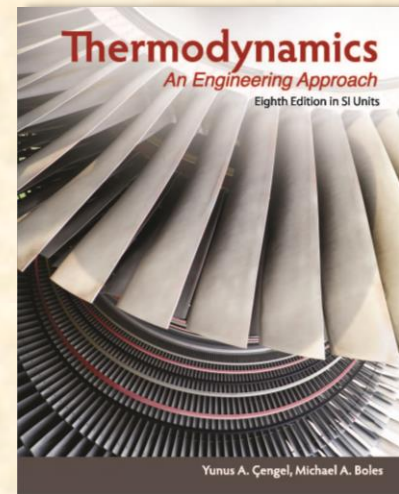


**Thermodynamics: An Engineering Approach**  
8th Edition in SI Units  
Yunus A. Çengel, Michael A. Boles  
McGraw-Hill, 2015



**CHAPTER 3**  
**PROPERTIES OF PURE**  
**SUBSTANCES**

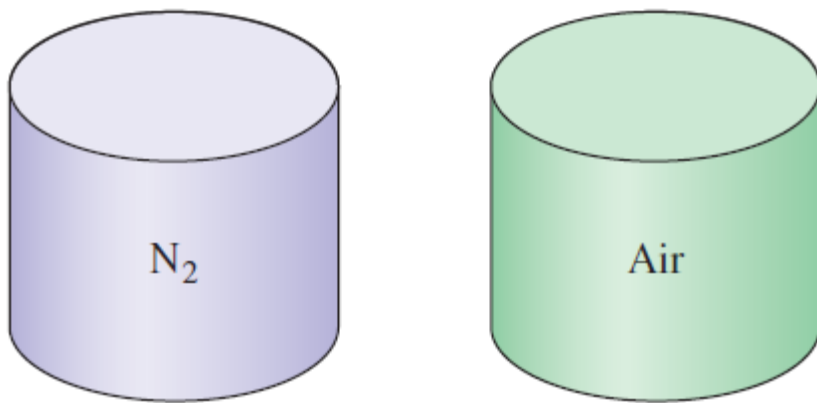
Lecture slides by  
**Mehmet Kanoglu**

# 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.

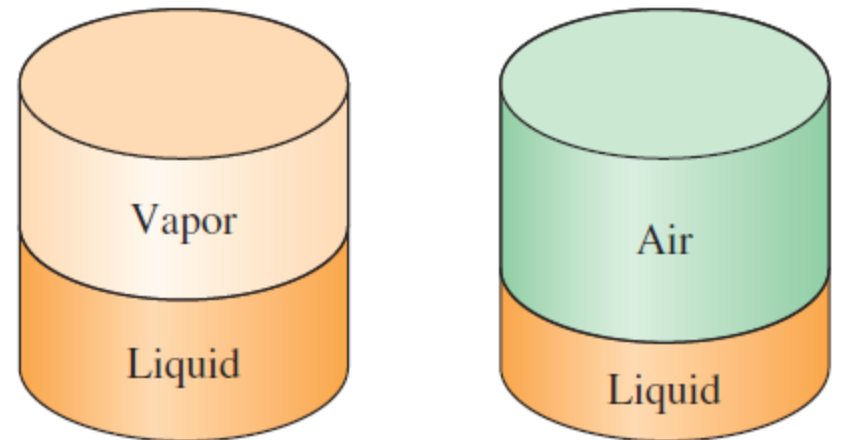
# PURE SUBSTANCE

- **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.



(a)  $H_2O$

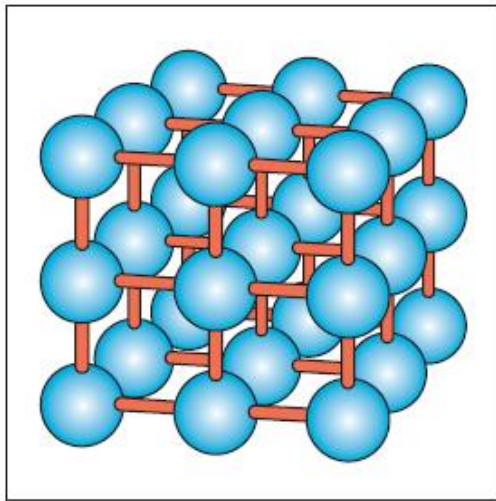
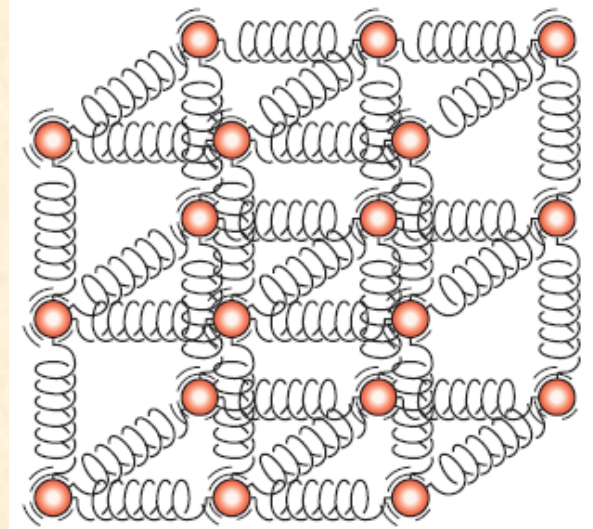
(b) Air

**FIGURE 3–2**

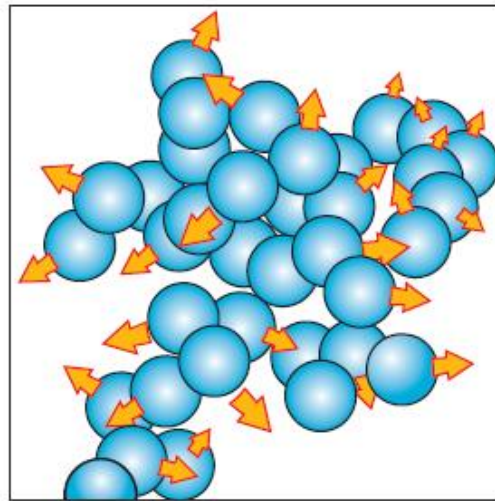
A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

# PHASES OF A PURE SUBSTANCE

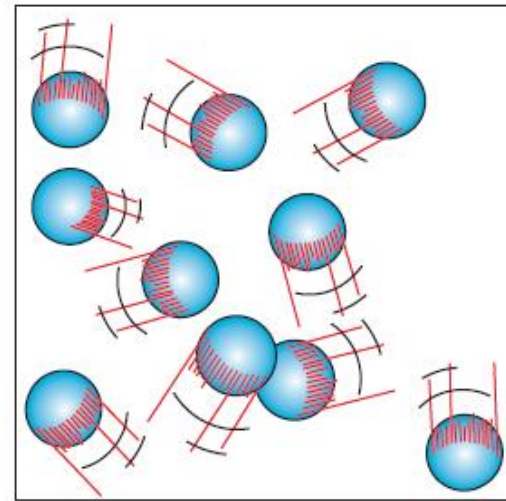
The molecules in a solid are kept at their positions by the large springlike inter-molecular forces.



(a)



(b)



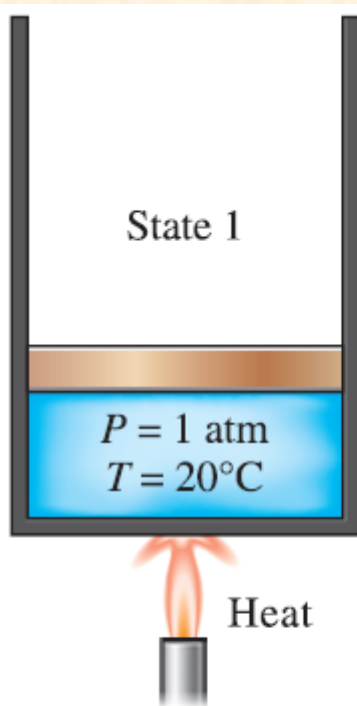
(c)

**FIGURE 3-4**

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.

# PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

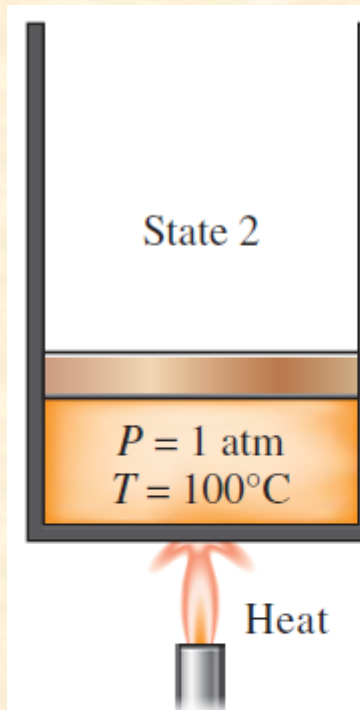
**Compressed liquid (subcooled liquid):** A substance that it is *not about to vaporize*



**FIGURE 3–5**

At 1 atm and  $20^\circ\text{C}$ , water exists in the liquid phase (*compressed liquid*).

**Saturated liquid:** A liquid that is *about to vaporize*

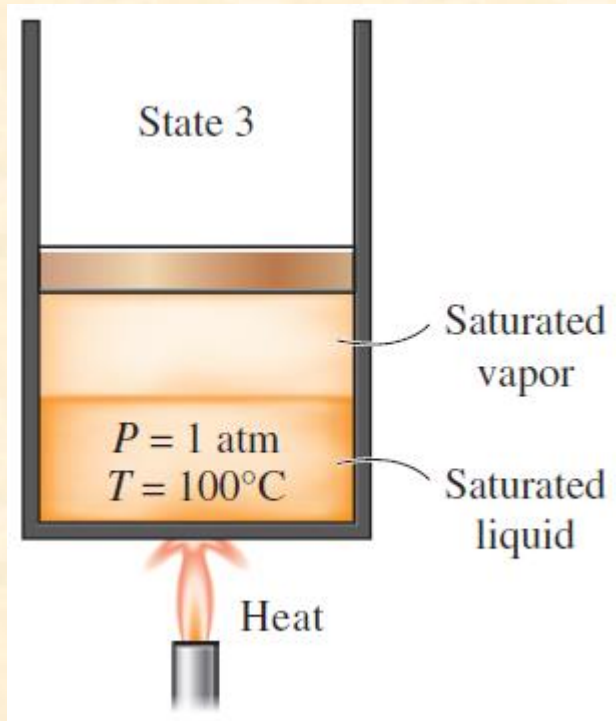


**FIGURE 3–6**

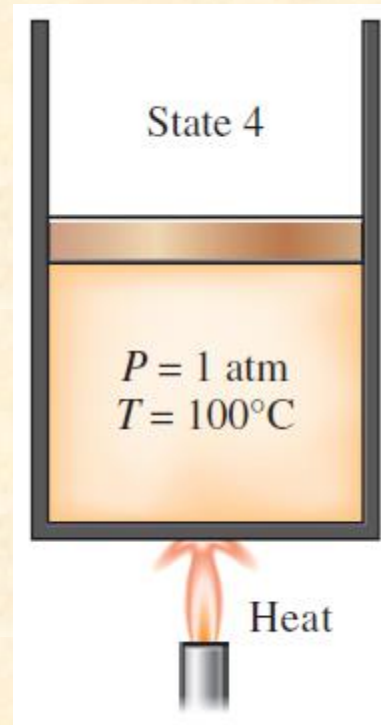
At 1 atm pressure and  $100^\circ\text{C}$ , water exists as a liquid that is ready to vaporize (*saturated liquid*).



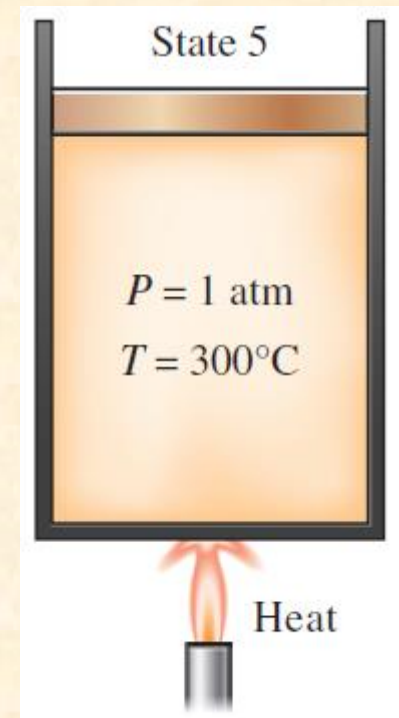
- **Saturated vapor:** A vapor that is *about to condense*.
- **Saturated liquid–vapor mixture:** The state at which the *liquid and vapor phases coexist* in equilibrium.
- **Superheated vapor:** A vapor that is *not about to condense* (i.e., not a saturated vapor).



