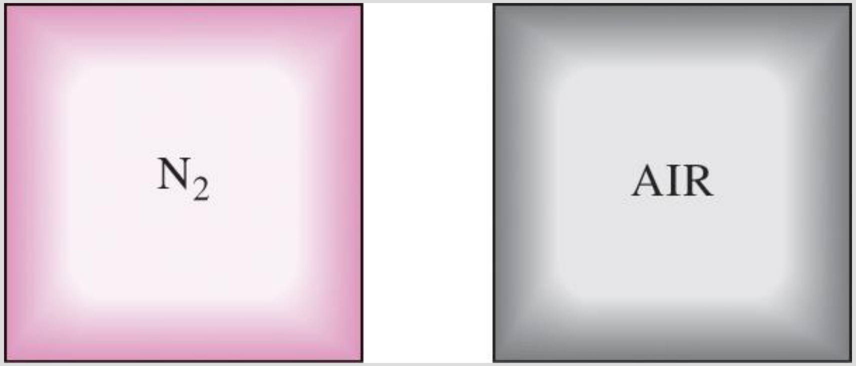
Chapter 3: PROPERTIES OF PURE SUBSTANCES

Objectives

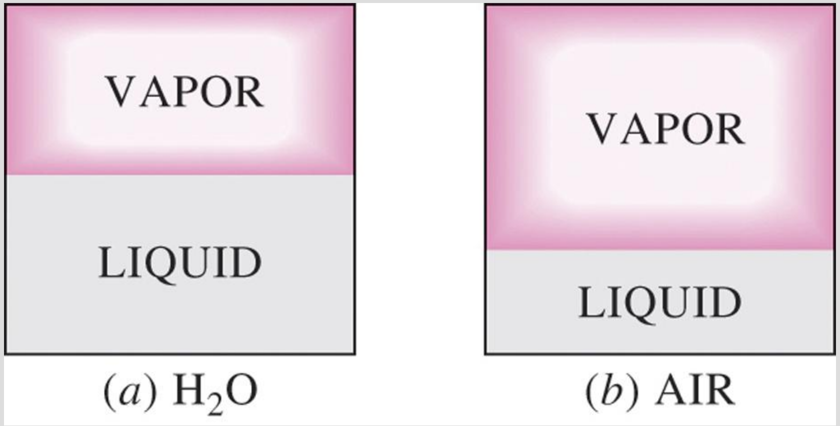
- Introduce the concept of a pure substance.
- Discuss the physics of phase-change processes.
- Illustrate the P-v, T-v, and P-T property diagrams and P-v-T surfaces of pure substances.
- Demonstrate the procedures for determining thermodynamic properties of pure substances from tables of property data.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



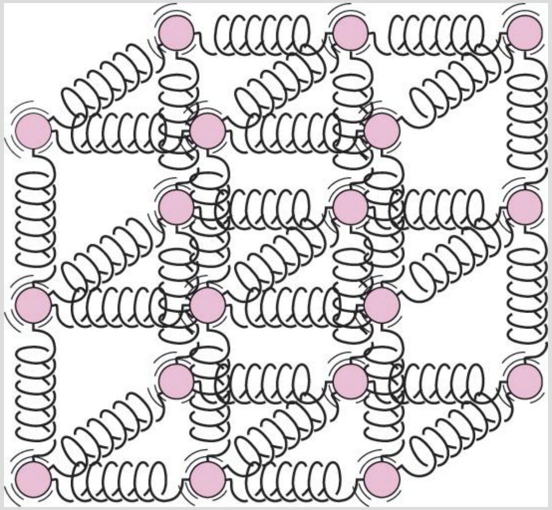
Nitrogen and gaseous air are pure substances.



(*a*) H_2O (*b*) AIR

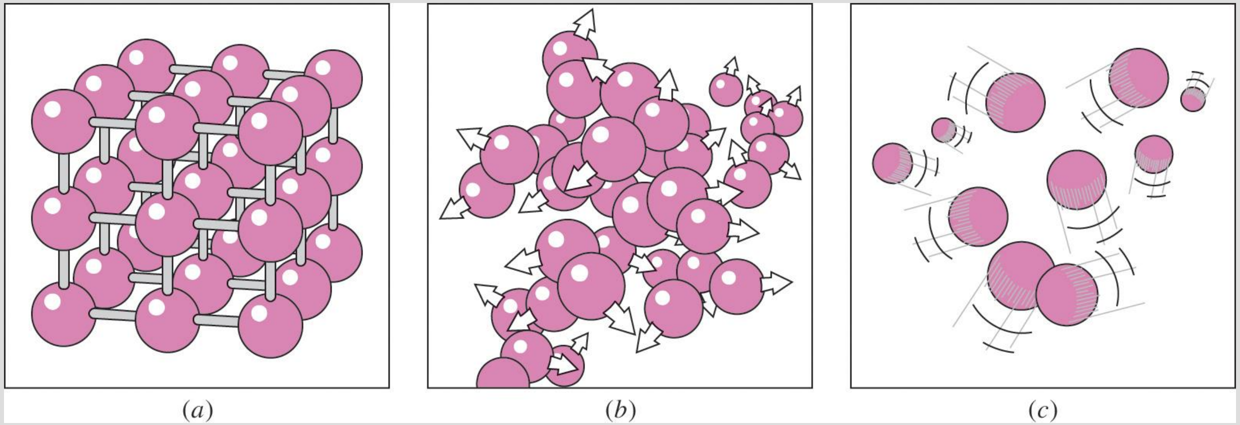
A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

PHASES OF A PURE SUBSTANCE



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

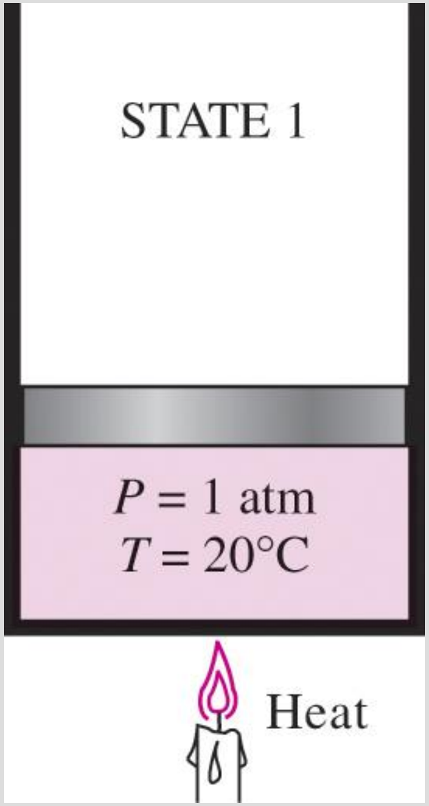
In a solid, the attractive and repulsive forces between the molecules tend to maintain them at relatively constant distances from each other.



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.

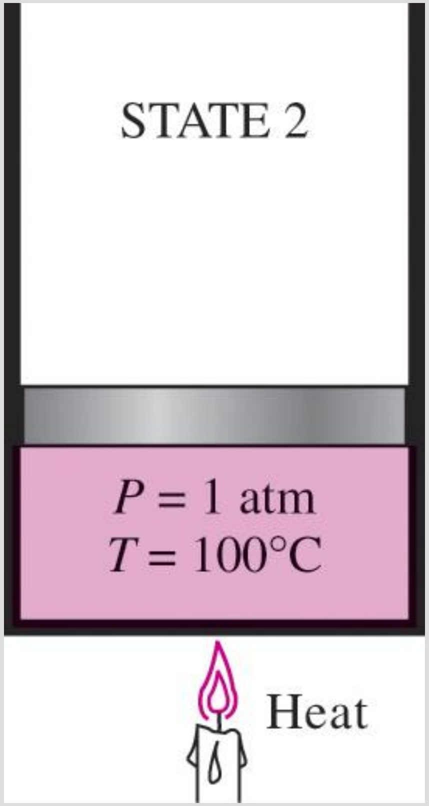
PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

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

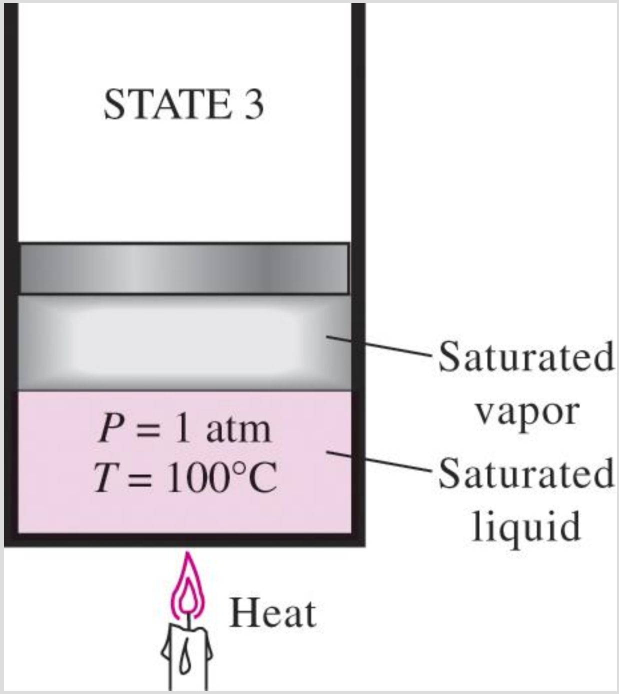


At 1 atm and 20° C, water exists in the liquid phase (***compressed liquid***).

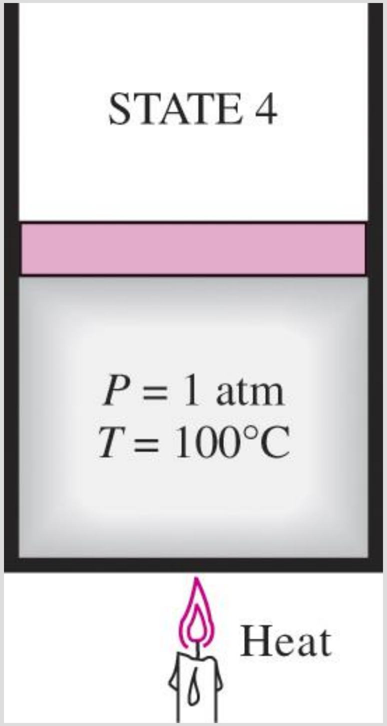
At 1 atm pressure and 100° C, water exists as a liquid that is ready to vaporize (***saturated liquid***).



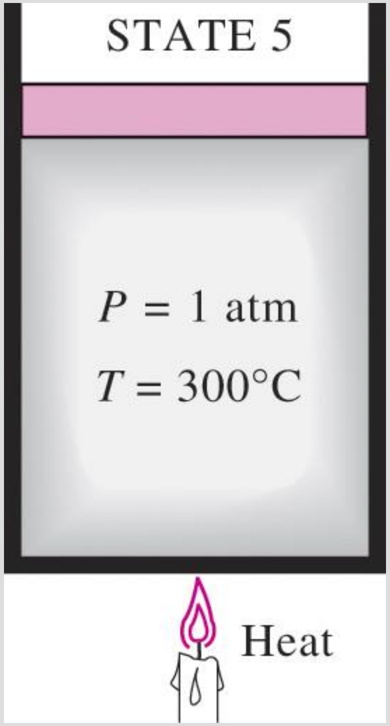
- **Saturated vapor**: A vapor that is *about to condense.*
- **Saturated liquid–vapor mixture**: The state at which the *liquid and vapor phases coexist* in equilibrium.
- **Superheated vapor**: A vapor that is *not about to condense* (i.e., not a saturated vapor).



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

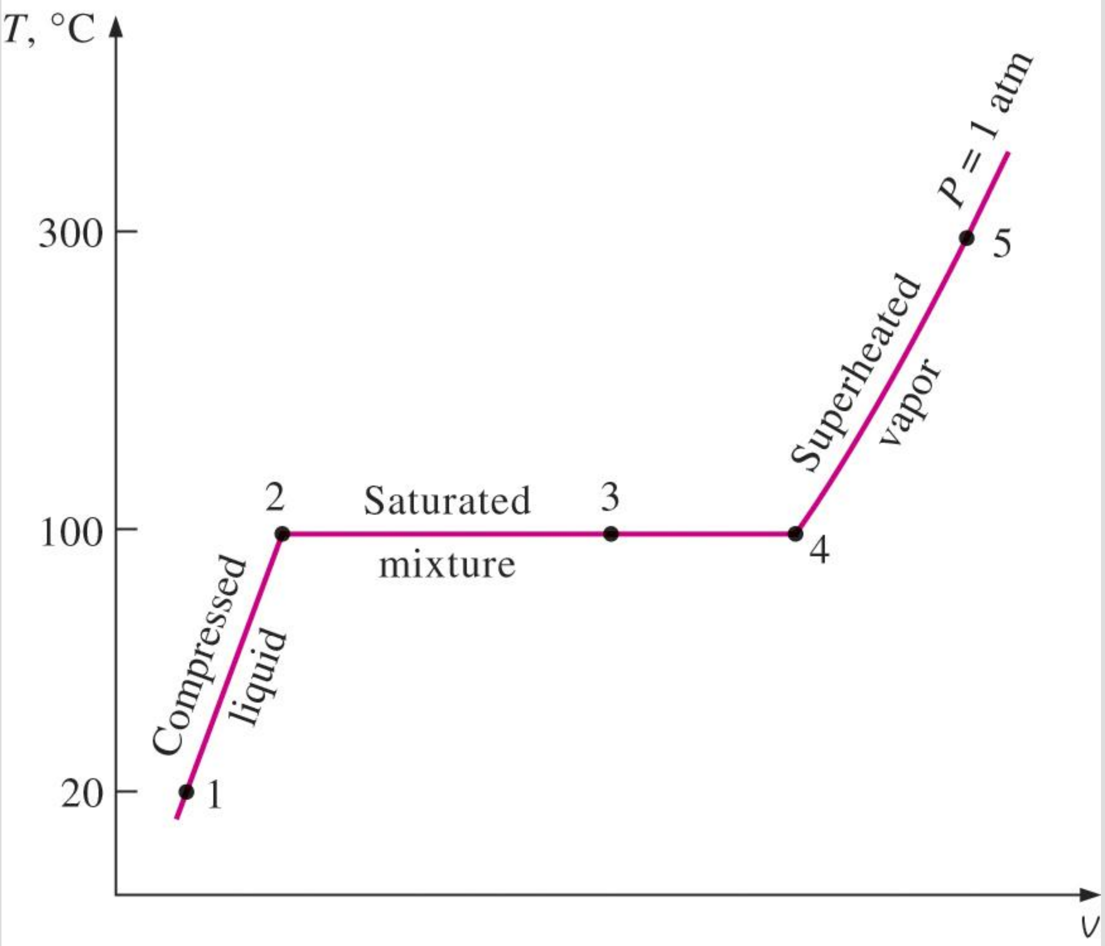


At 1 atm pressure, the temperature remains constant at 100° C until the last drop of liquid is vaporized (***saturated vapor***).



