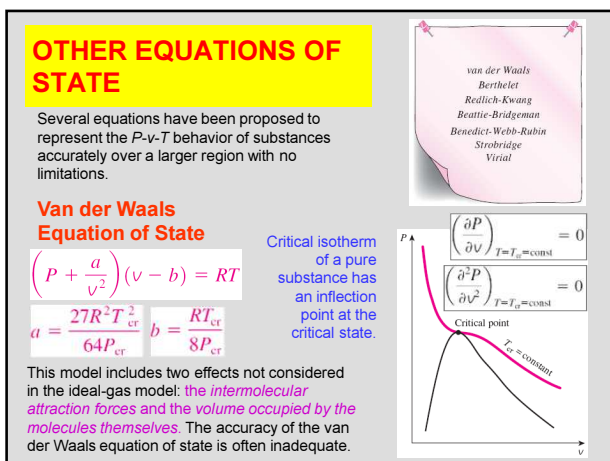
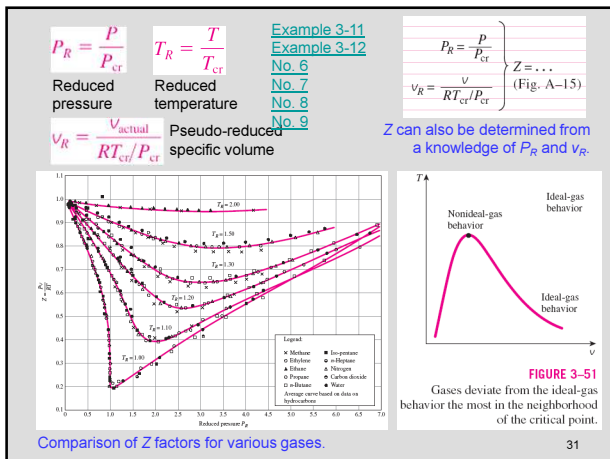


TABLE 3-4

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	$4.80 \times 10^4$

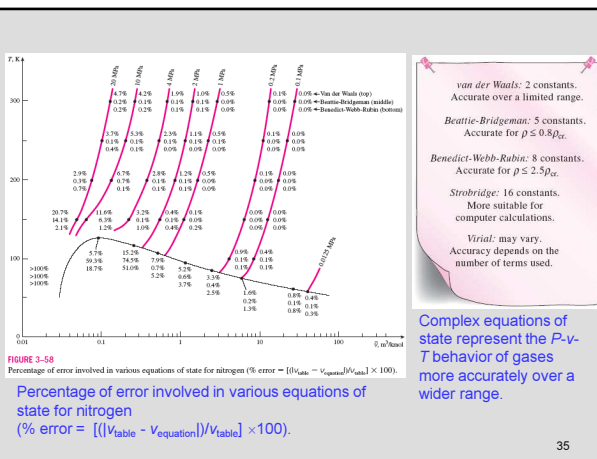
Source: Gordon J. Van Wylen and Richard E. Sonntag, *Fundamentals of Classical Thermodynamics*, English/SI Version, 3rd ed. (New York: John Wiley & Sons, 1986), p. 46, table 3.3.

(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	$1.054 \times 10^6$	$8.673 \times 10^6$	$1.350 \times 10^{-4}$	0.0060
Methane, $\text{CH}_4$	5.00	187.91	0.003380	0.04260	$2.578 \times 10^6$	$2.286 \times 10^6$	$1.244 \times 10^{-4}$	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

Source: Kenneth Wark, *Thermodynamics*, 4th ed. (New York: McGraw-Hill, 1983), p. 815, table A-21M. Originally published in H. W. Cooper and J. C. Goldfrank, *Hydrocarbon Processing* 46, no. 12 (1967), p. 141.

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## Summary

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