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

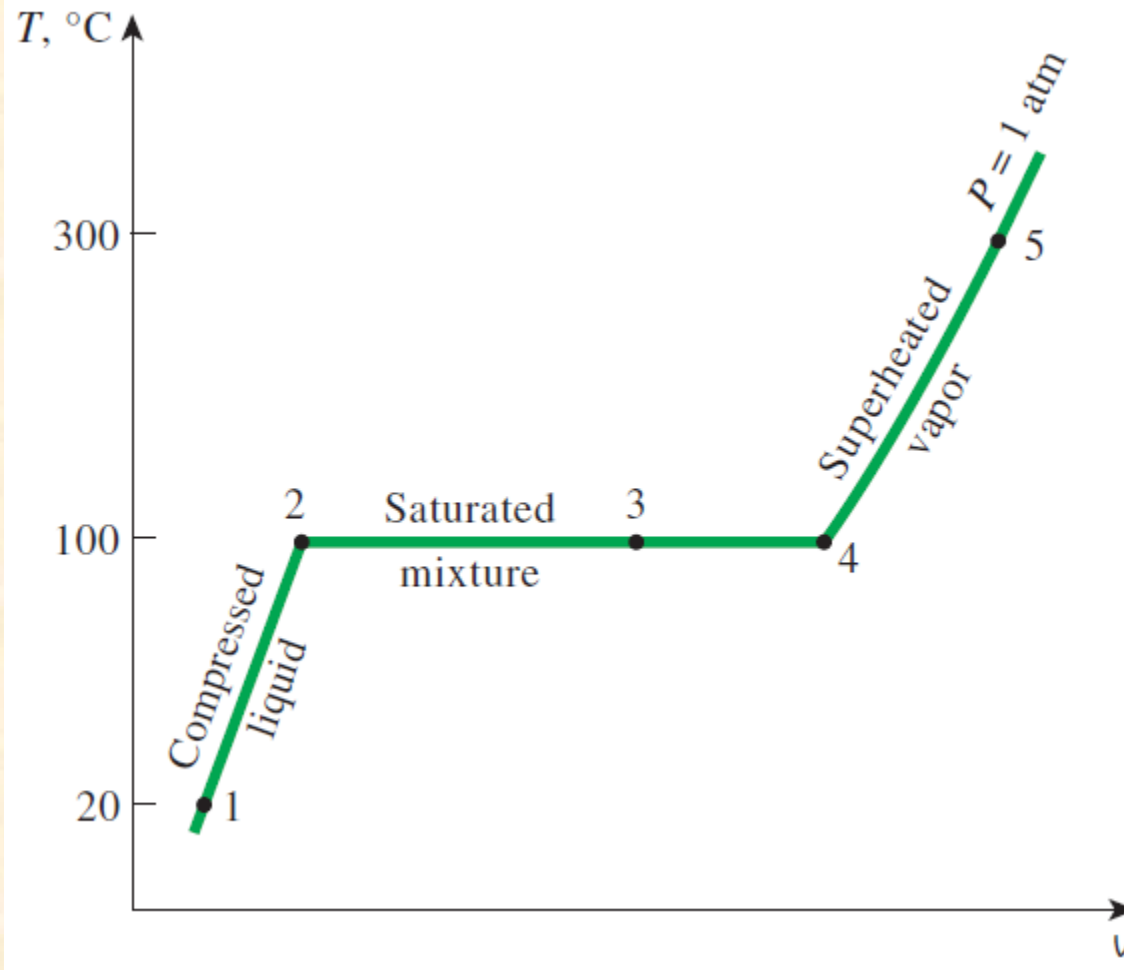


At 1 atm pressure, the temperature remains constant at  $100^\circ\text{C}$  until the last drop of liquid is vaporized (**saturated vapor**).



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

If the entire process between state 1 and 5 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.*

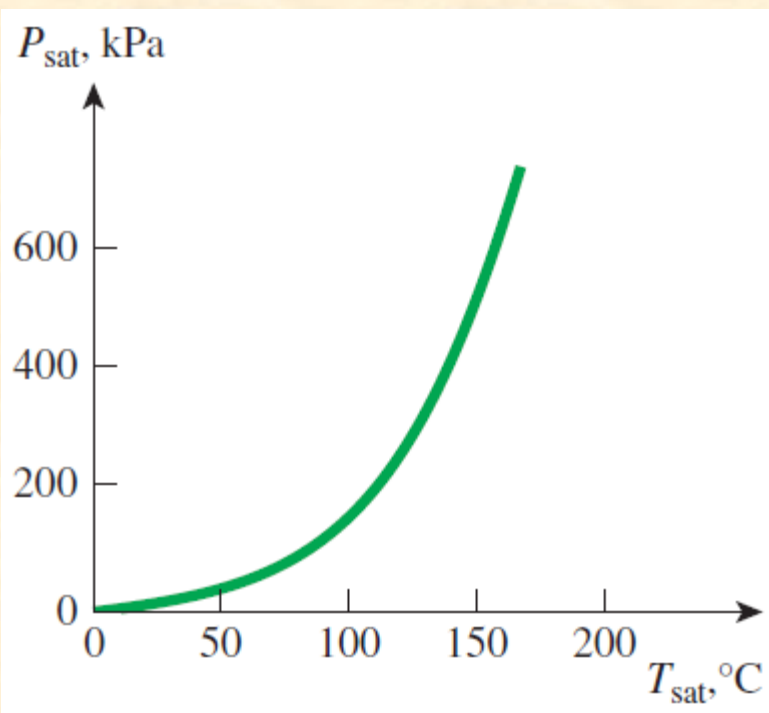
# Saturation Temperature and Saturation Pressure

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  $T_{\text{sat}}$ :** The temperature at which a pure substance changes phase at a given pressure.

**Saturation pressure  $P_{\text{sat}}$ :** 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 (or vapor) pressure of water at various temperatures

Temperature $T$ , °C	Saturation Pressure $P_{\text{sat}}$ , kPa
–10	0.260
–5	0.403
0	0.611
5	0.872
10	1.23
15	1.71
20	2.34
25	3.17
30	4.25
40	7.38
50	12.35
100	101.3 (1 atm)
150	475.8
200	1554
250	3973
300	8581



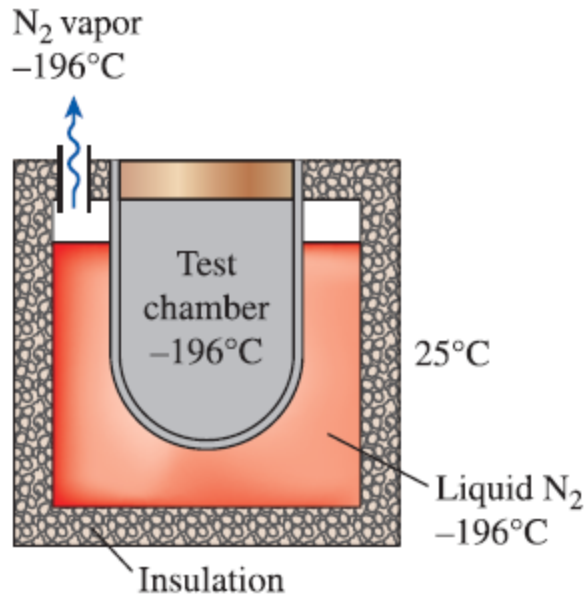
- **Latent heat:** The amount of energy absorbed or released during a phase-change process.
- **Latent heat of fusion:** The amount of energy absorbed during melting. It is equivalent to the amount of energy released during freezing.
- **Latent heat of vaporization:** The amount of energy absorbed during 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

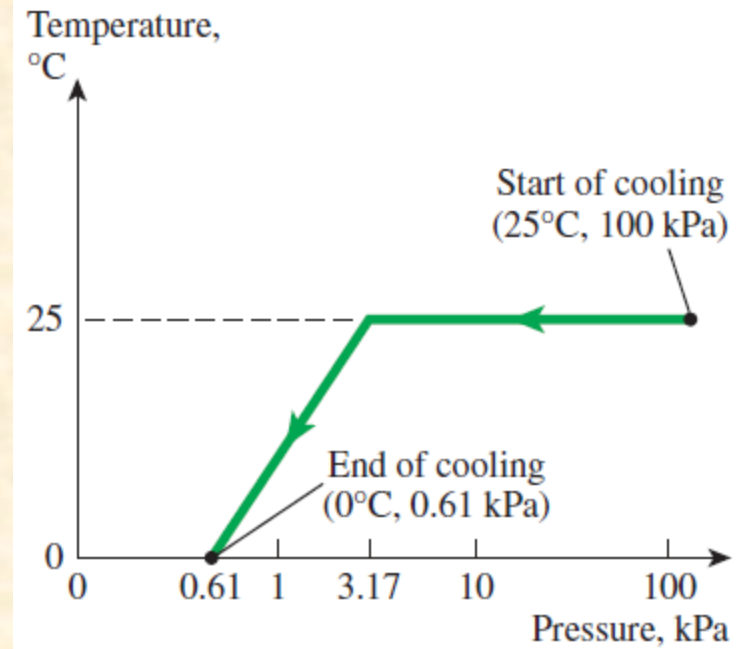
# Some Consequences of $T_{\text{sat}}$ and $P_{\text{sat}}$ Dependence



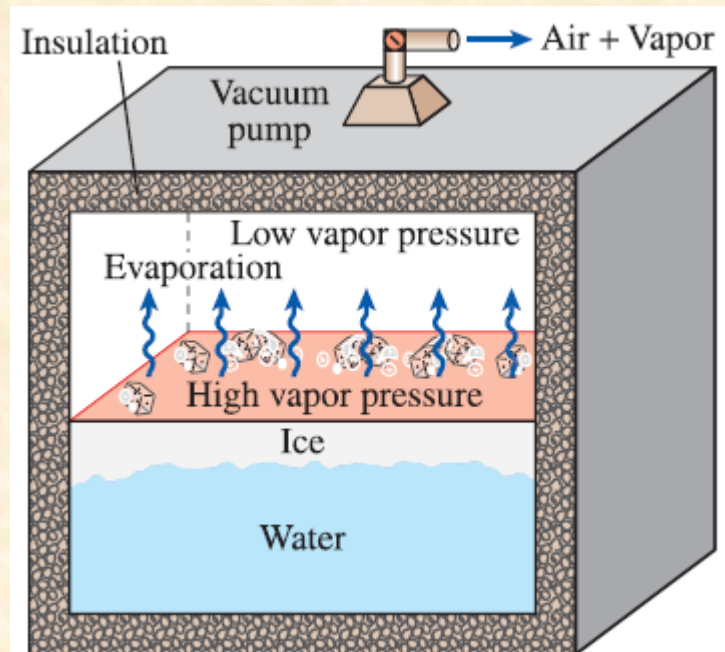
**FIGURE 3-12**

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  $0^{\circ}\text{C}$ .