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

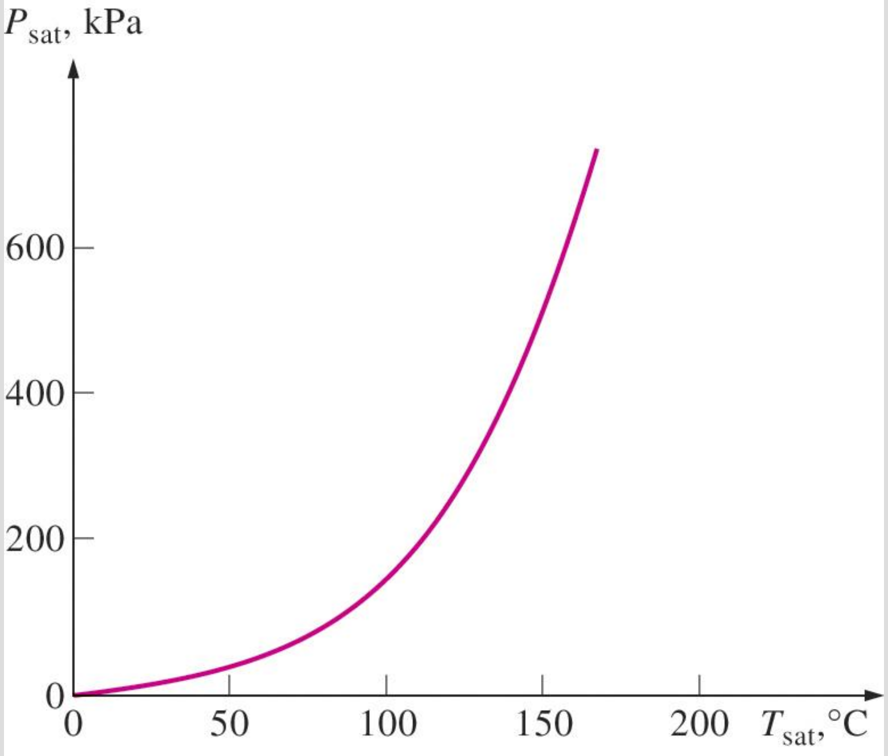
If the entire process between state 1 and 5 described in the figure is reversed by cooling the water while maintaining the pressure at the same value, the water will go back to state 1, retracing the same path, and in so doing, the amount of heat released will exactly match the amount of heat added during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



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

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.

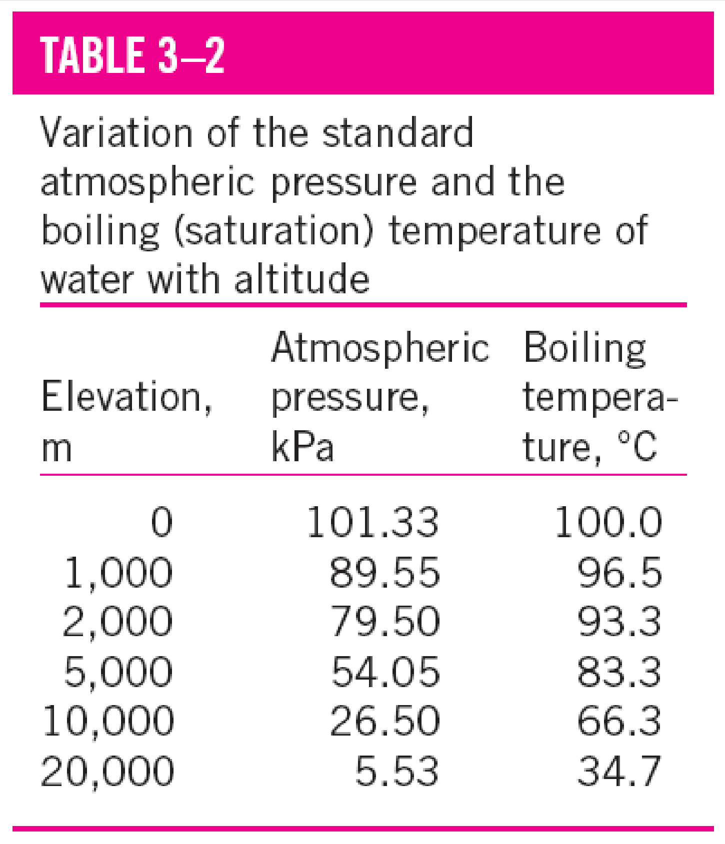
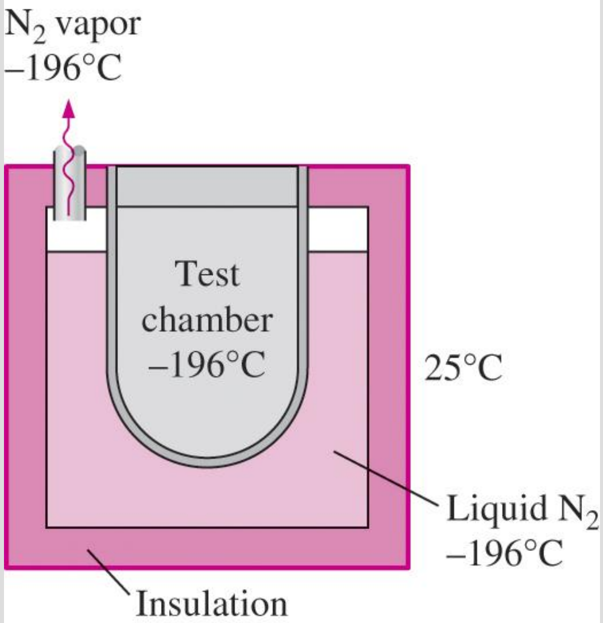


TABLE 3–2

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

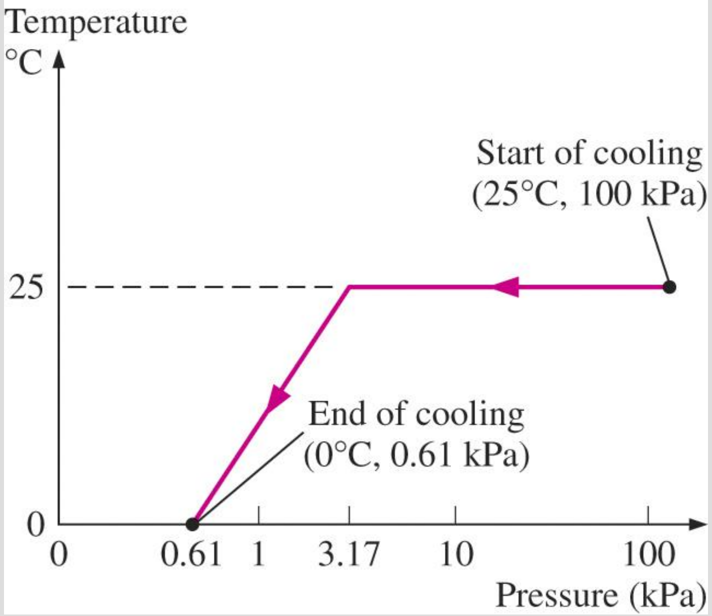
Elevation, m	Atmospheric pressure, kPa	Boiling temperature, °C
0	101.33	100.0
1,000	89.55	96.5
2,000	79.50	93.3
5,000	54.05	83.3
10,000	26.50	66.3
20,000	5.53	34.7

Some Consequences of T_{sat} and P_{sat} Dependence

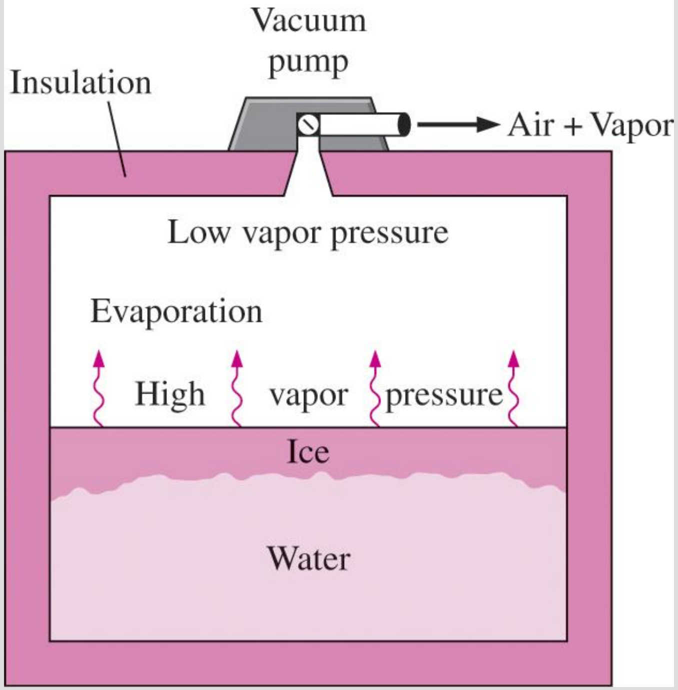


The temperature of liquid nitrogen exposed to the atmosphere remains constant at 196° C, and thus it maintains the test chamber at 196° C.

The variation of the temperature of fruits and vegetables with pressure during vacuum cooling from 25° C to 0° C.

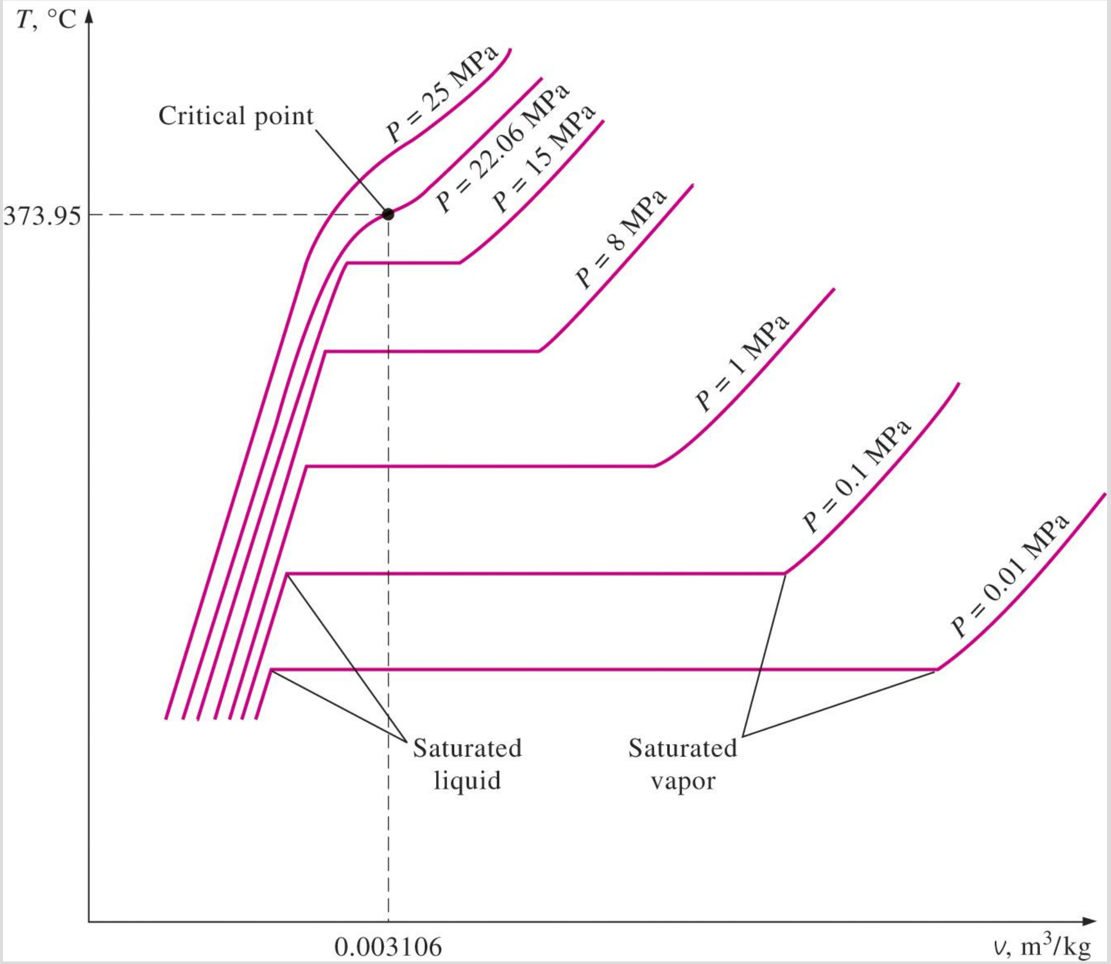


In 1775, ice was made by evacuating the air space in a water tank.



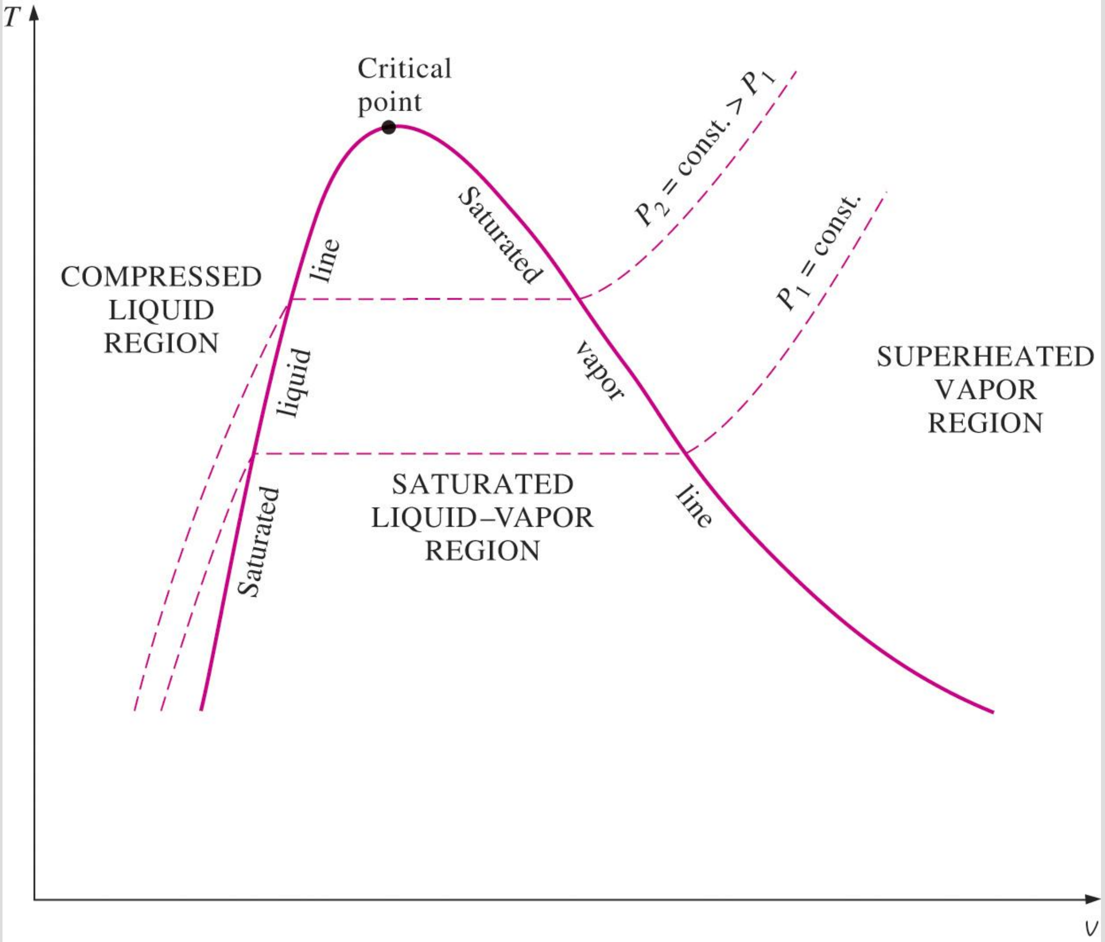
PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

- 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.

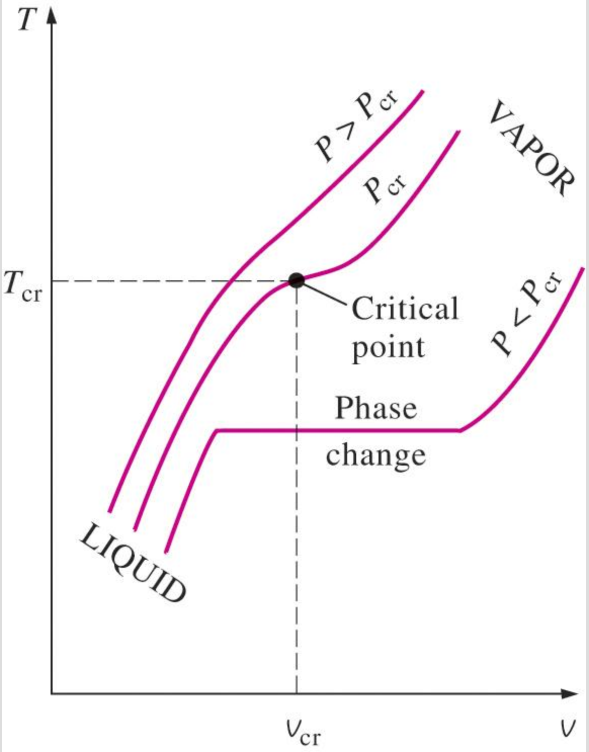


T-*v* diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

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

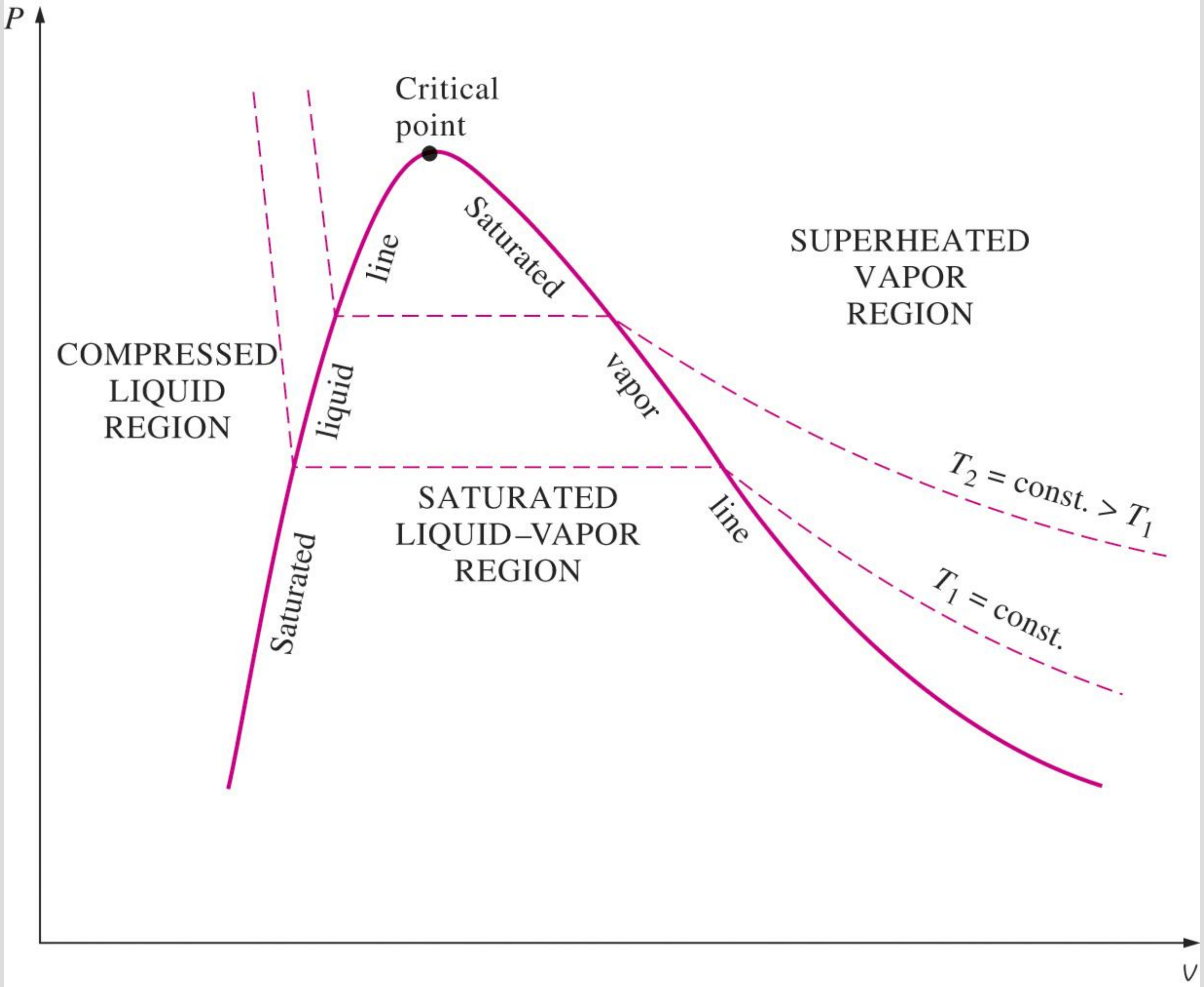


T-*v* diagram of a pure substance.

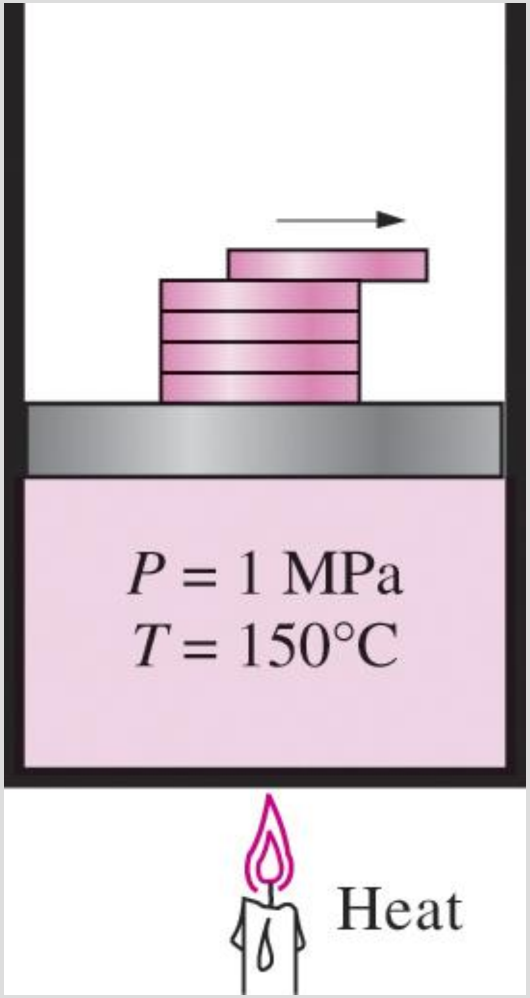


At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.

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



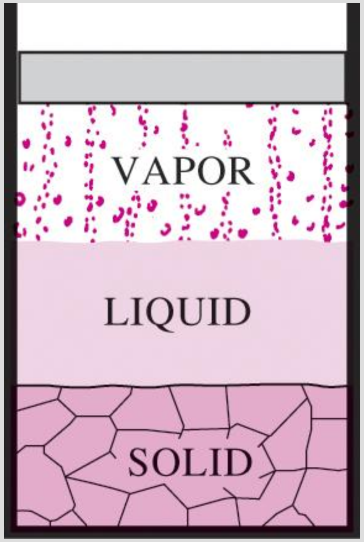
P-*v* diagram of a pure substance.



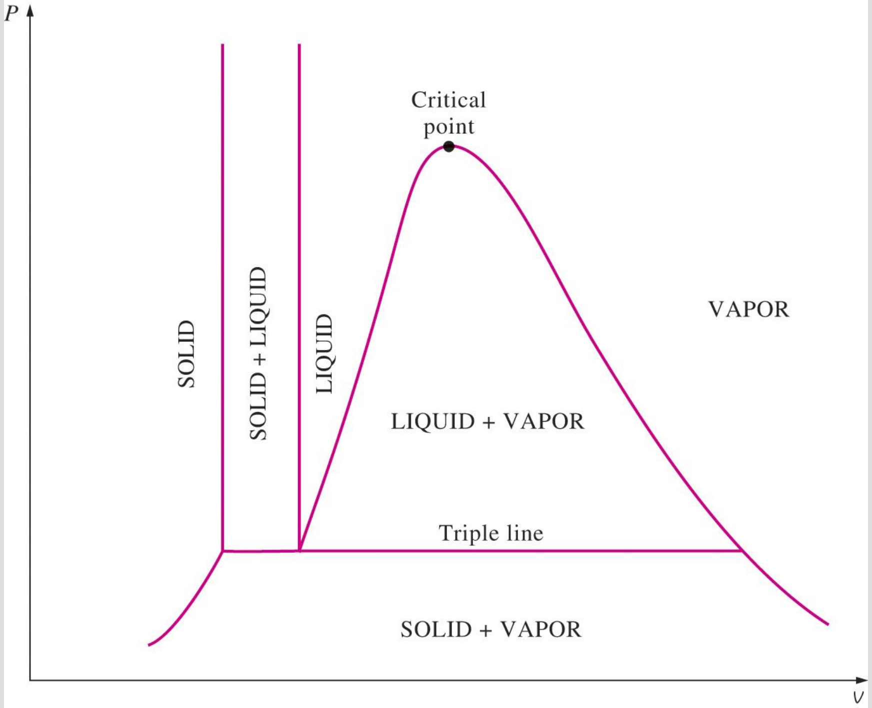
The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

Extending the Diagrams to Include the Solid Phase

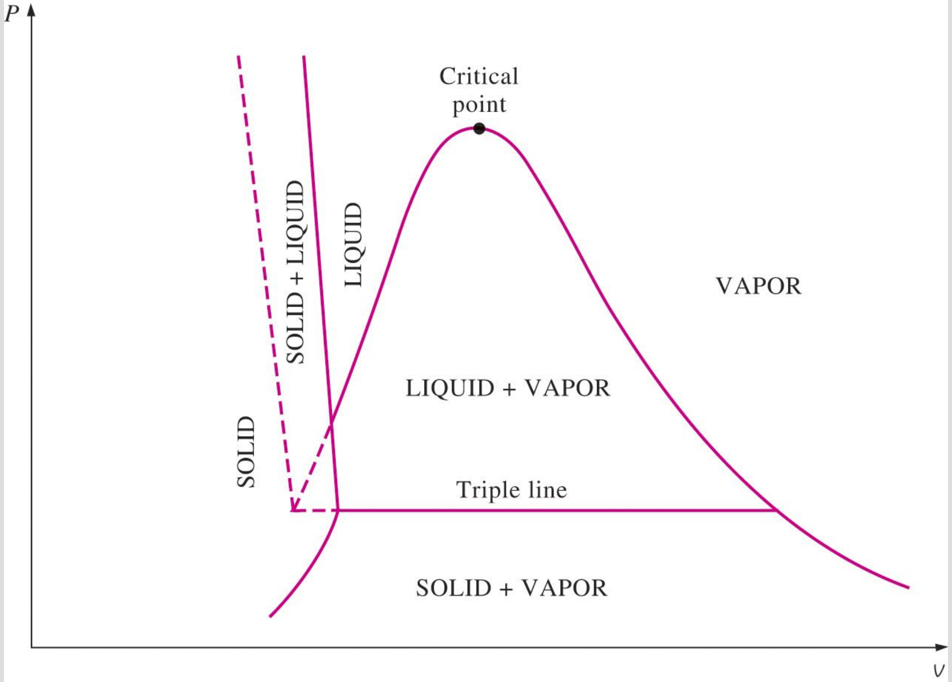
For water,
$T_{tp} = 0.01^\circ$ C
$P_{tp} = 0.6117$ kPa



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



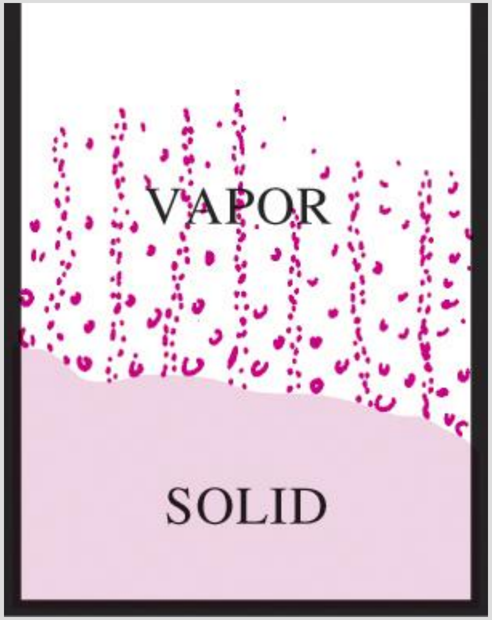
P-*v* diagram of a substance that contracts on freezing.