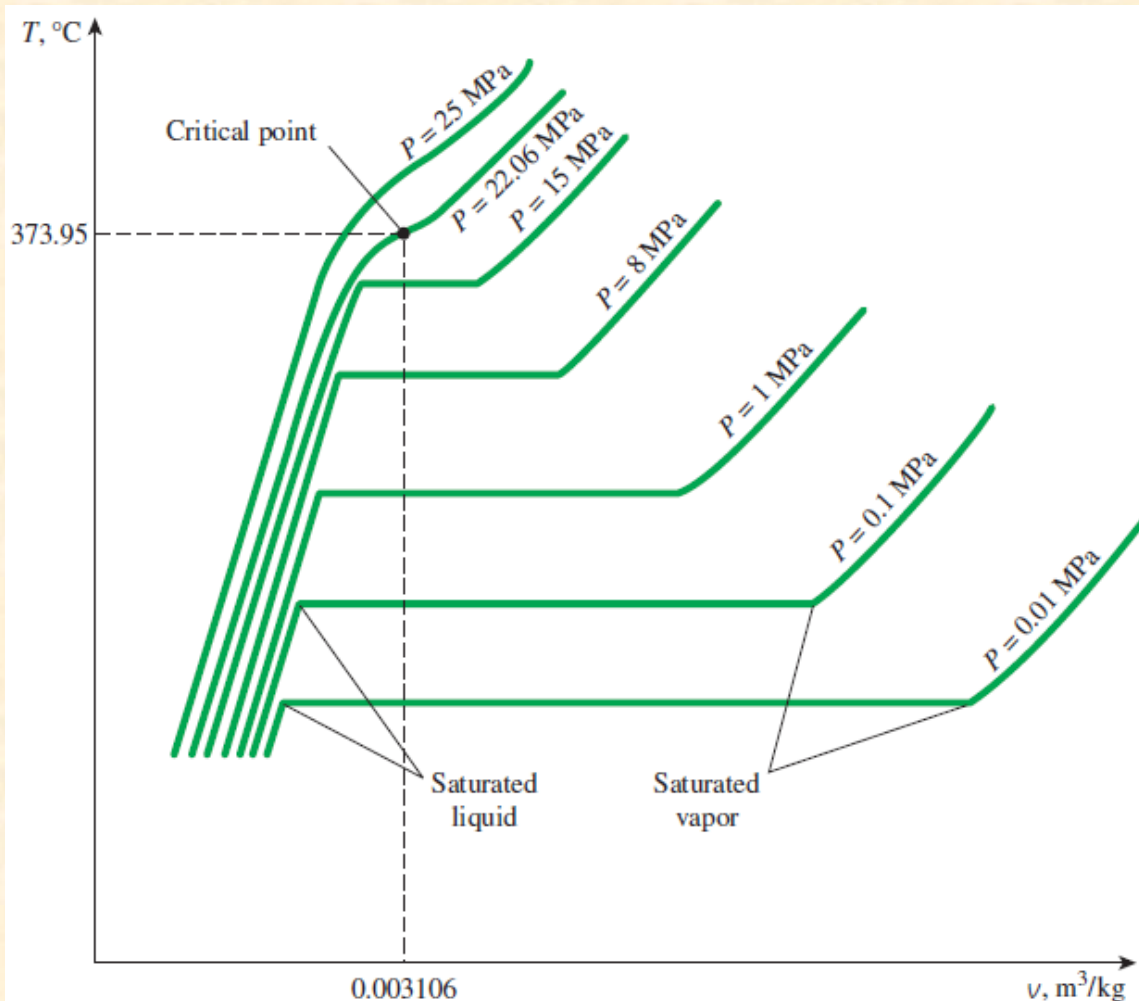


In 1775, ice was made by evacuating the air space in a water tank.



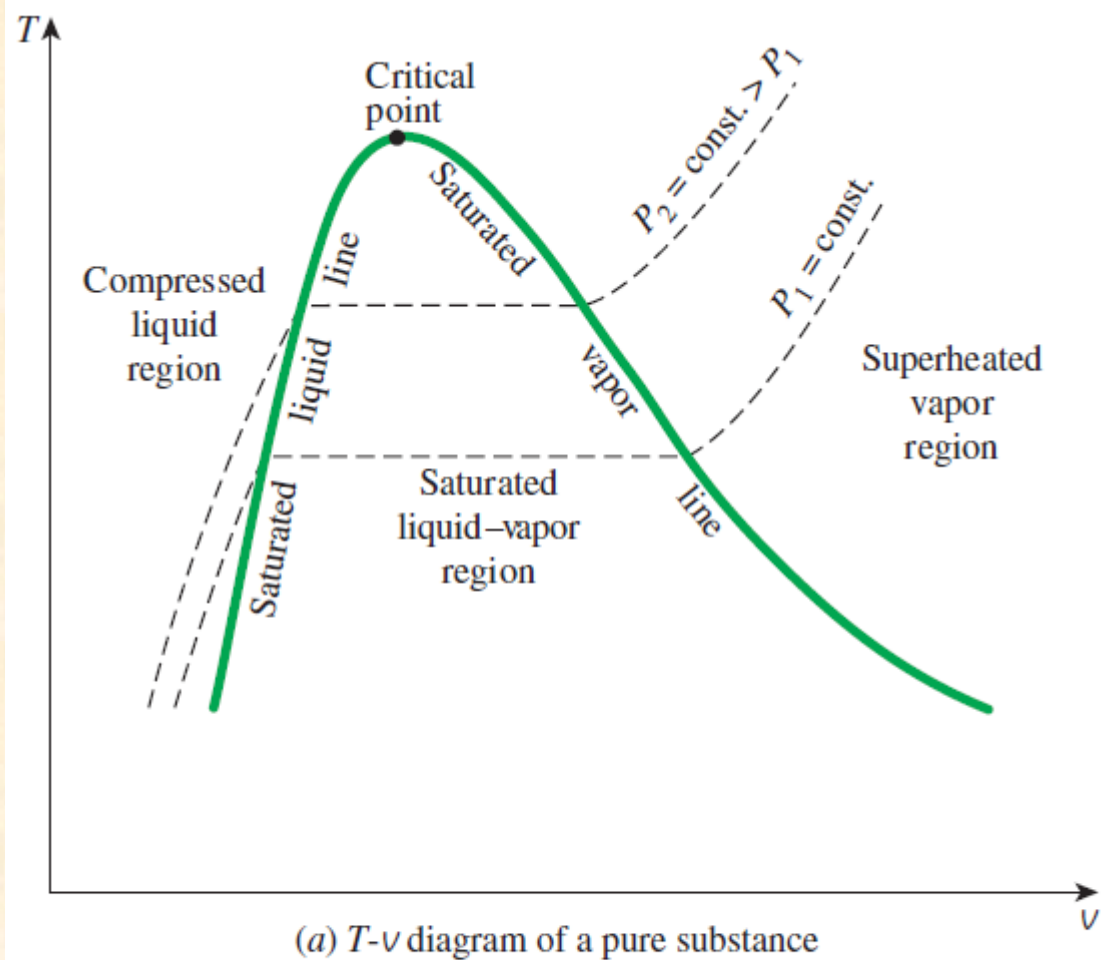
# PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

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.



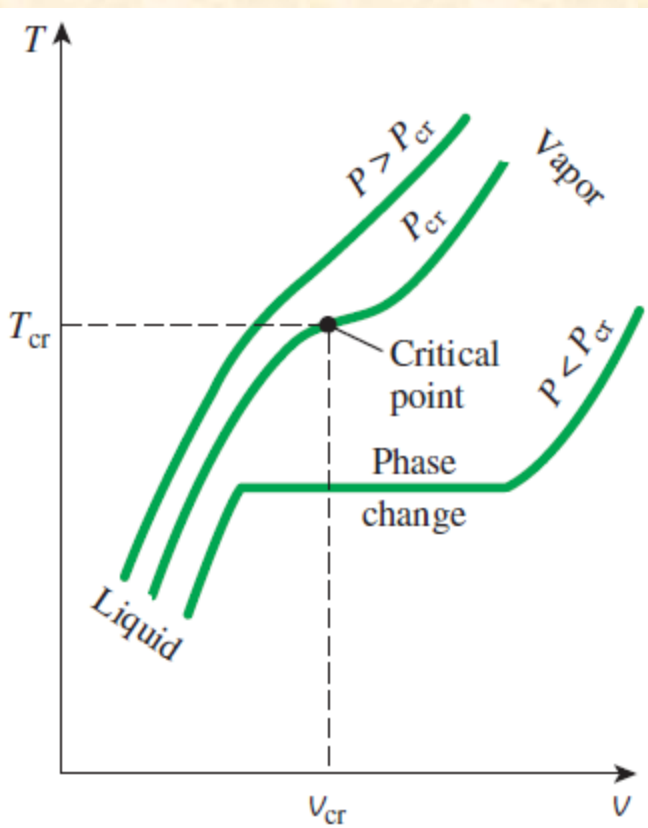
$T$ - $v$  diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

- saturated liquid line
- saturated vapor line
- compressed liquid region
- superheated vapor region
- saturated liquid–vapor mixture region (wet region)



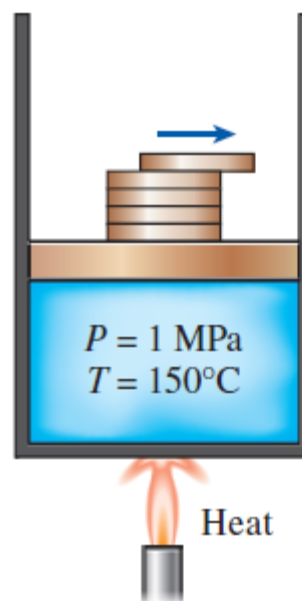
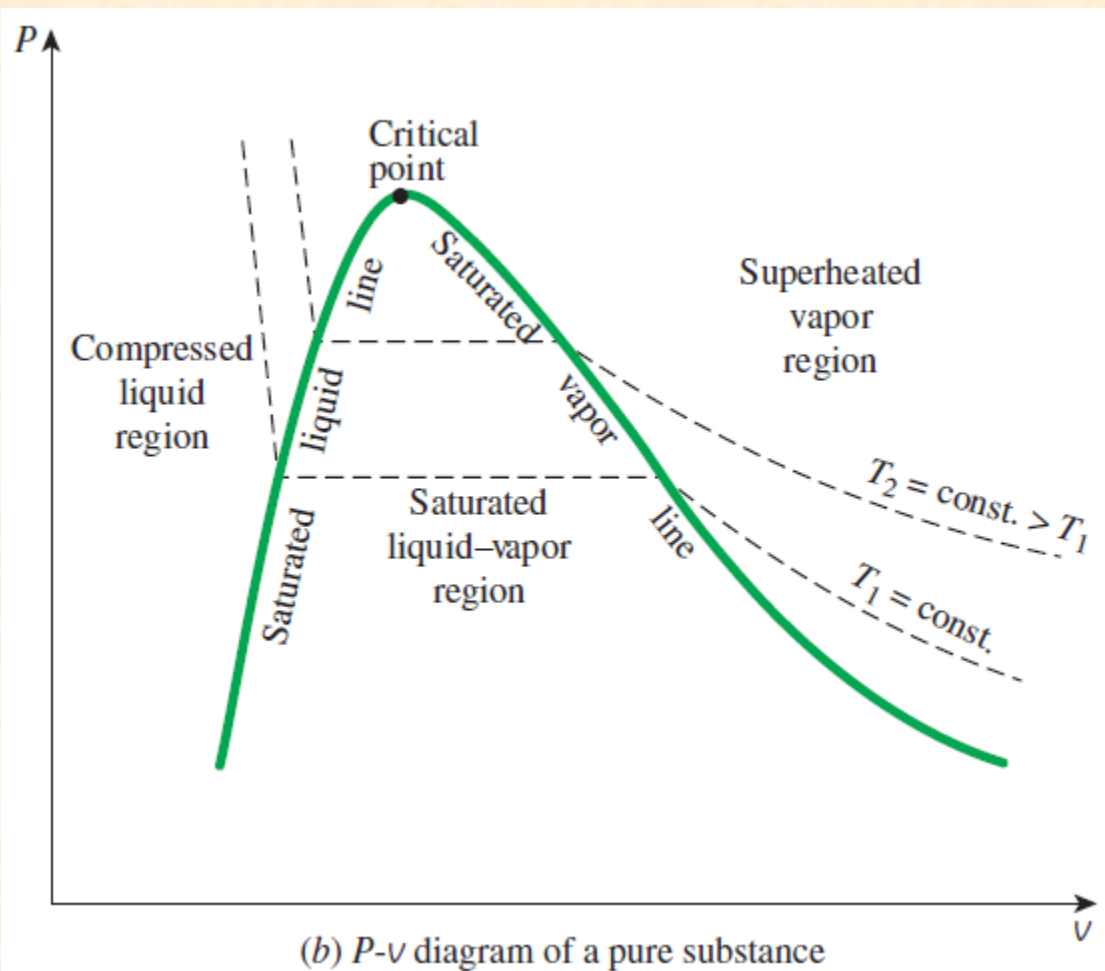
**FIGURE 3–17**

Property diagrams of a pure substance.



At supercritical pressures ( $P > P_{cr}$ ), there is no distinct phase-change (boiling) process.

**Critical point:** The point at which the saturated liquid and saturated vapor states are identical.



**FIGURE 3-18**

The pressure in a piston-cylinder device can be reduced by reducing the weight of the piston.