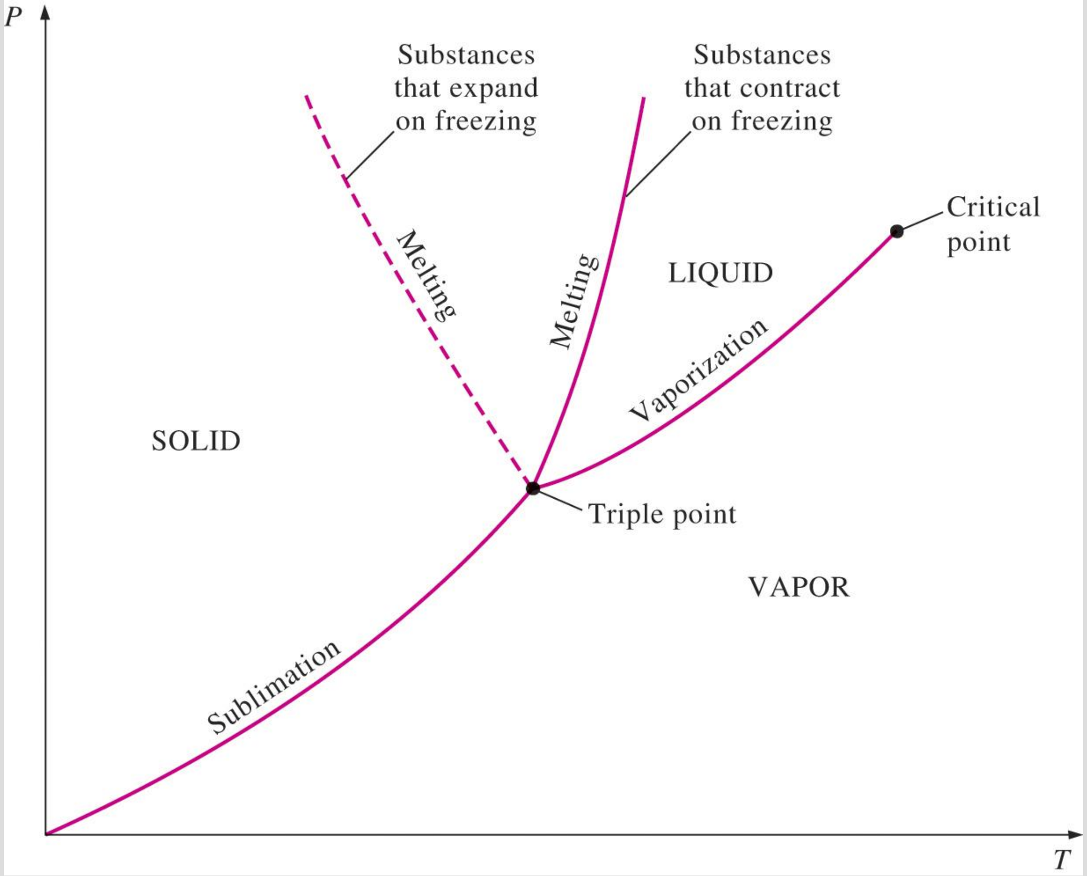
P-*v* diagram of a substance that expands on freezing (such as water).

Sublimation: Passing from the solid phase directly into the vapor phase.

Phase Diagram

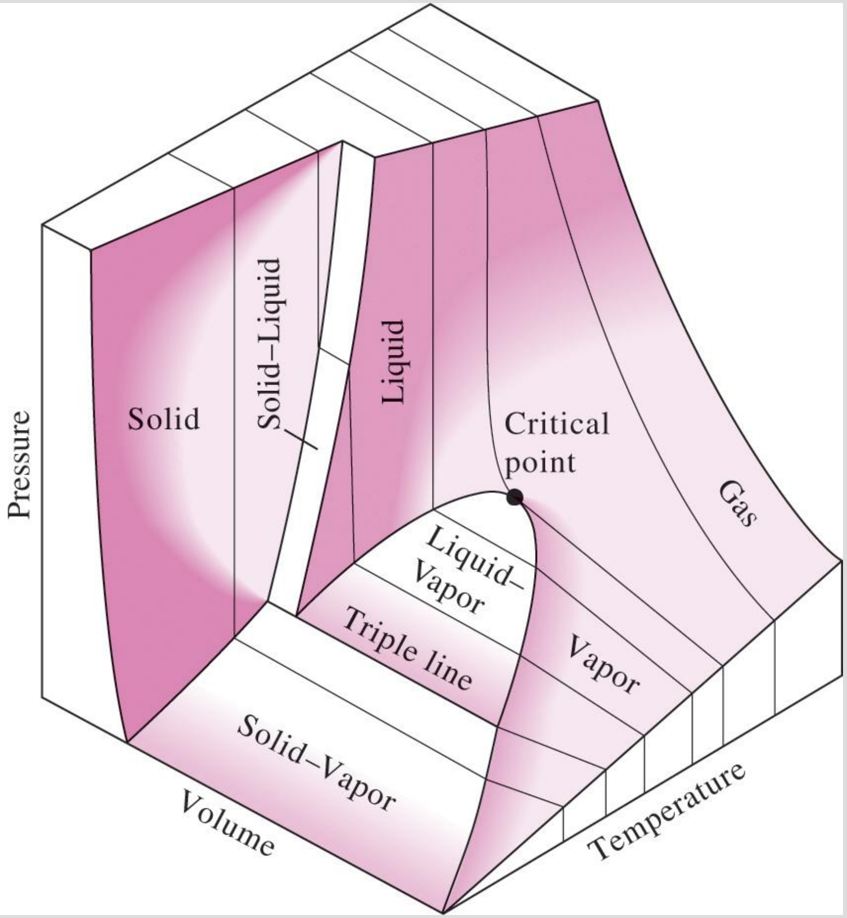


At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).

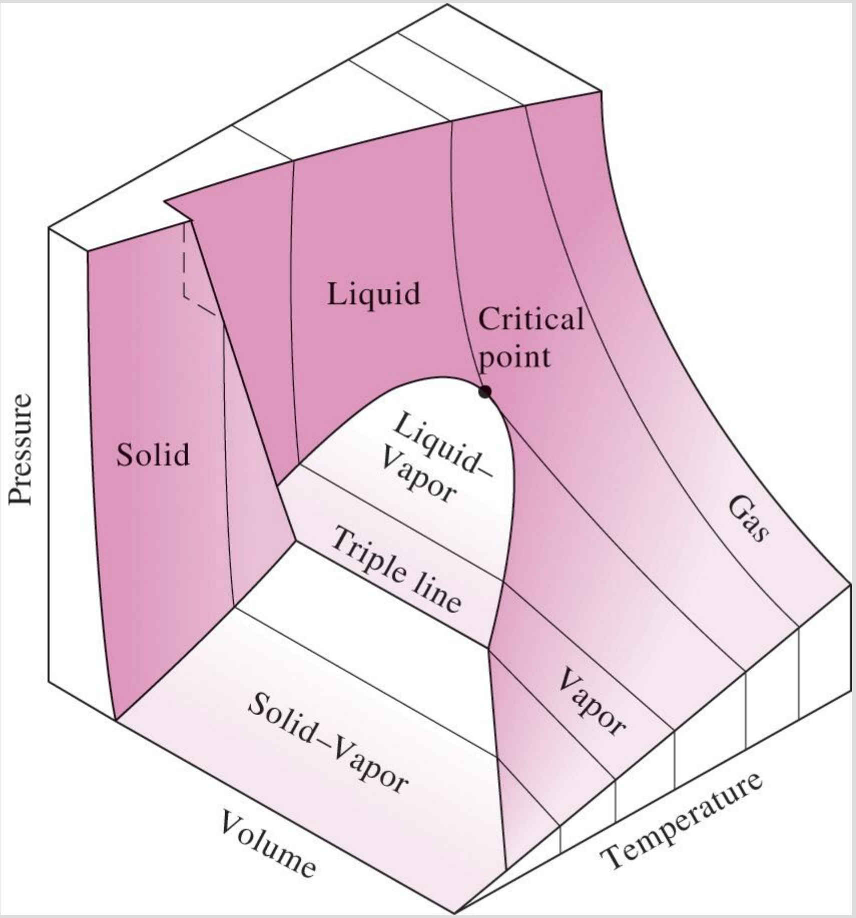


P-T diagram of pure substances.

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.



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



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

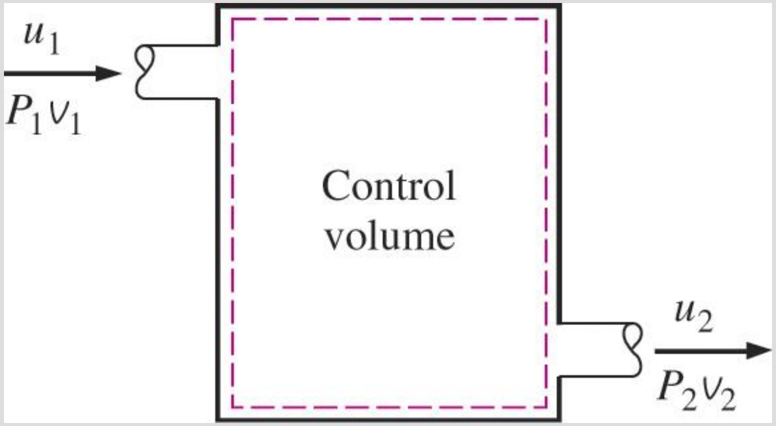
PROPERTY TABLES

- 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

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

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



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

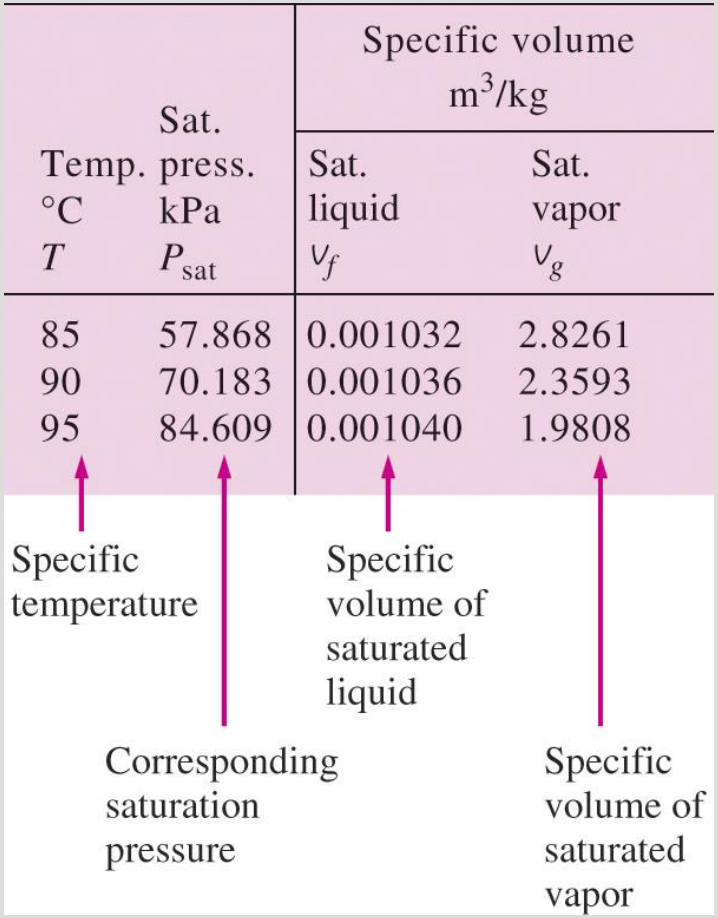
$$\text{kPa} \cdot \text{m}^3 \equiv \text{kJ}$$
$$\text{kPa} \cdot \text{m}^3/\text{kg} \equiv \text{kJ/kg}$$
$$\text{bar} \cdot \text{m}^3 \equiv 100 \text{ kJ}$$
$$\text{MPa} \cdot \text{m}^3 \equiv 1000 \text{ kJ}$$
$$\text{psi} \cdot \text{ft}^3 \equiv 0.18505 \text{ Btu}$$

The product *pressure* × *volume* has energy units.

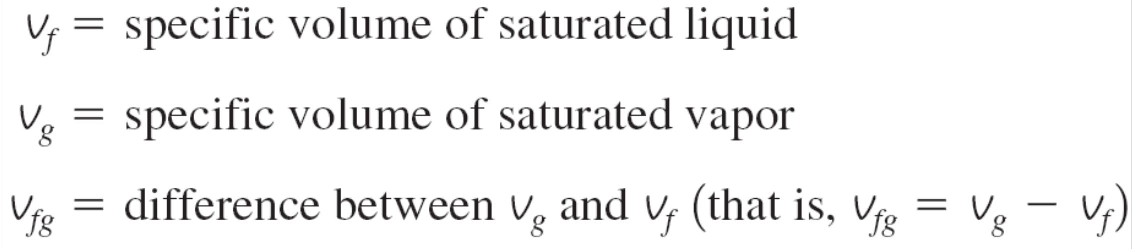
Saturated Liquid and Saturated Vapor States

- **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_{sat}	Specific volume m^3/kg Sat. liquid v_f	Specific volume m^3/kg 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



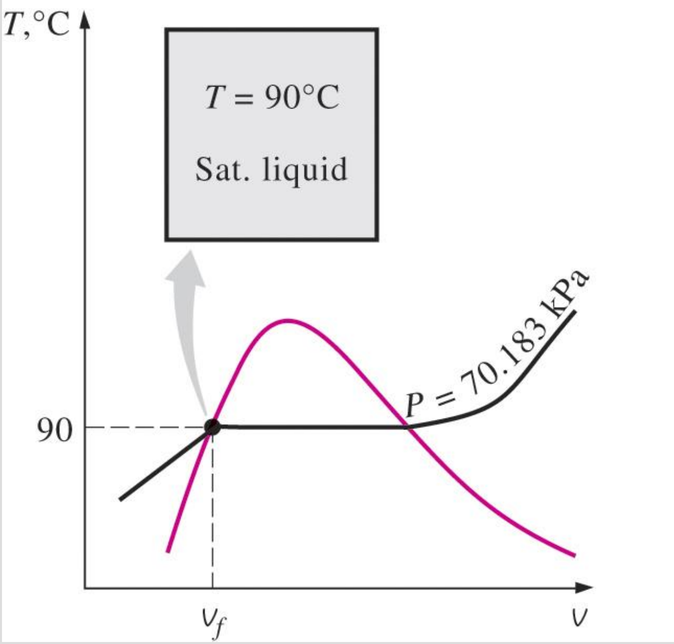
v_f = specific volume of saturated liquid

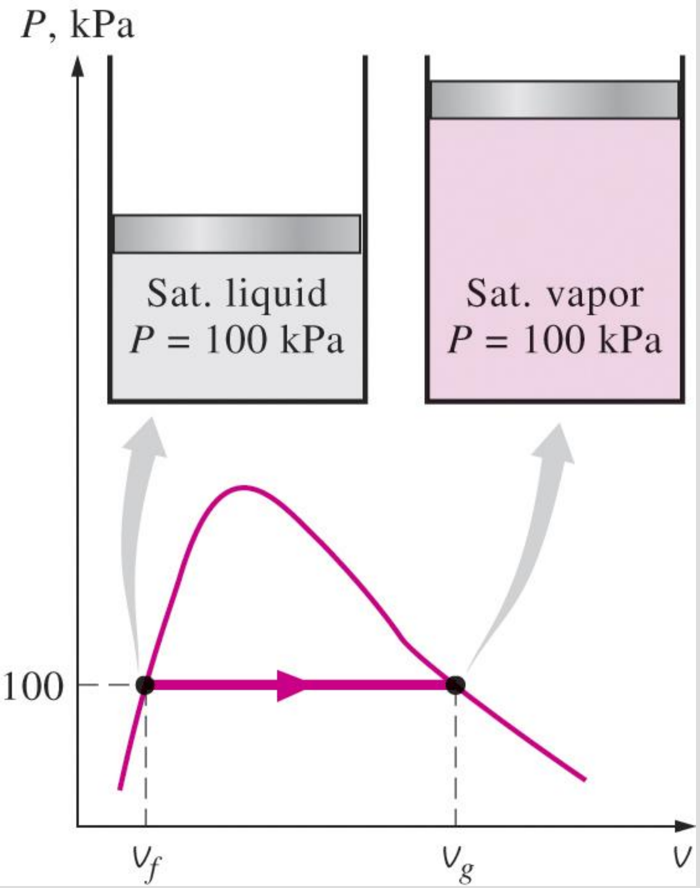
v_g = specific volume of saturated vapor

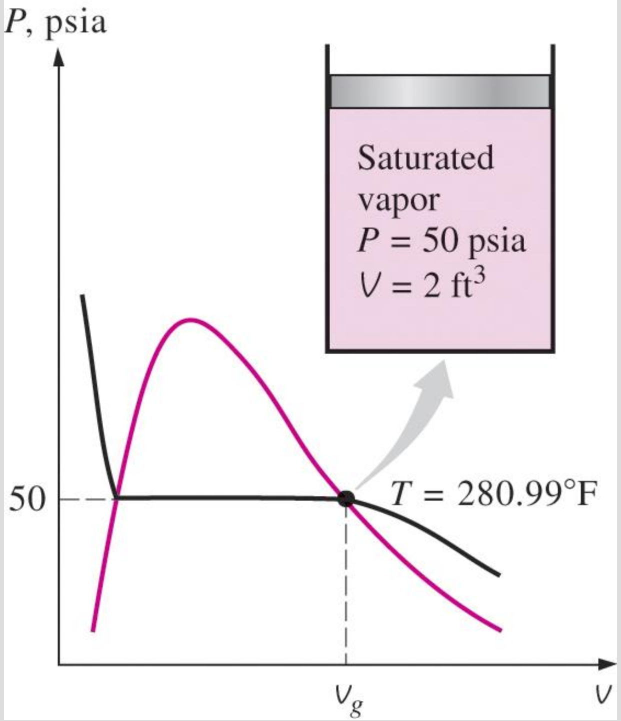
v_{fg} = difference between v_g and v_f (that is, $v_{fg} = v_g - v_f$)

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.

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







EXAMPLE 3–1 Pressure of Saturated Liquid in a Tank

A rigid tank contains 50 kg of saturated liquid water at 90°C. Determine the pressure in the tank and the volume of the tank.

Solution A rigid tank contains saturated liquid water. The pressure and volume of the tank are to be determined.

Analysis The state of the saturated liquid water is shown on a *T-v* diagram in Fig. 3–31. Since saturation conditions exist in the tank, the pressure must be the saturation pressure at 90°C:

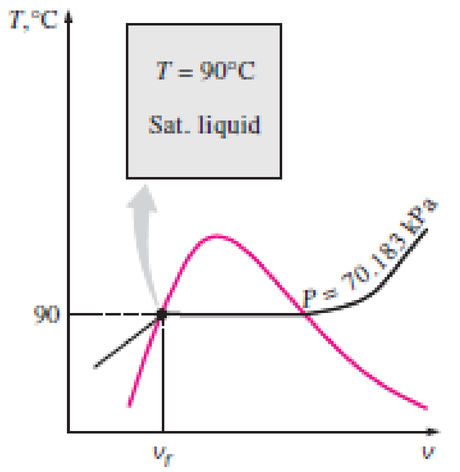
$$P = P_{\text{sat @ }90^\circ\text{C}} = \mathbf{70.183\ kPa} \qquad (\text{Table A–4})$$

The specific volume of the saturated liquid at 90°C is

$$v = v_{f\text{ @ }90^\circ\text{C}} = 0.001036\ \text{m}^3/\text{kg} \qquad (\text{Table A–4})$$

Then the total volume of the tank becomes

$$V = mv = (50\ \text{kg})(0.001036\ \text{m}^3/\text{kg}) = \mathbf{0.0518\ m^3}$$



EXAMPLE 3–2 Temperature of Saturated Vapor in a Cylinder

A piston–cylinder device contains 2 ft^3 of saturated water vapor at 50-psia pressure. Determine the temperature and the mass of the vapor inside the cylinder.

Solution A cylinder contains saturated water vapor. The temperature and the mass of vapor are to be determined.

Analysis The state of the saturated water vapor is shown on a *P-v* diagram in Fig. 3–32. Since the cylinder contains saturated vapor at 50 psia, the temperature inside must be the saturation temperature at this pressure:

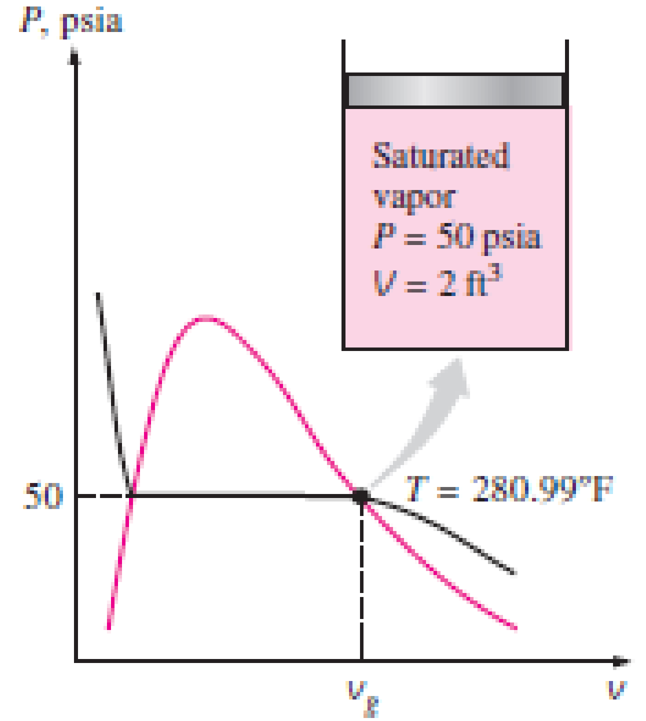
$$T = T_{\text{sat @ 50 psia}} = \mathbf{280.99°F} \qquad \text{(Table A–5E)}$$

The specific volume of the saturated vapor at 50 psia is

$$v = v_{g\text{ @ 50 psia}} = 8.5175\ \text{ft}^3/\text{lbm} \qquad \text{(Table A–5E)}$$

Then the mass of water vapor inside the cylinder becomes

$$m = \frac{V}{v} = \frac{2\ \text{ft}^3}{8.5175\ \text{ft}^3/\text{lbm}} = \mathbf{0.235\ lbm}$$



EXAMPLE 3–3 Volume and Energy Change during Evaporation

A mass of 200 g of saturated liquid water is completely vaporized at a constant pressure of 100 kPa. Determine (*a*) the volume change and (*b*) the amount of energy transferred to the water.

Solution Saturated liquid water is vaporized at constant pressure. The volume change and the energy transferred are to be determined.

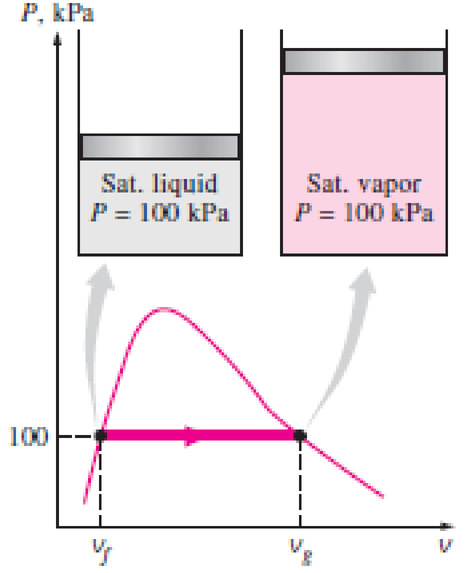
$$v_{fg} = v_g - v_f = 1.6941 - 0.001043 = 1.6931 \text{ m}^3/\text{kg}$$

Thus,

$$\Delta V = mv_{fg} = (0.2 \text{ kg})(1.6931 \text{ m}^3/\text{kg}) = \mathbf{0.3386 \text{ m}^3}$$

(*b*) The amount of energy needed to vaporize a unit mass of a substance at a given pressure is the enthalpy of vaporization at that pressure, which is h_{fg} = 2257.5 kJ/kg for water at 100 kPa. Thus, the amount of energy transferred is

$$mh_{fg} = (0.2 \text{ kg})(2257.5 \text{ kJ/kg}) = \mathbf{451.5 \text{ kJ}}$$



Saturated Liquid–Vapor Mixture

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

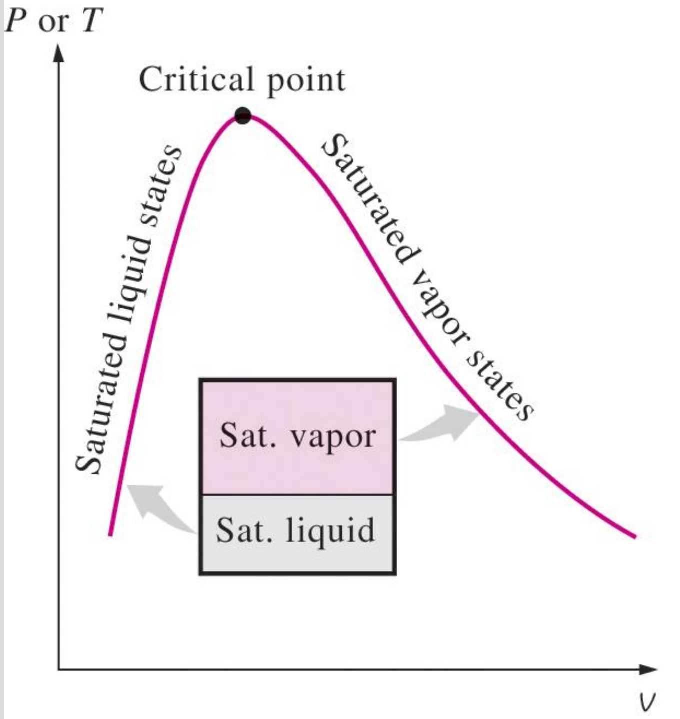
Quality is between 0 and 1 → 0: sat. liquid, 1: sat. vapor

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

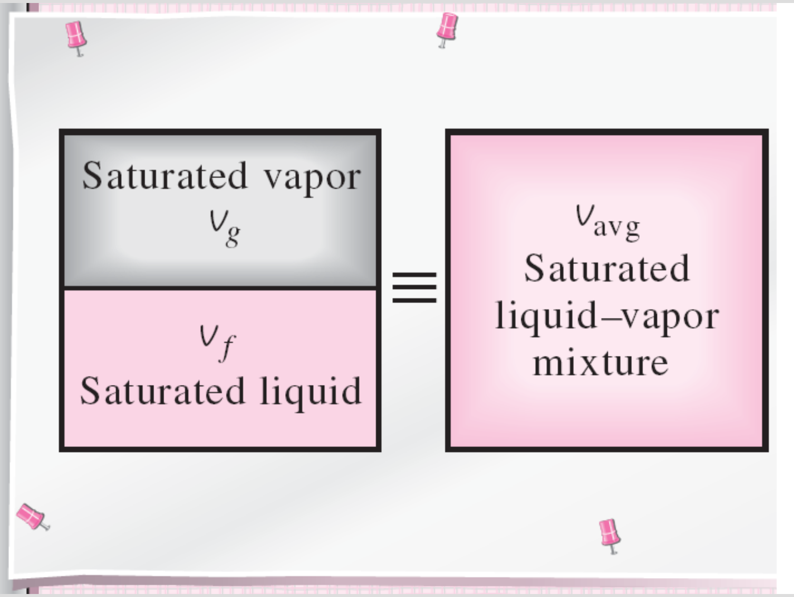
Temperature and pressure are dependent properties for a mixture.

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

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



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.

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

$$x = m_g / m_t$$

$$x = \frac{v_{avg} - v_f}{v_{fg}}$$

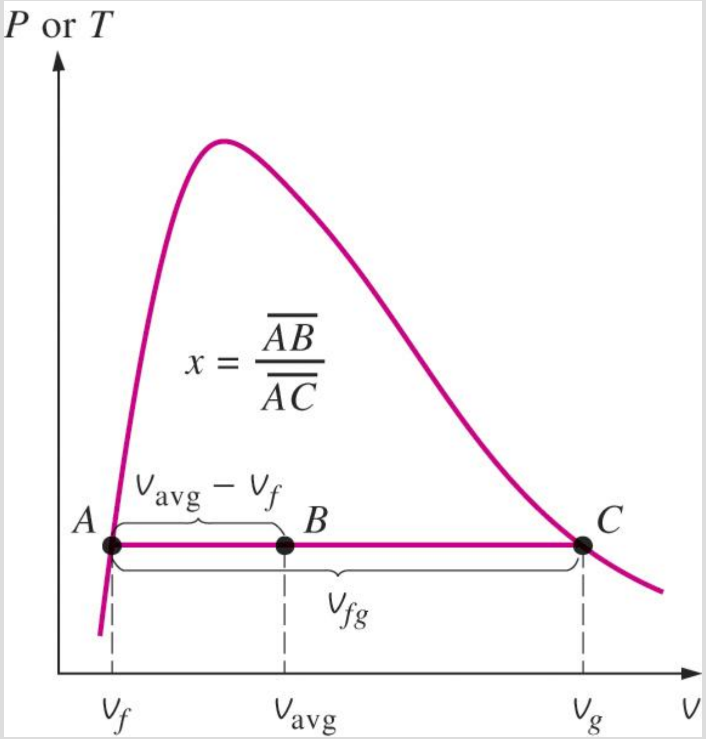
$$u_{avg} = u_f + x u_{fg} \qquad (\mathrm{kJ/kg})$$

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

y → *v*, *u*, or *h*.