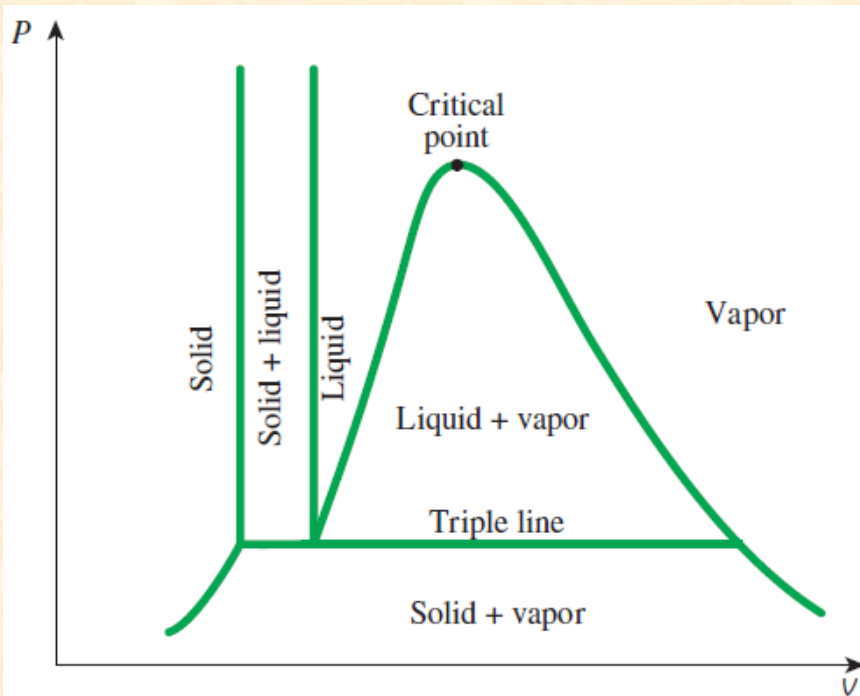


# Extending the Diagrams to Include the Solid Phase

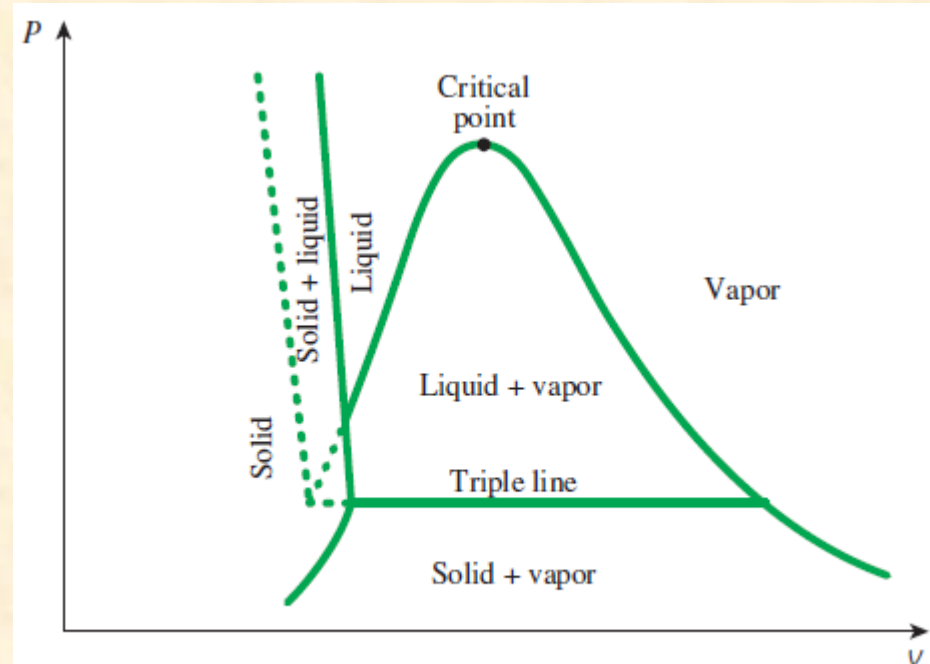
For water,  
 $T_{\text{tp}} = 0.01^{\circ}\text{C}$   
 $P_{\text{tp}} = 0.6117 \text{ kPa}$



At triple-point pressure and temperature, a substance exists in three phases in equilibrium.



(a)  $P$ - $v$  diagram of a substance that contracts on freezing



(b)  $P$ - $v$  diagram of a substance that expands on freezing (such as water)

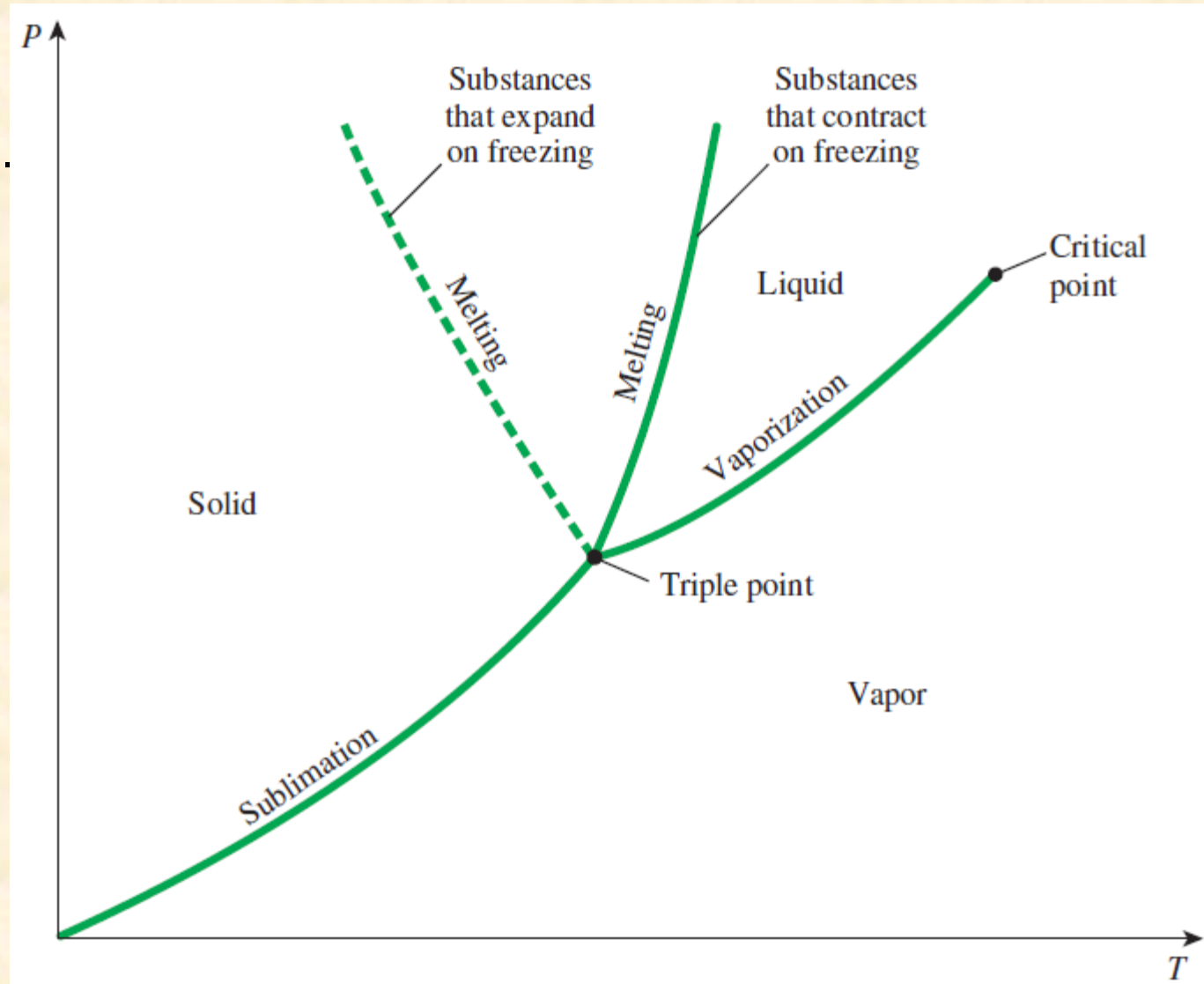
# Phase Diagram

## Sublimation:

Passing from the solid phase directly into the vapor phase.

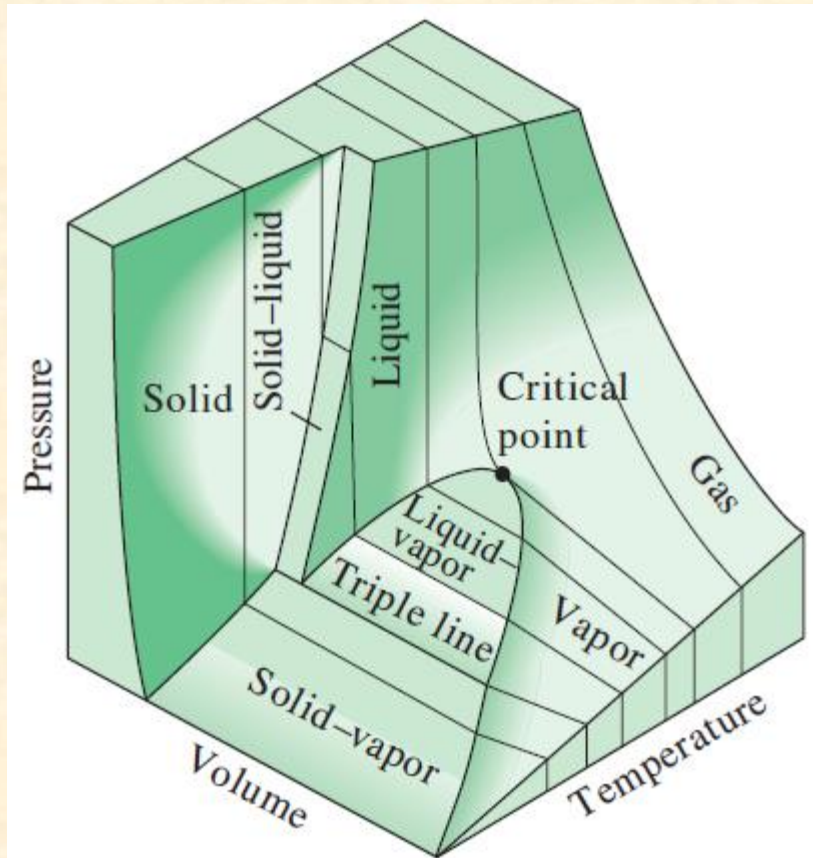


At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).



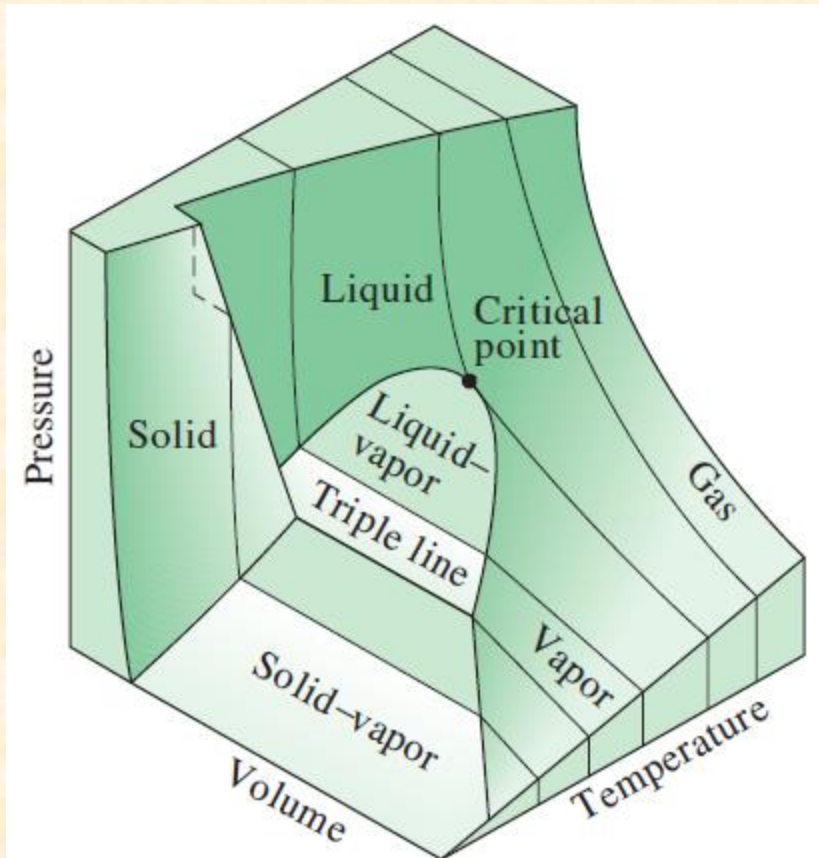
*P-T* diagram of pure substances.