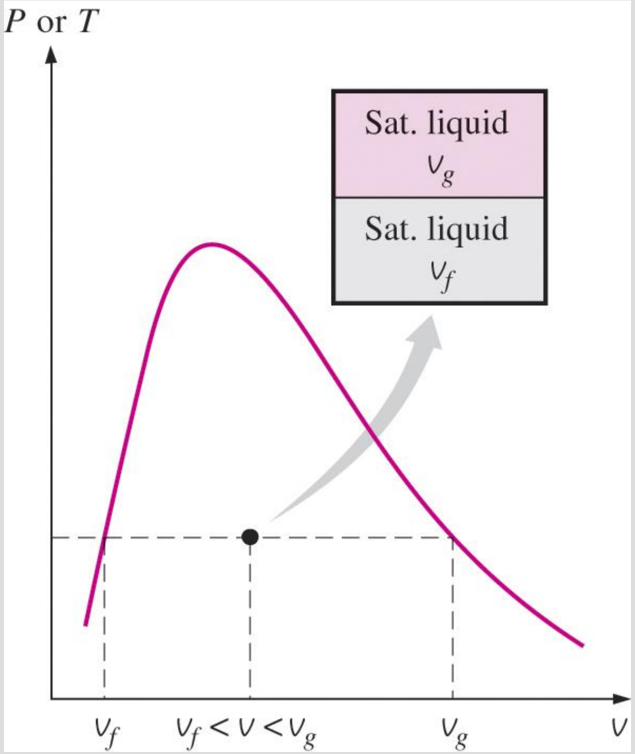
$$y_{avg} = y_f + x y_{fg}$$

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

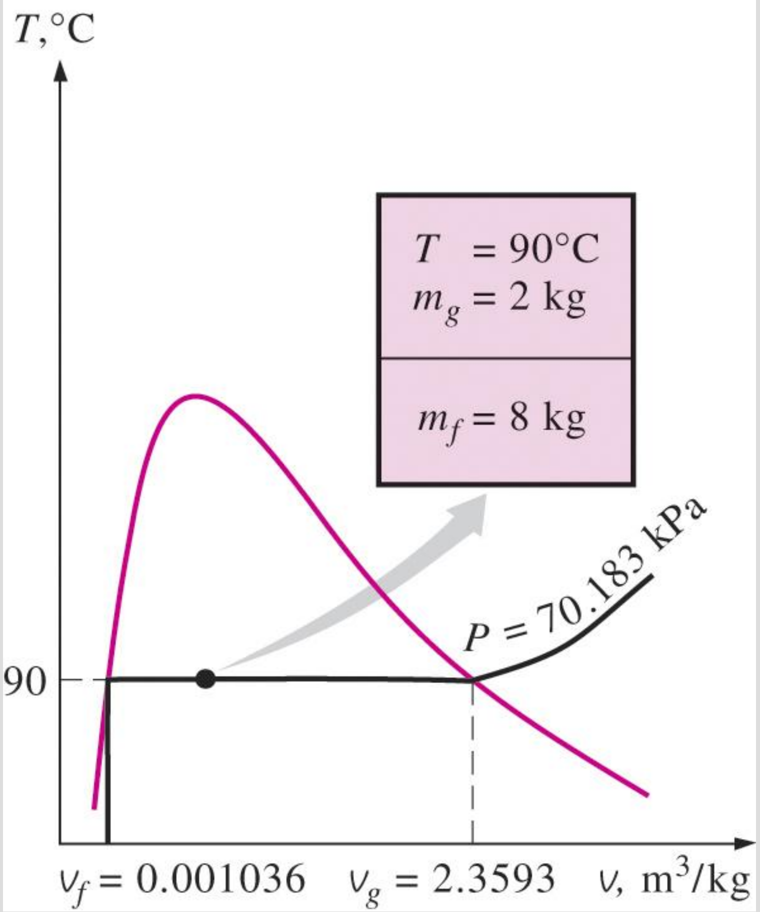


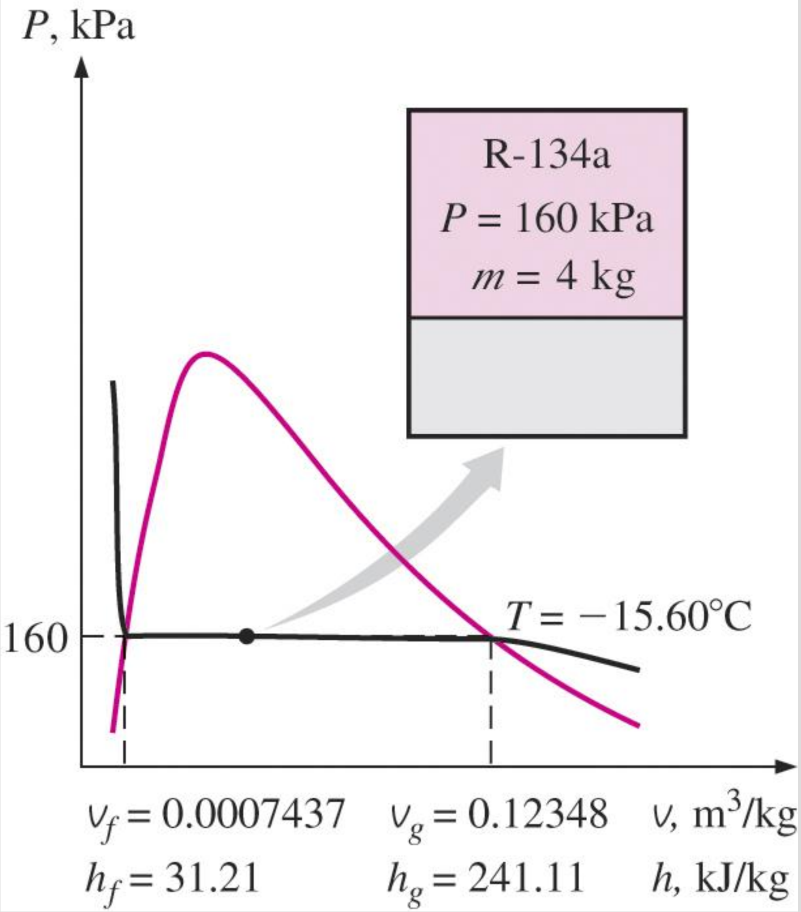
Quality is related to the horizontal distances on *P*-*v* and *T*-*v* diagrams.

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.



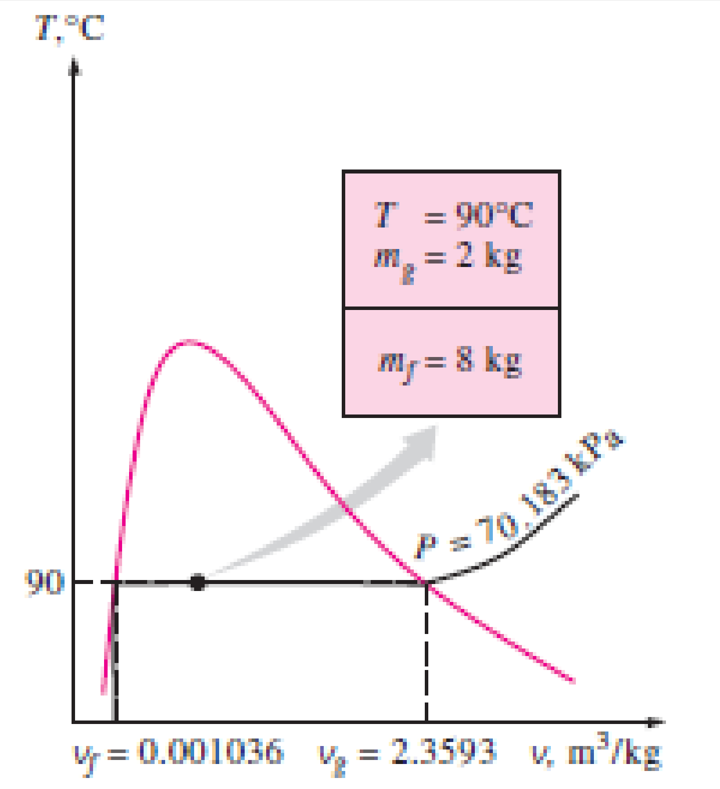


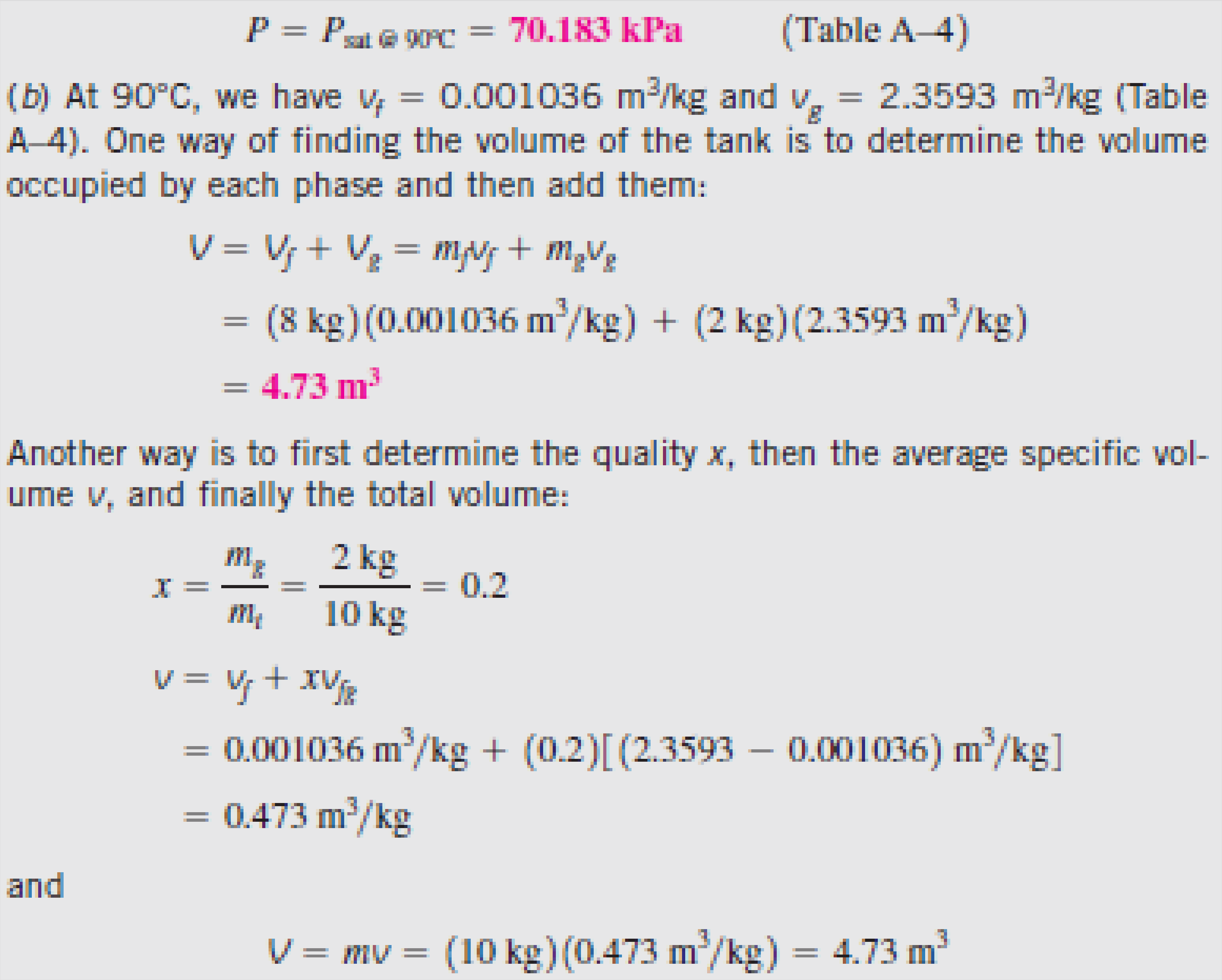
EXAMPLE 3–4 Pressure and Volume of a Saturated Mixture

A rigid tank contains 10 kg of water at 90°C. If 8 kg of the water is in the liquid form and the rest is in the vapor form, determine (*a*) the pressure in the tank and (*b*) the volume of the tank.

Solution A rigid tank contains saturated mixture. The pressure and the volume of the tank are to be determined.

Analysis (*a*) The state of the saturated liquid–vapor mixture is shown in Fig. 3–38. Since the two phases coexist in equilibrium, we have a saturated mixture, and the pressure must be the saturation pressure at the given temperature:





$$P = P_{\mathrm{sat\,@\,90^\circ C}} = \mathbf{70.183\ kPa} \qquad \text{(Table A–4)}$$

(*b*) At 90°C, we have $v_f = 0.001036\ \mathrm{m^3/kg}$ and $v_g = 2.3593\ \mathrm{m^3/kg}$ (Table A–4). One way of finding the volume of the tank is to determine the volume occupied by each phase and then add them:

$$\begin{aligned} V &= V_f + V_g = m_f v_f + m_g v_g \\ &= (8\ \mathrm{kg})(0.001036\ \mathrm{m^3/kg}) + (2\ \mathrm{kg})(2.3593\ \mathrm{m^3/kg}) \\ &= \mathbf{4.73\ m^3} \end{aligned}$$

Another way is to first determine the quality x, then the average specific volume v, and finally the total volume:

$$x = \frac{m_g}{m_t} = \frac{2\ \mathrm{kg}}{10\ \mathrm{kg}} = 0.2$$

$$\begin{aligned} v &= v_f + x v_{fg} \\ &= 0.001036\ \mathrm{m^3/kg} + (0.2)[(2.3593 - 0.001036)\ \mathrm{m^3/kg}] \\ &= 0.473\ \mathrm{m^3/kg} \end{aligned}$$

and

$$V = mv = (10\ \mathrm{kg})(0.473\ \mathrm{m^3/kg}) = 4.73\ \mathrm{m^3}$$

EXAMPLE 3–5 Properties of Saturated Liquid–Vapor Mixture

An 80-L vessel contains 4 kg of refrigerant-134a at a pressure of 160 kPa. Determine (*a*) the temperature, (*b*) the quality, (*c*) the enthalpy of the refrigerant, and (*d*) the volume occupied by the vapor phase.

Solution A vessel is filled with refrigerant-134a. Some properties of the refrigerant are to be determined.