The  $P$ - $v$ - $T$  surfaces present a great deal of information at once, but in a thermodynamic analysis it is more convenient to work with two-dimensional diagrams, such as the  $P$ - $v$  and  $T$ - $v$  diagrams.



**FIGURE 3-23**

$P$ - $v$ - $T$  surface of a substance that *contracts* on freezing.



**FIGURE 3-24**

$P$ - $v$ - $T$  surface of a substance that *expands* on freezing (like water).

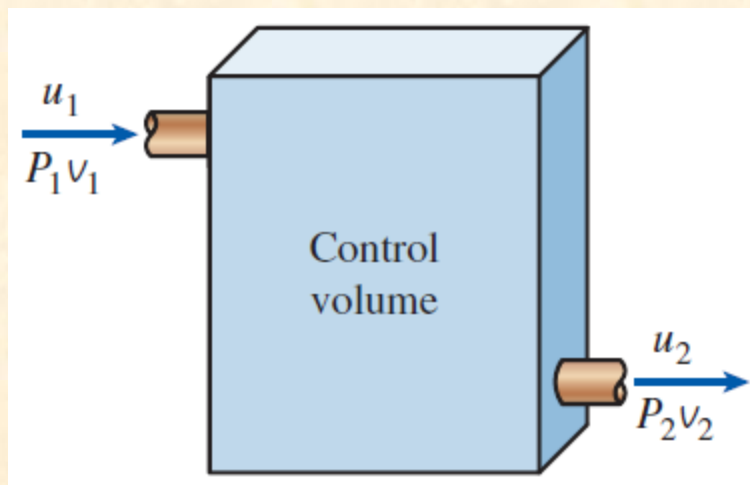
# PROPERTY TABLES

- 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.

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

The product *pressure*  $\times$  *volume* has energy units. 17



# Saturated Liquid and Saturated Vapor States

$v_f$  = specific volume of saturated liquid

$v_g$  = specific volume of saturated vapor

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

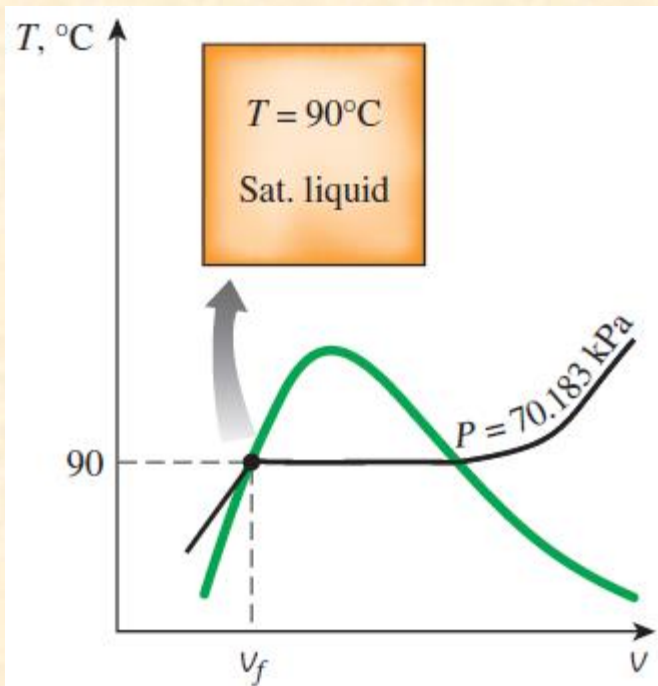
A partial list of Table A–4.

Temp. °C $T$	Sat. press. kPa $P_{sat}$	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

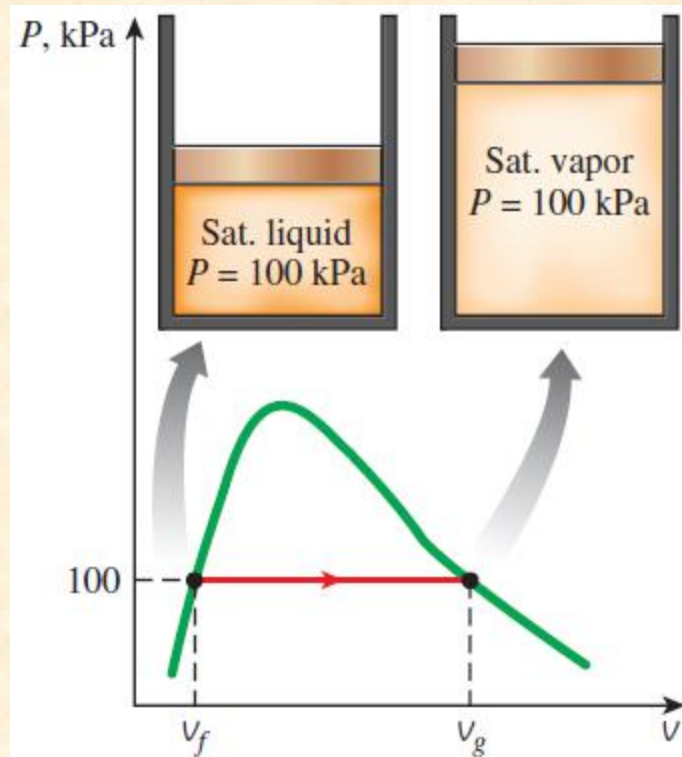
- **Table A–4:** Saturation properties of water under temperature.
- **Table A–5:** Saturation properties of water under pressure.

**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.





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



# Saturated Liquid–Vapor Mixture

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

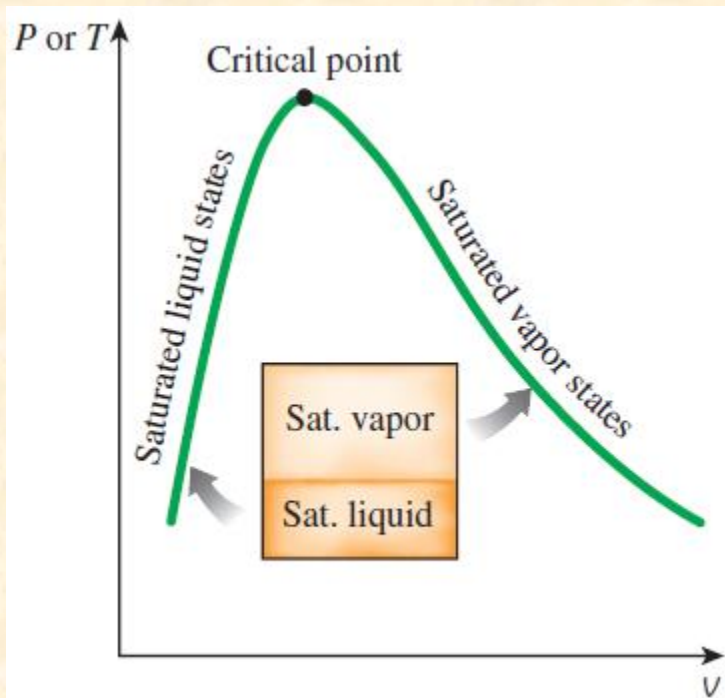
**Quality is between 0 and 1  $\rightarrow$  0: sat. liquid, 1: sat. vapor.**

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

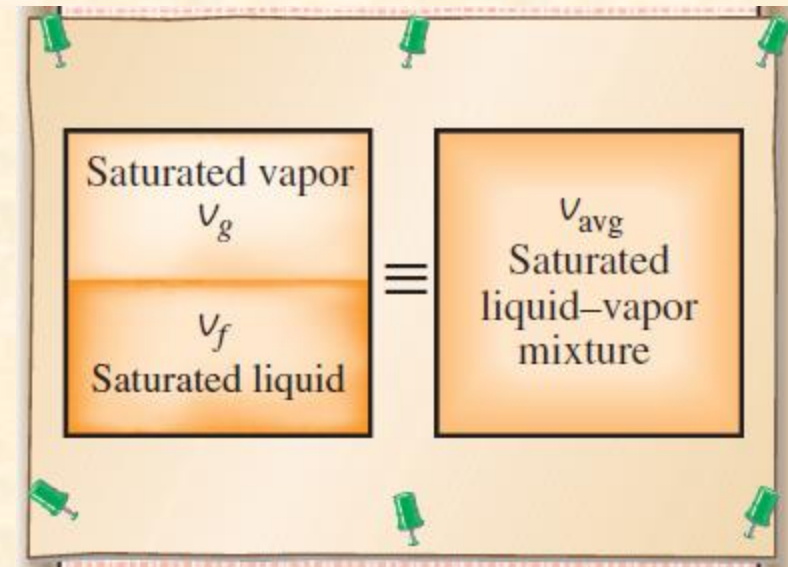
$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}}$$

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

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.

$$v_{\text{avg}} = v_f + x v_{fg} \quad (\text{m}^3/\text{kg})$$

$$x = m_g/m_t \quad x = \frac{v_{\text{avg}} - v_f}{v_{fg}}$$

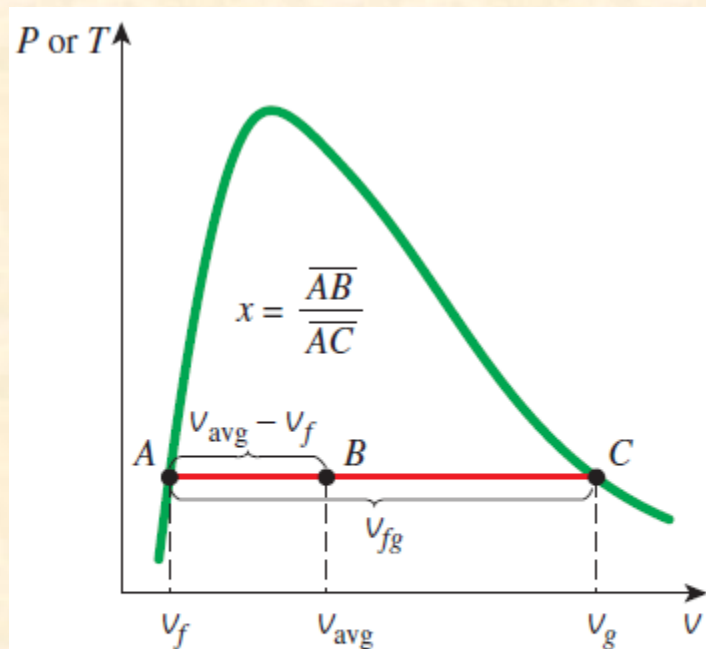
$$u_{\text{avg}} = u_f + x u_{fg} \quad (\text{kJ/kg})$$