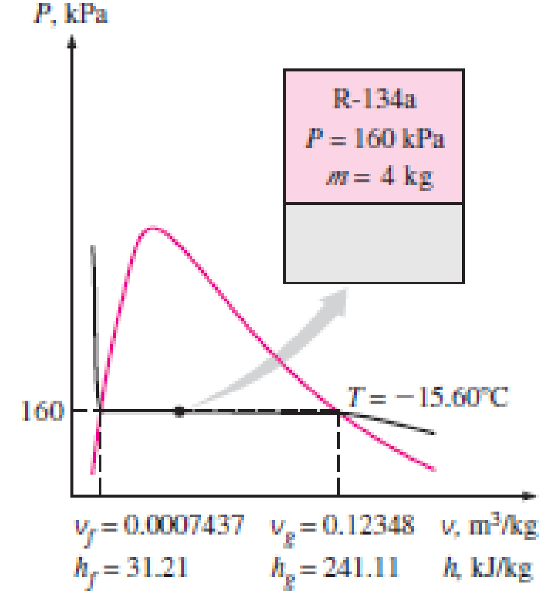
$$v = \frac{V}{m} = \frac{0.080\ \mathrm{m^3}}{4\ \mathrm{kg}} = 0.02\ \mathrm{m^3/kg}$$

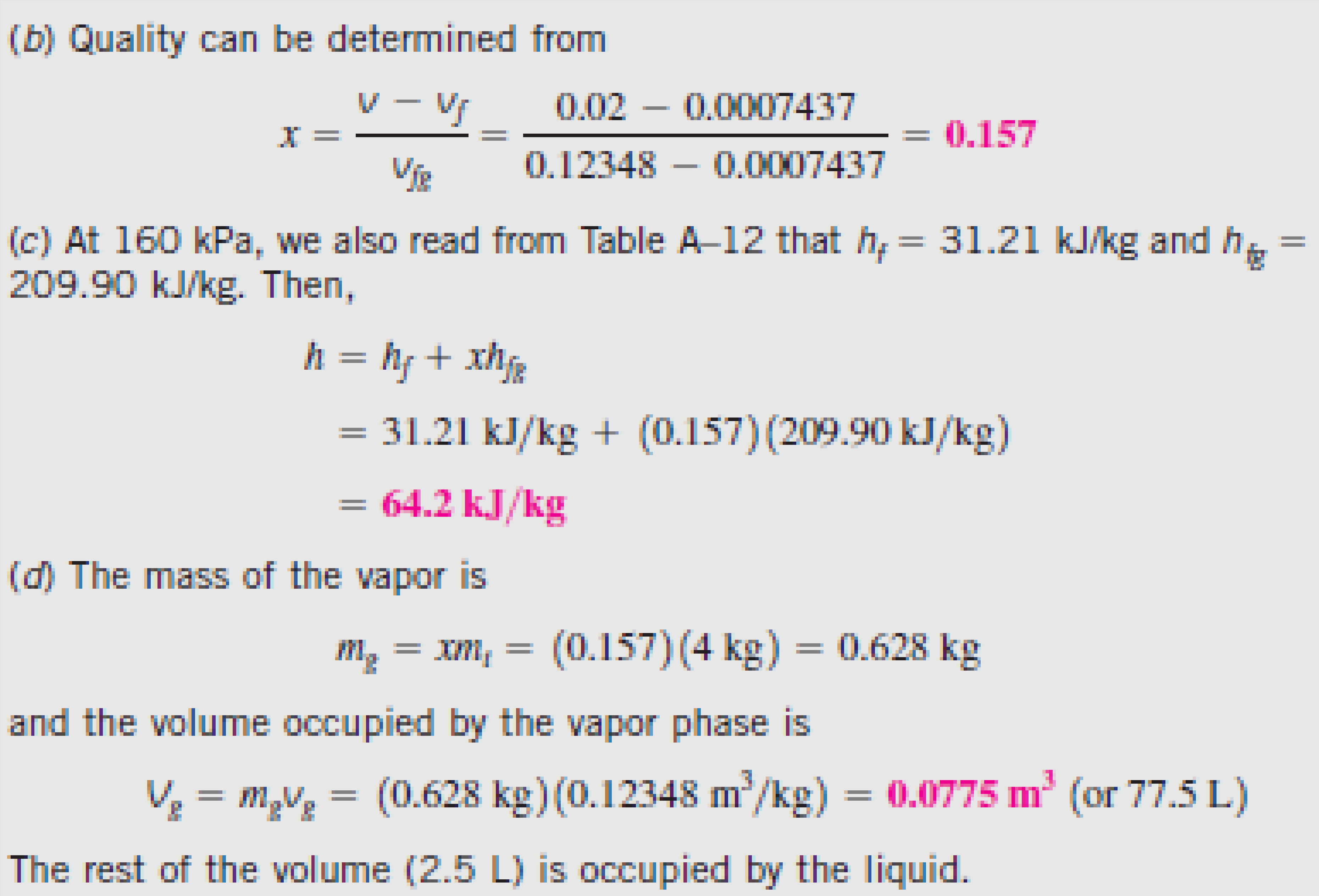
At 160 kPa, we read

$$\begin{aligned} v_f &= 0.0007437\ \mathrm{m^3/kg} \\ v_g &= 0.12348\ \mathrm{m^3/kg} \end{aligned} \qquad \text{(Table A–12)}$$

Obviously, $v_f < v < v_g$, and, the refrigerant is in the saturated mixture region. Thus, the temperature must be the saturation temperature at the specified pressure:

$$T = T_{\mathrm{sat\ @\ 160\ kPa}} = \mathbf{-15.60°C}$$





(*b*) Quality can be determined from

$$x = \frac{v - v_f}{v_{fg}} = \frac{0.02 - 0.0007437}{0.12348 - 0.0007437} = \mathbf{0.157}$$

(*c*) At 160 kPa, we also read from Table A–12 that $h_f = 31.21$ kJ/kg and $h_{fg} =$ 209.90 kJ/kg. Then,

$$\begin{aligned} h &= h_f + xh_{fg} \\ &= 31.21\ \text{kJ/kg} + (0.157)(209.90\ \text{kJ/kg}) \\ &= \mathbf{64.2\ kJ/kg} \end{aligned}$$

(*d*) The mass of the vapor is

$$m_g = xm_t = (0.157)(4\ \text{kg}) = 0.628\ \text{kg}$$

and the volume occupied by the vapor phase is

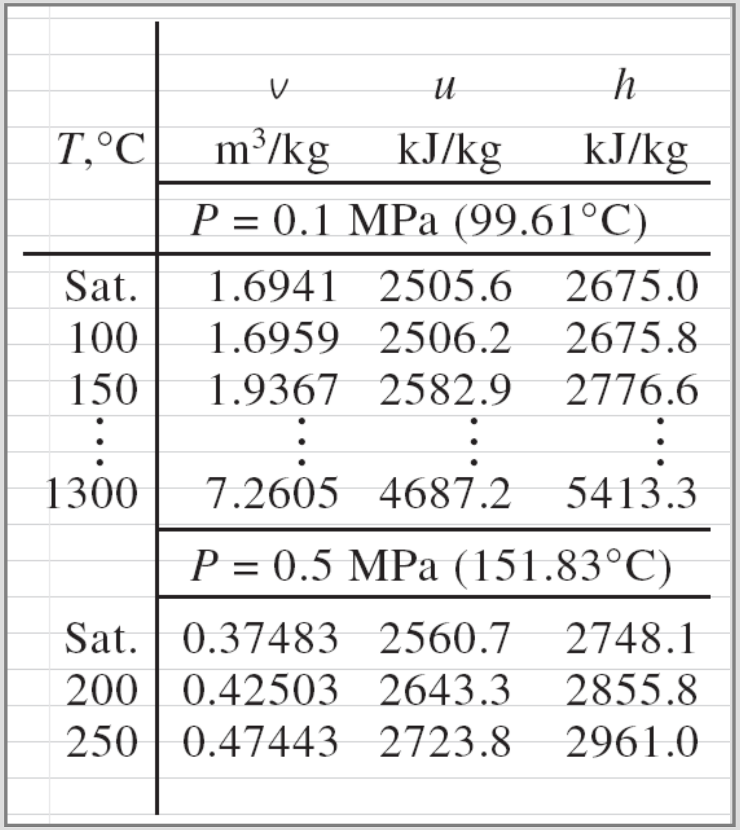
$$V_g = m_g v_g = (0.628\ \text{kg})(0.12348\ \text{m}^3/\text{kg}) = \mathbf{0.0775\ m^3}\ (\text{or } 77.5\ \text{L})$$

The rest of the volume (2.5 L) is occupied by the liquid.

Superheated Vapor

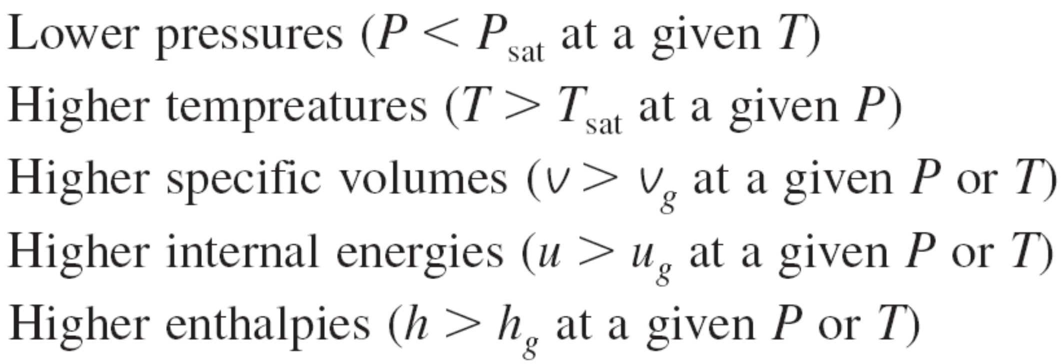
In the region to the right of the saturated vapor line and at temperatures above the critical point temperature, a substance exists as superheated vapor.

In this region, temperature and pressure are independent properties.



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

Compared to saturated vapor, superheated vapor is characterized by



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

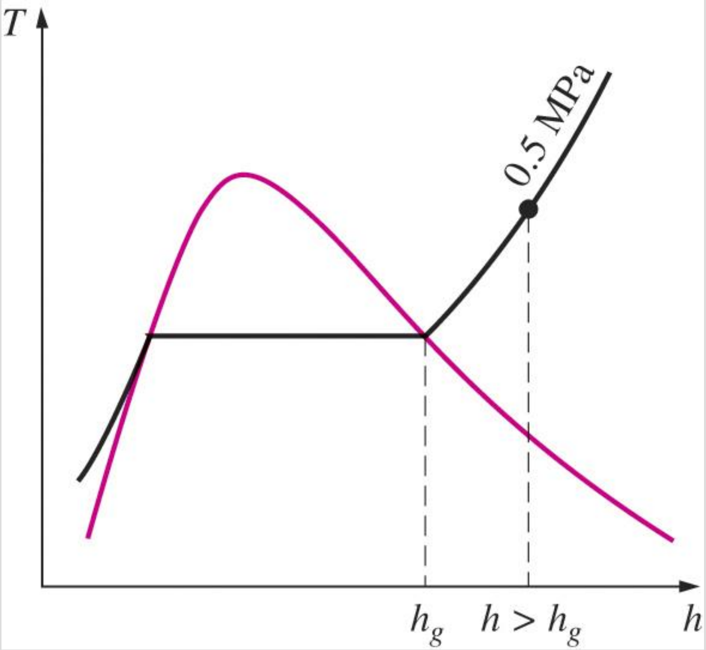
Higher tempreatures ($T > T_{\mathrm{sat}}$ at a given P)

Higher specific volumes ($v > v_g$ at a given P or T)

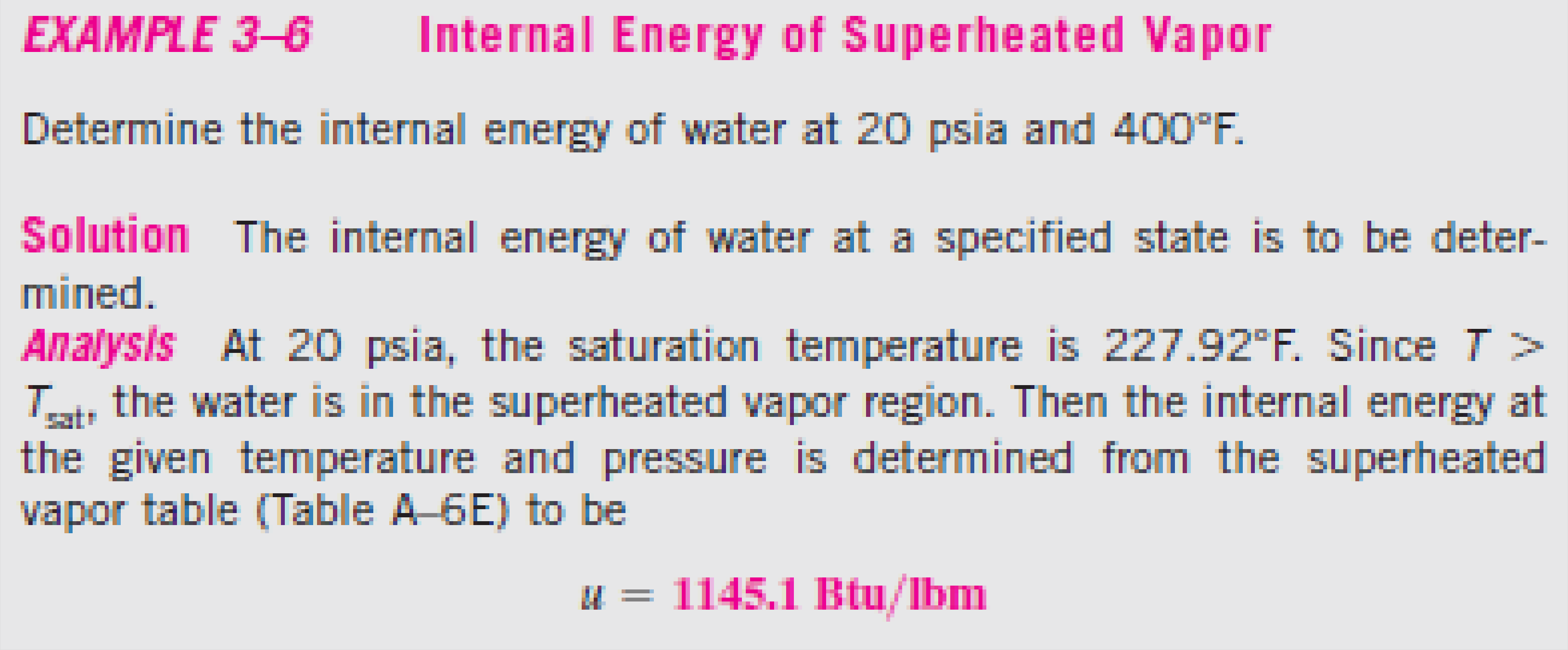
Higher internal energies ($u > u_g$ at a given P or T)

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.



EXAMPLE 3–6 **Internal Energy of Superheated Vapor**

Determine the internal energy of water at 20 psia and 400°F.

Solution The internal energy of water at a specified state is to be determined.

Analysis At 20 psia, the saturation temperature is 227.92°F. Since $T > T_{\mathrm{sat}}$, the water is in the superheated vapor region. Then the internal energy at the given temperature and pressure is determined from the superheated vapor table (Table A–6E) to be

$$u = \mathbf{1145.1\ Btu/lbm}$$

EXAMPLE 3–7 Temperature of Superheated Vapor

Determine the temperature of water at a state of $P = 0.5$ MPa and $h = 2890$ kJ/kg.