$$h_{\text{avg}} = h_f + x h_{fg} \quad (\text{kJ/kg})$$

$y \rightarrow v, u, \text{ or } h.$

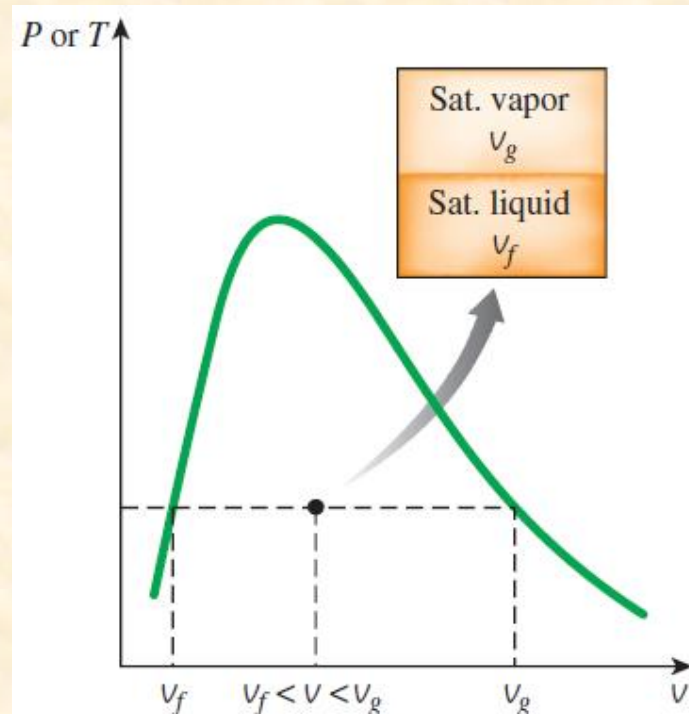
$$y_{\text{avg}} = y_f + x y_{fg}$$

$$y_f \leq y_{\text{avg}} \leq y_g$$



**FIGURE 3–33**

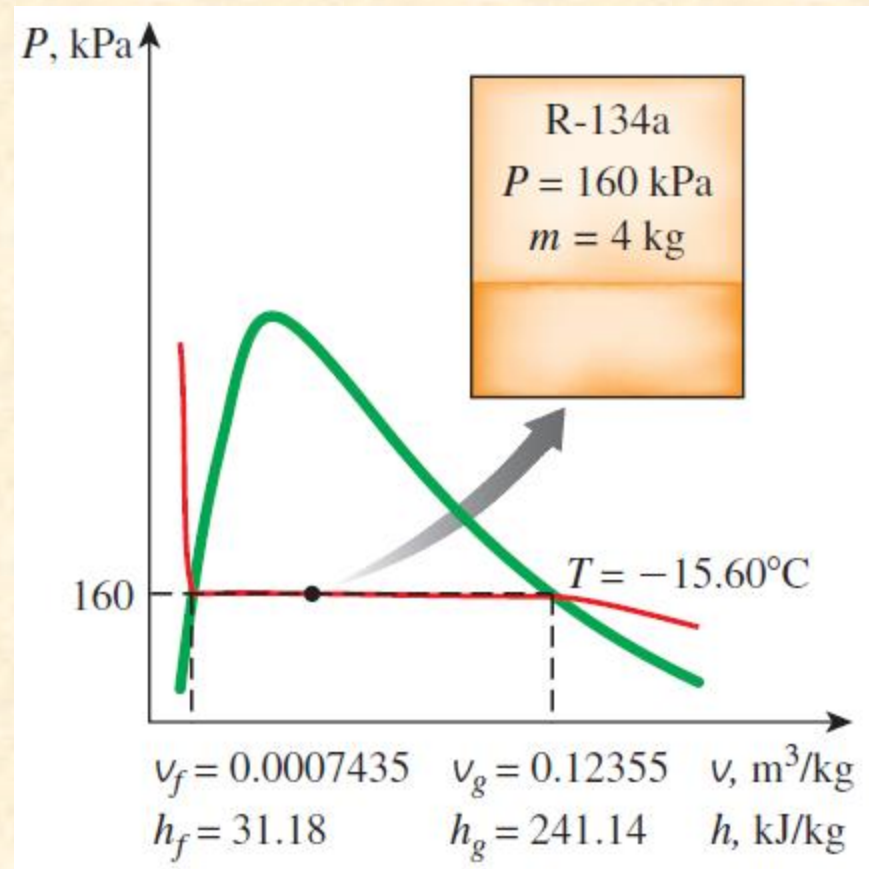
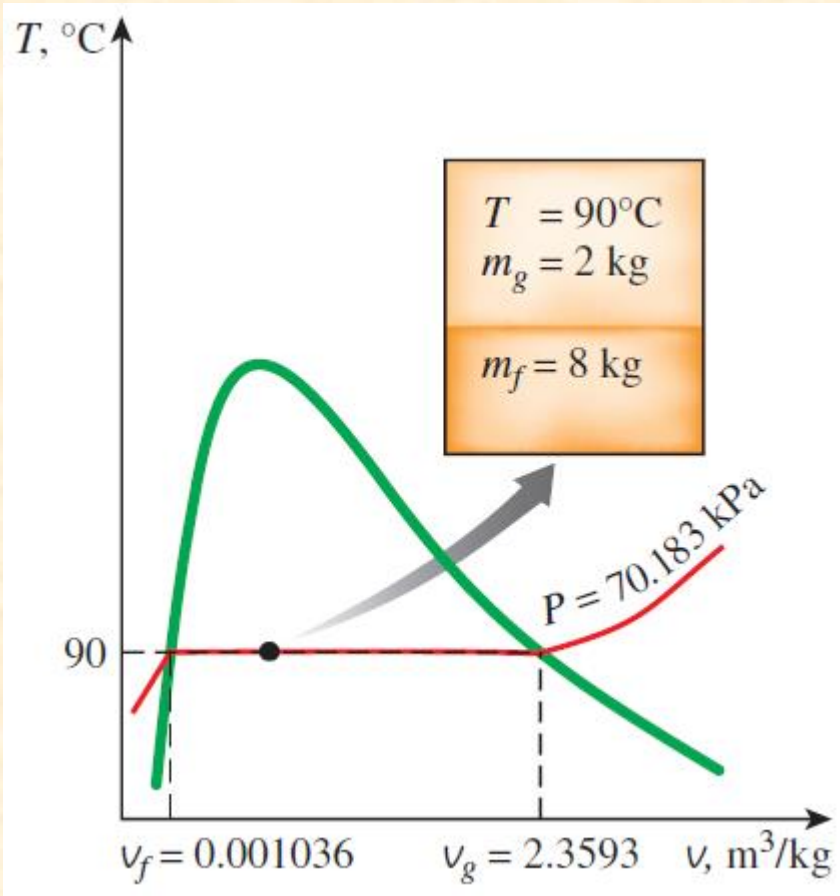
Quality is related to the horizontal distances on  $P$ - $v$  and  $T$ - $v$  diagrams.



**FIGURE 3–34**

The  $v$  value of a saturated liquid–vapor mixture lies between the  $v_f$  and  $v_g$  values at the specified  $T$  or  $P$ .

**Examples:** Saturated liquid-vapor mixture states on  $T$ - $v$  and  $P$ - $v$  diagrams.



In the region to the right of the saturated vapor line and at temperatures above the critical point temperature, a substance exists as superheated vapor.

In this region, temperature and pressure are independent properties.

	$\nu$	$u$	$h$
$T, ^\circ\text{C}$	$\text{m}^3/\text{kg}$	$\text{kJ/kg}$	$\text{kJ/kg}$
$P = 0.1 \text{ MPa} (99.61^\circ\text{C})$			
Sat.	1.6941	2505.6	2675.0
100	1.6959	2506.2	2675.8
150	1.9367	2582.9	2776.6
$\vdots$	$\vdots$	$\vdots$	$\vdots$
1300	7.2605	4687.2	5413.3
$P = 0.5 \text{ MPa} (151.83^\circ\text{C})$			
Sat.	0.37483	2560.7	2748.1
200	0.42503	2643.3	2855.8
250	0.47443	2723.8	2961.0

## Superheated Vapor

Compared to saturated vapor, superheated vapor is characterized by

Lower pressures ( $P < P_{\text{sat}}$  at a given  $T$ )

Higher temperatures ( $T > T_{\text{sat}}$  at a given  $P$ )

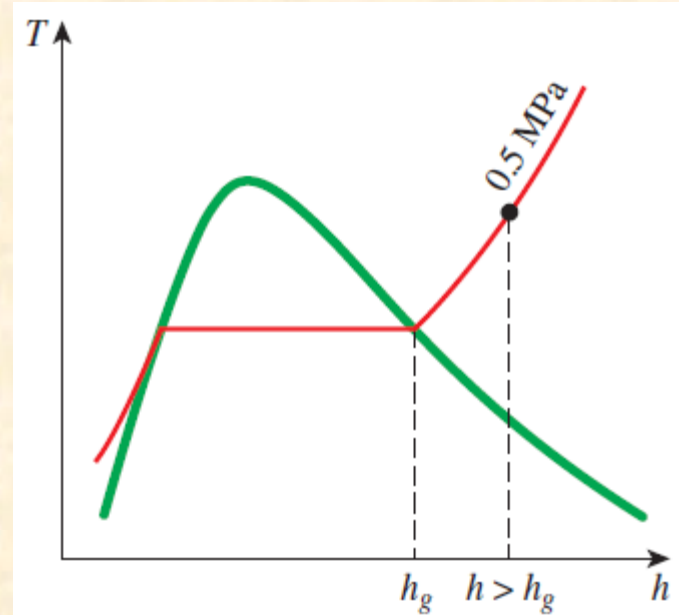
Higher specific volumes ( $\nu > \nu_g$  at a given  $P$  or  $T$ )

Higher internal energies ( $u > u_g$  at a given  $P$  or  $T$ )

Higher enthalpies ( $h > h_g$  at a given  $P$  or  $T$ )

At a specified  $P$ , superheated vapor exists at a higher  $h$  than the saturated vapor.

A partial listing of Table A–6.





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

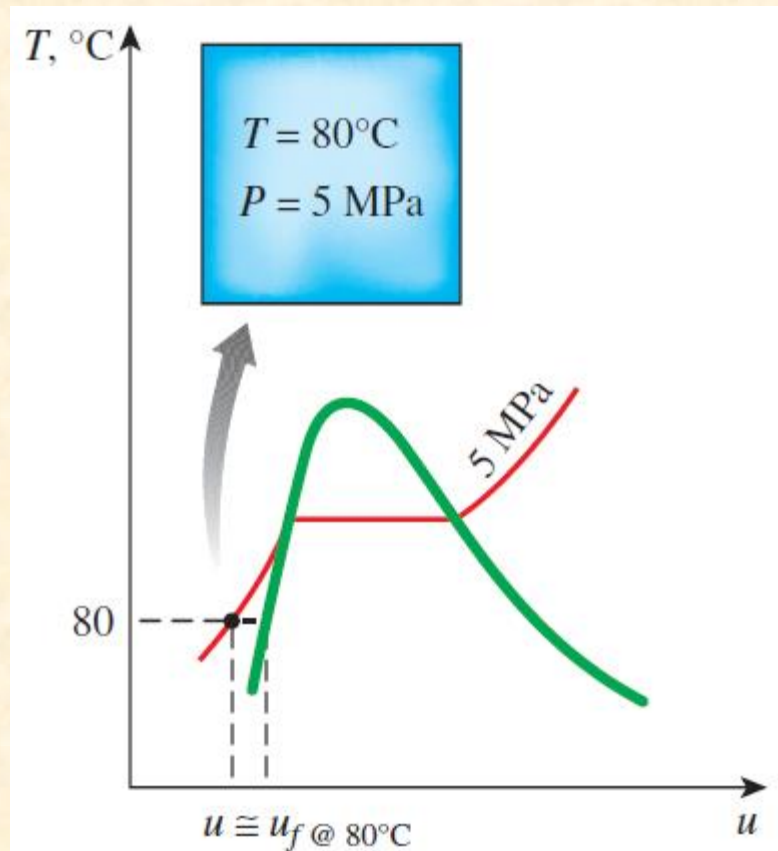
Higher pressures ( $P > P_{\text{sat}}$  at a given  $T$ )

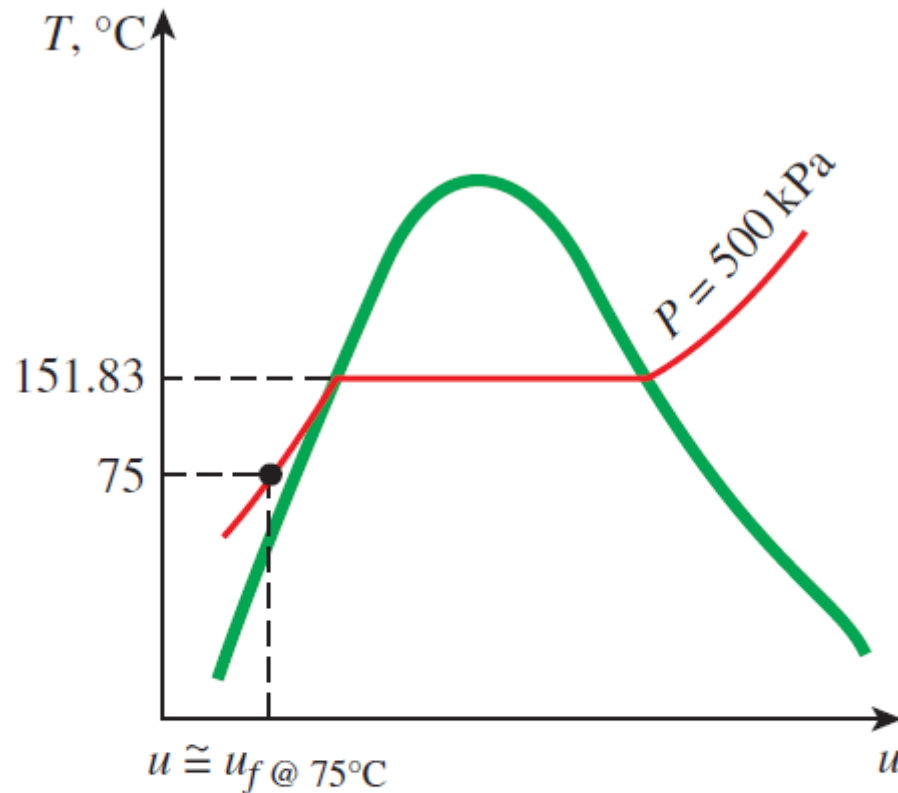
Lower temperatures ( $T < T_{\text{sat}}$  at a given  $P$ )

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  $T$ )





**FIGURE 3–41**

At a given  $P$  and  $T$ , a pure substance will exist as a compressed liquid if  $T < T_{\text{sat}} @ P$ .

# 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.

Saturated water—Temperature table

Temp., $T$ °C	Sat. press., $P_{\text{sat}}$ kPa	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	0.6117	0.001000	206.00	0.000	2374.9	2374.9	0.001	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	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., $T$ °C	Sat. press., $P_{\text{sat}}$ kPa	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

# 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

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

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Ideal gas  
equation at two  
states for a fixed  
mass

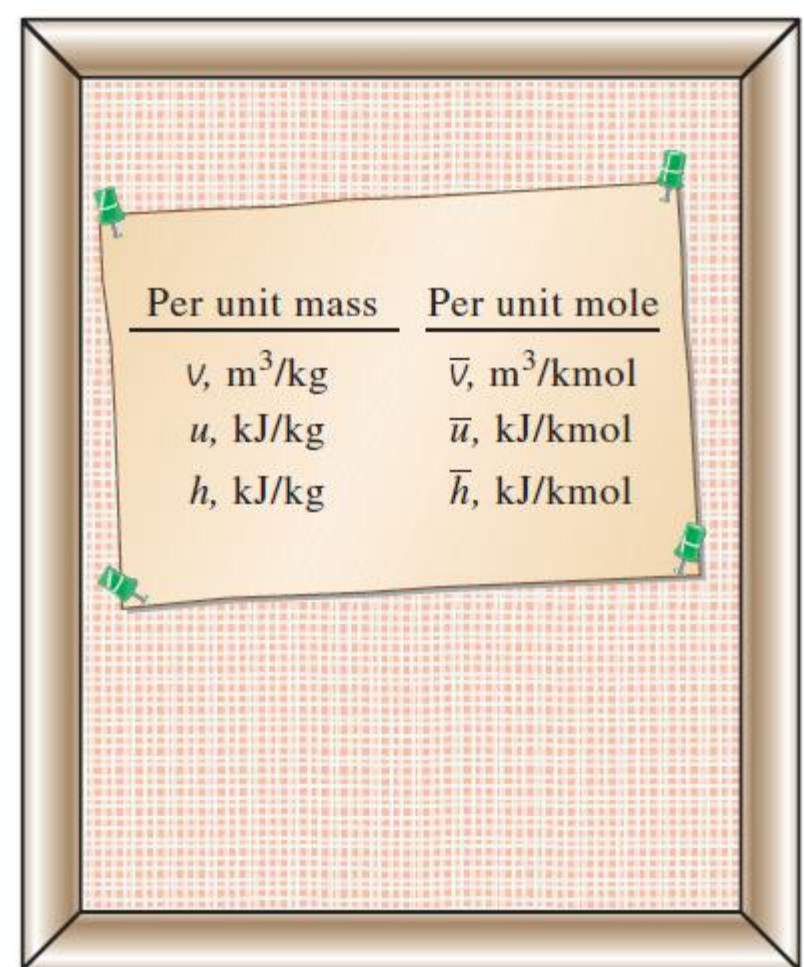
Various expressions  
of ideal gas equation

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

$$mR = (MN)R = NR_u \longrightarrow P\upsilon = NR_u T$$

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

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



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

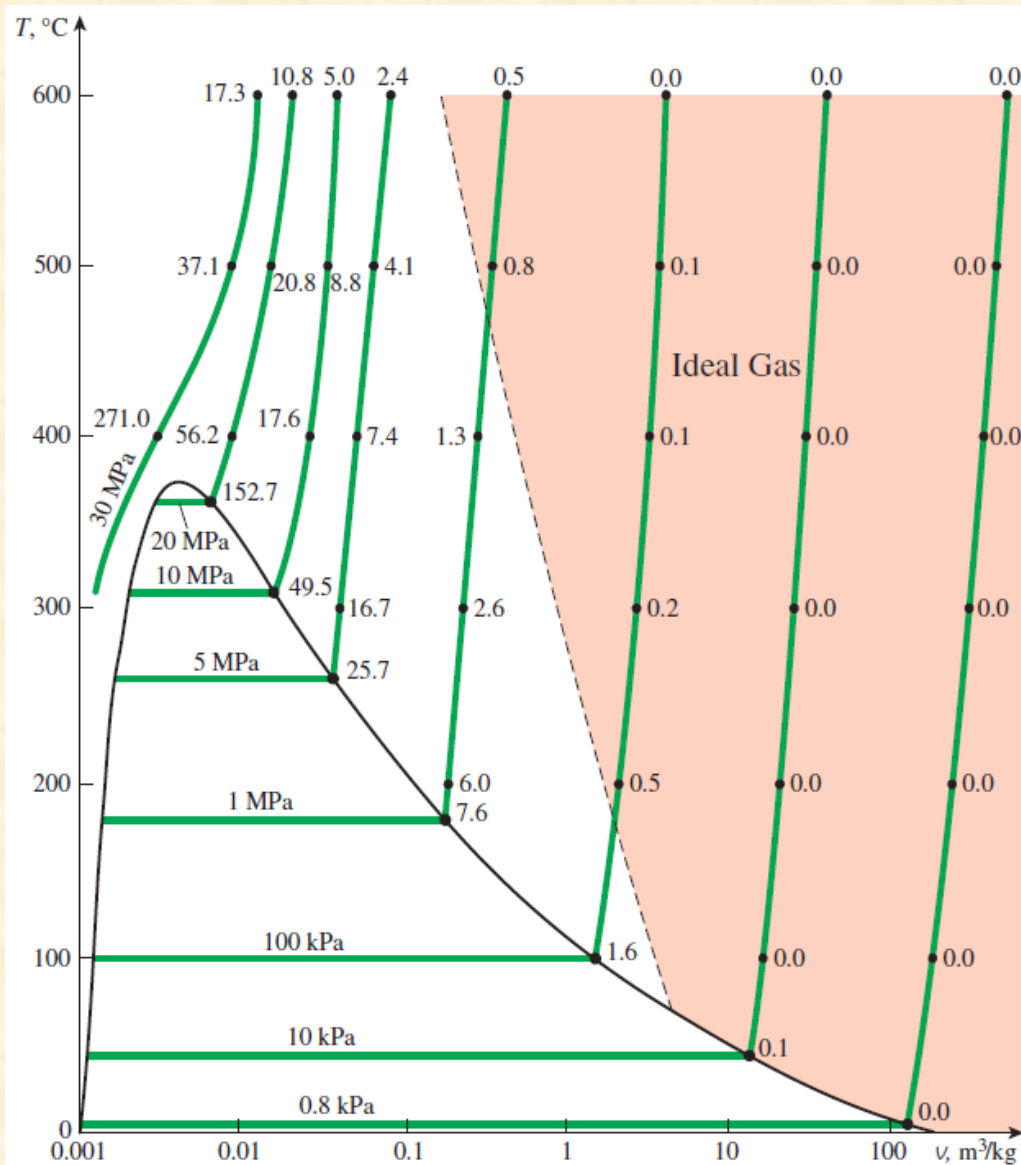
**FIGURE 3–43**

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



# 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

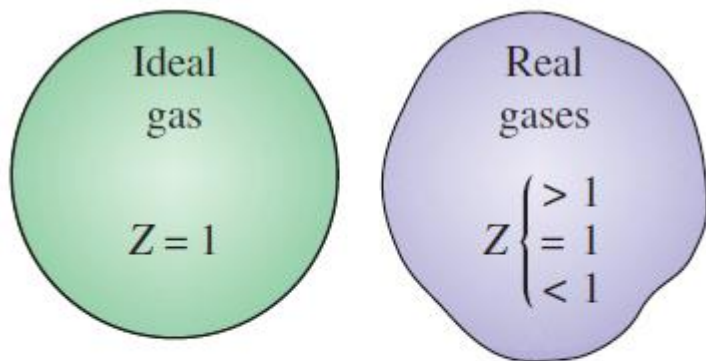
## Compressibility factor $Z$

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

$$PV = ZRT$$

$$Z = \frac{PV}{RT}$$

$$Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}$$



**FIGURE 3–46**

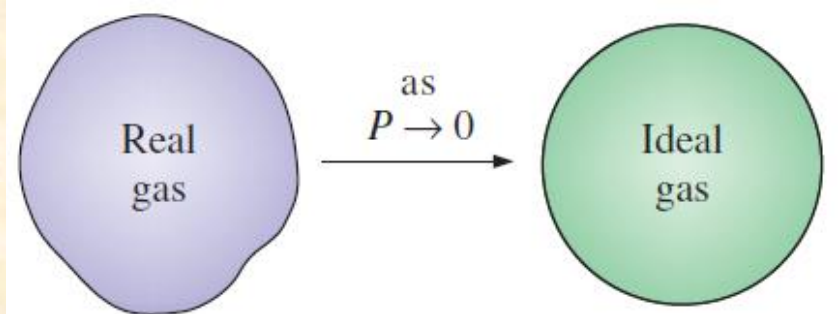
The compressibility factor is unity for ideal gases.

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).

$$P_R = \frac{P}{P_{cr}}$$

Reduced  
pressure

$$T_R = \frac{T}{T_{cr}}$$

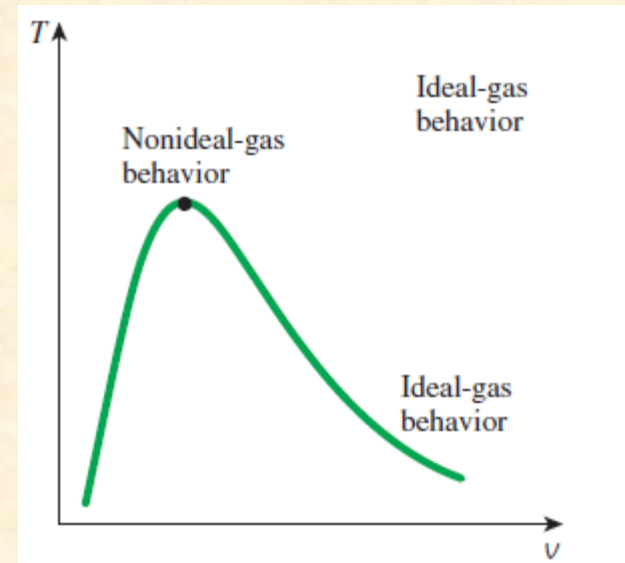
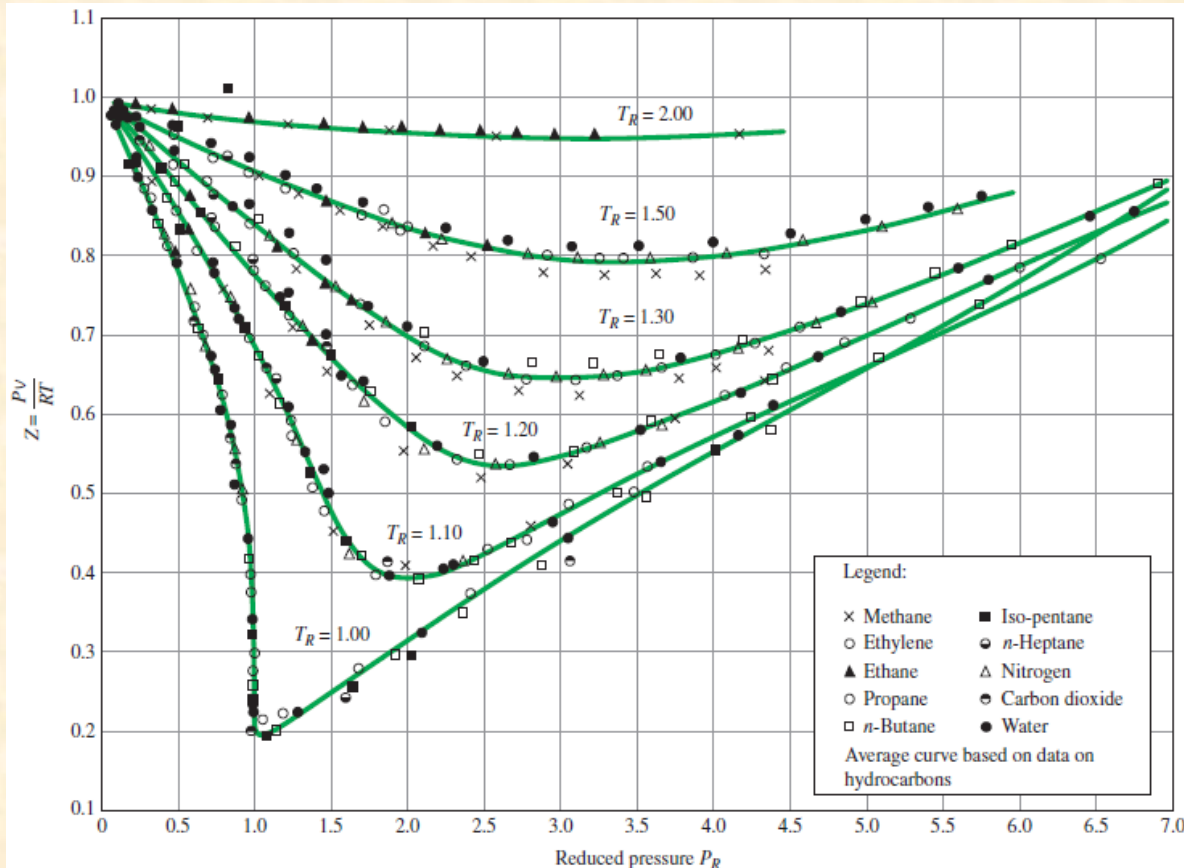
Reduced  
temperature

$$V_R = \frac{V_{actual}}{RT_{cr}/P_{cr}}$$

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.

# 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.

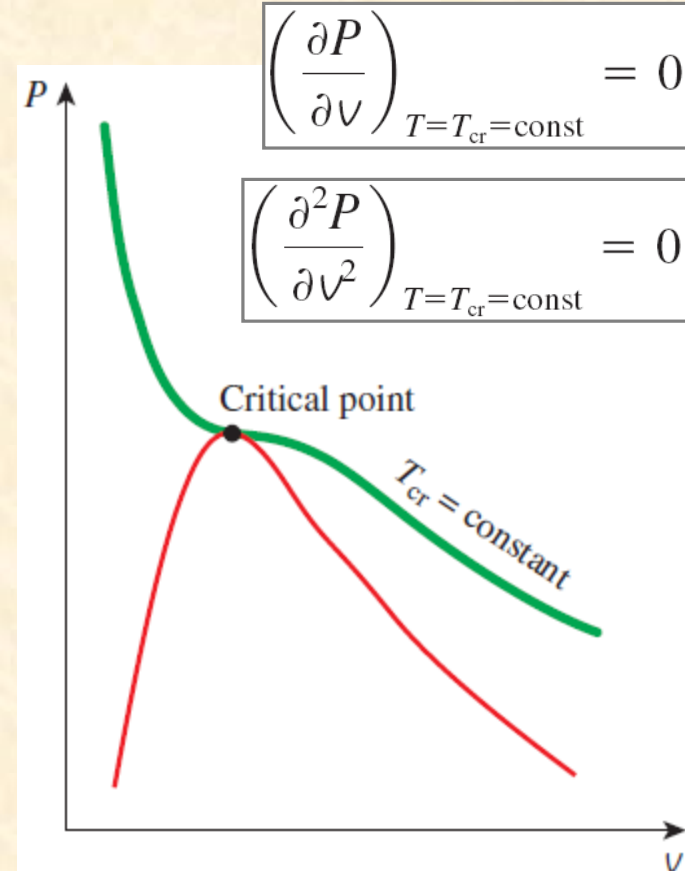
## Van der Waals Equation of State

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

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

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

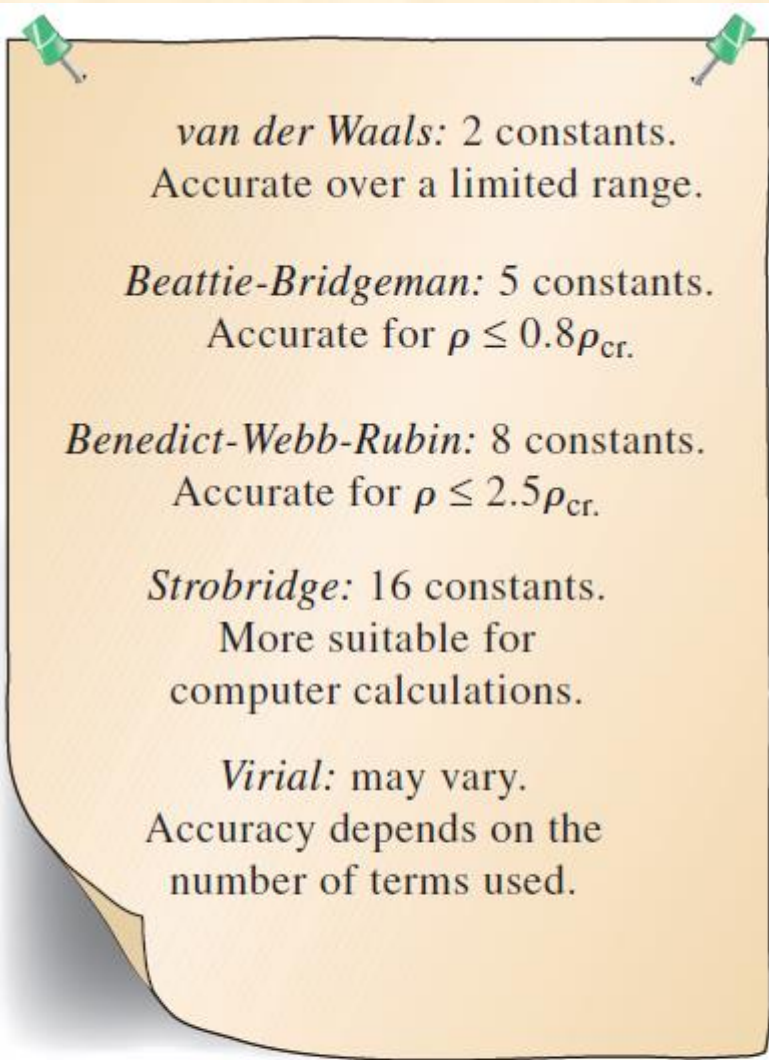
(a) When  $P$  is in kPa,  $\bar{v}$  is in  $\text{m}^3/\text{kmol}$ ,  $T$  is in K, and  $R_u = 8.314 \text{ kPa}\cdot\text{m}^3/\text{kmol}\cdot\text{K}$ , the five constants in the Beattie-Bridgeman equation are as follows:

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



*van der Waals*: 2 constants.  
Accurate over a limited range.

*Beattie-Bridgeman*: 5 constants.  
Accurate for  $\rho \leq 0.8\rho_{\text{cr}}$ .

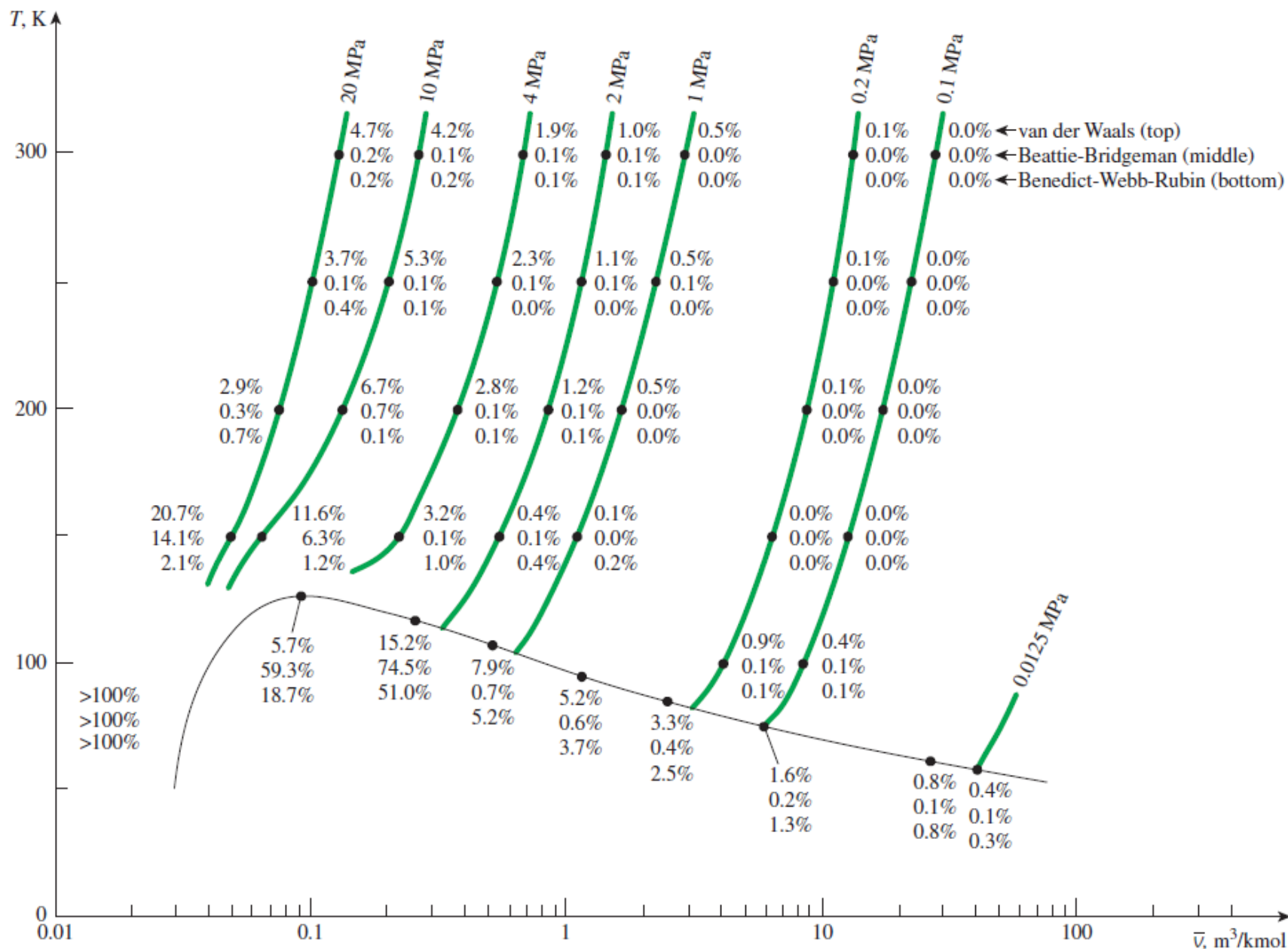
*Benedict-Webb-Rubin*: 8 constants.  
Accurate for  $\rho \leq 2.5\rho_{\text{cr}}$ .

*Strobridge*: 16 constants.  
More suitable for  
computer calculations.

*Virial*: may vary.  
Accuracy depends on the  
number of terms used.

### 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 =  $[(v_{\text{table}} - v_{\text{equation}})/v_{\text{table}}] \times 100$ ).

# Summary

- Pure substance
- Phases of a pure substance
- Phase-change processes of pure substances
  - ✓ Compressed liquid, Saturated liquid, Saturated vapor, Superheated vapor
  - ✓ Saturation temperature and Saturation pressure
- Property diagrams for phase change processes
  - ✓ The  $T$ - $v$  diagram, The  $P$ - $v$  diagram, The  $P$ - $T$  diagram, The  $P$ - $v$ - $T$  surface
- Property tables
  - ✓ Enthalpy
  - ✓ Saturated liquid, saturated vapor, Saturated liquid vapor mixture, Superheated vapor, compressed liquid
  - ✓ Reference state and reference values
- 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