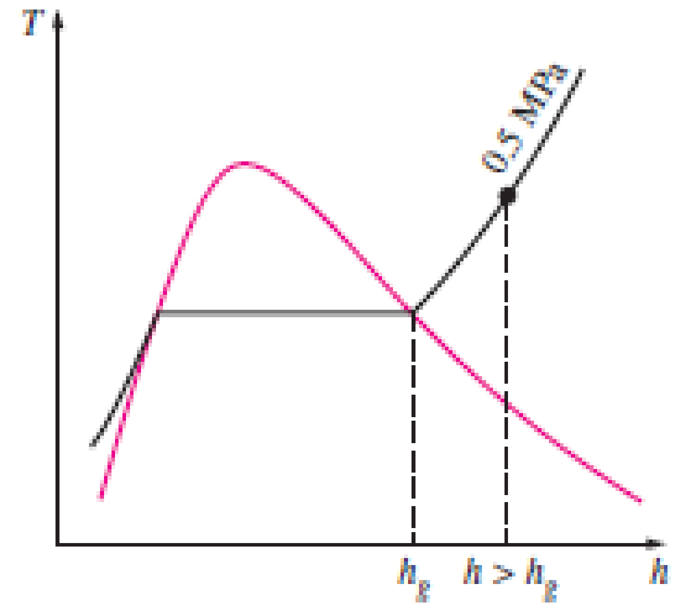
Solution The temperature of water at a specified state is to be determined.

Analysis At 0.5 MPa, the enthalpy of saturated water vapor is $h_g = 2748.1$ kJ/kg. Since $h > h_g$, as shown in Fig. 3–41, we again have superheated vapor. Under 0.5 MPa in Table A–6 we read

T, °C	h, kJ/kg
200	2855.8
250	2961.0

Obviously, the temperature is between 200 and 250°C. By linear interpolation it is determined to be

$$T = \mathbf{216.3°C}$$



Compressed Liquid

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

$y \cong y_{f\,@\,T}$ ***y*** → *v*, *u*, or *h*

A more accurate relation for *h*

$$h \cong h_{f\,@\,T} + v_{f\,@\,T}\,(P - P_{\text{sat}\,@\,T})$$

Compressed liquid is characterized by

- Higher pressures ($P > P_{\text{sat}}$ at a given T)
- Lower tempreatures ($T < T_{\text{sat}}$ 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)

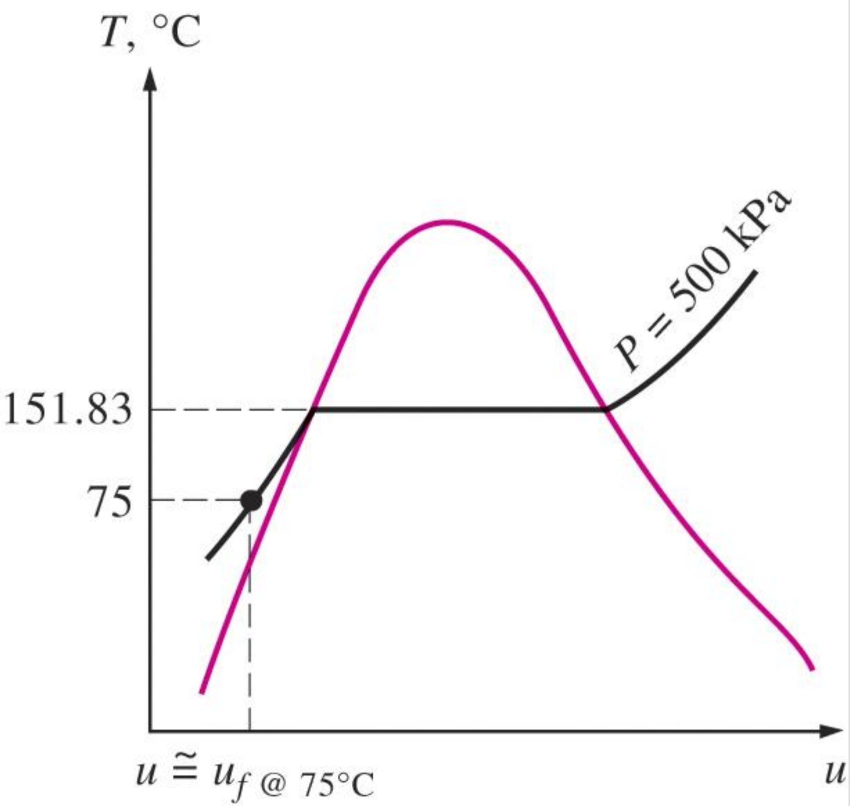
Given: P and T

$$v \cong v_{f\,@T}$$
$$u \cong u_{f\,@T}$$
$$h \cong h_{f\,@T}$$

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

At a given *P* and *T*, a pure substance will exist as a compressed liquid if

$$T < T_{\text{sat}\,@\,P}$$



EXAMPLE 3–8 Approximating Compressed Liquid as Saturated Liquid

Determine the internal energy of compressed liquid water at 80°C and 5 MPa, using (*a*) data from the compressed liquid table and (*b*) saturated liquid data. What is the error involved in the second case?

Solution The exact and approximate values of the internal energy of liquid water are to be determined.

Analysis At 80°C, the saturation pressure of water is 47.416 kPa, and since 5 MPa > P_{sat}, we obviously have compressed liquid, as shown in Fig. 3–43.

(*a*) From the compressed liquid table (Table A–7)

$$\left.\begin{aligned} P &= 5 \text{ MPa} \\ T &= 80°\text{C} \end{aligned}\right\} \quad u = \mathbf{333.82\ kJ/kg}$$

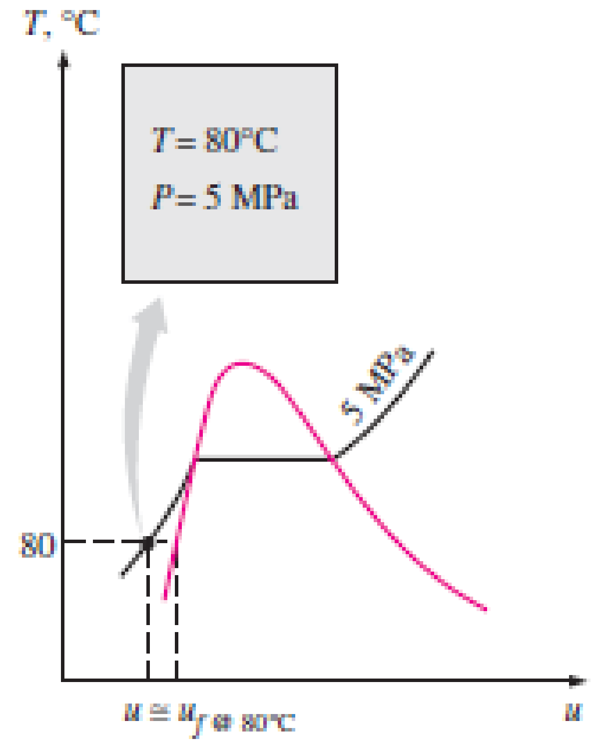
(*b*) From the saturation table (Table A–4), we read

$$u \cong u_{f\,@\,80°\text{C}} = \mathbf{334.97\ kJ/kg}$$

The error involved is

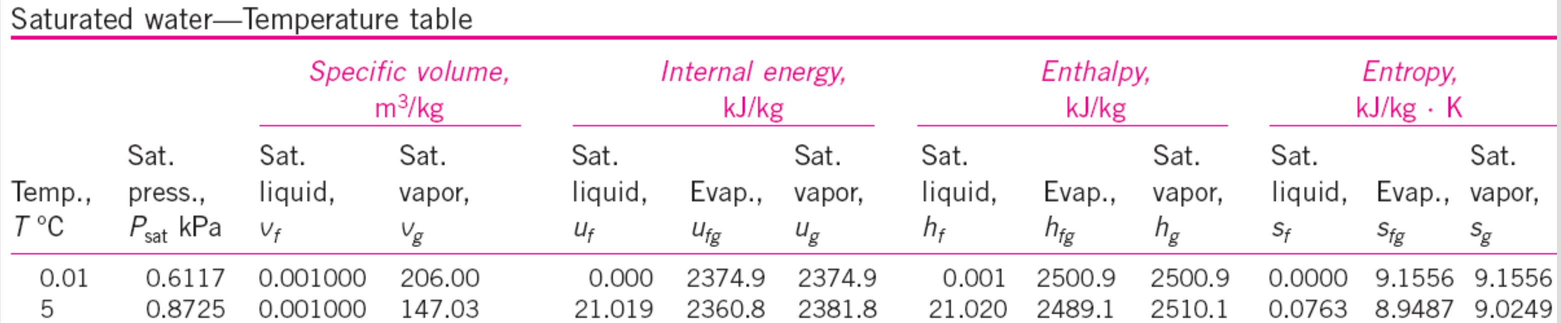
$$\frac{334.97 - 333.82}{333.82} \times 100 = \mathbf{0.34\%}$$

which is less than 1 percent.



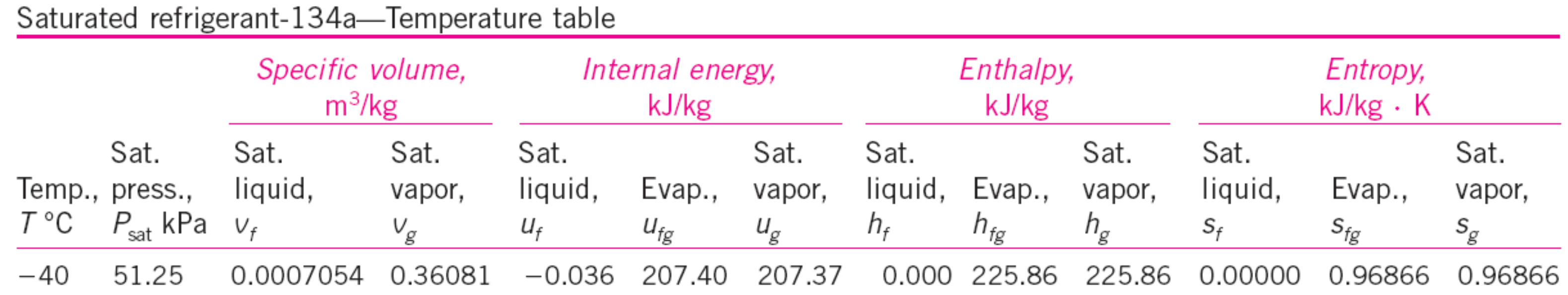
Reference State and Reference Values

- 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 referance state for water is 0.01° C and for R-134a is -40° 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.



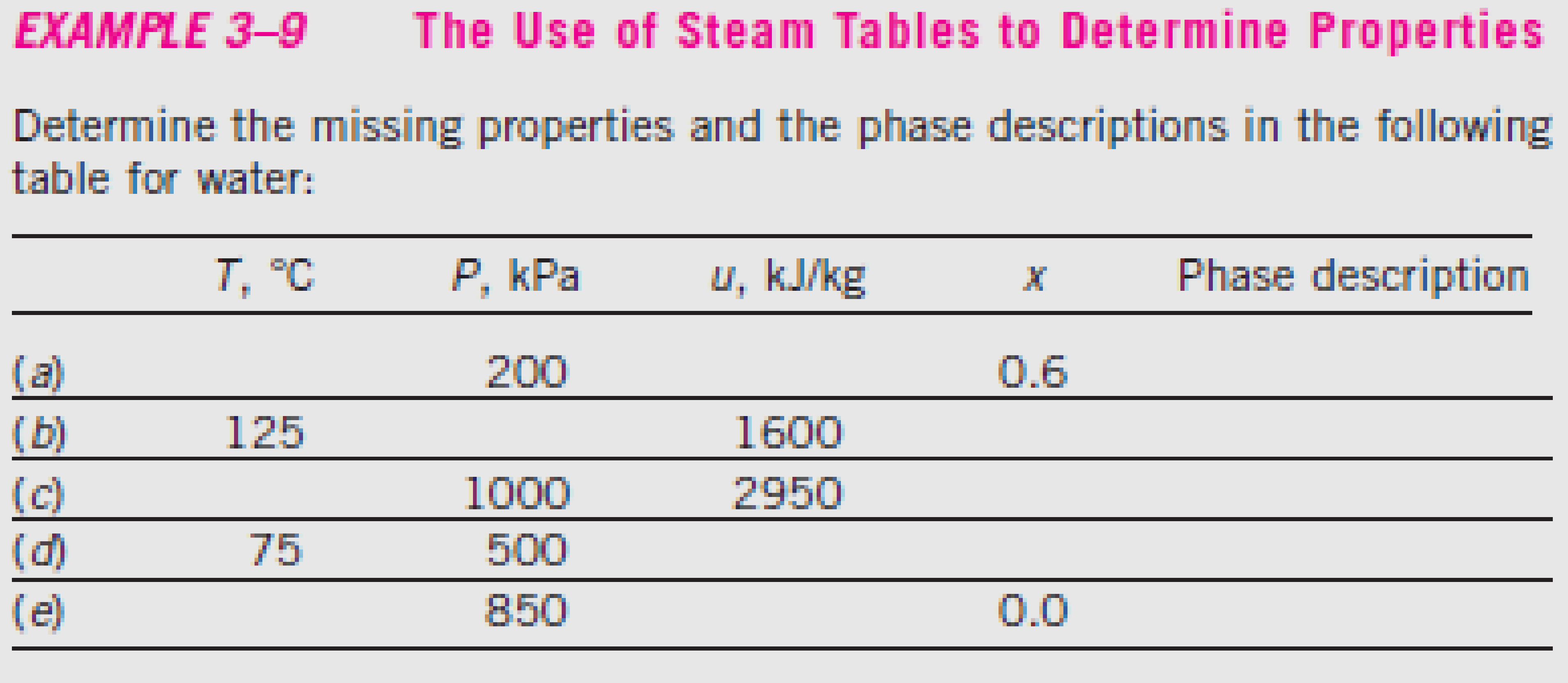
Saturated water—Temperature table

		Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg · K		
Temp., T °C	Sat. press., P_{sat} kPa	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

		Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg · K		
Temp., T °C	Sat. press., P_{sat} kPa	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



EXAMPLE 3–9 The Use of Steam Tables to Determine Properties

Determine the missing properties and the phase descriptions in the following table for water:

	T, °C	P, kPa	u, kJ/kg	x	Phase description
(*a*)		200		0.6	
(*b*)	125		1600		
(*c*)		1000	2950		
(*d*)	75	500			
(*e*)		850		0.0	

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.

$$P = R\left(\frac{T}{v}\right)$$

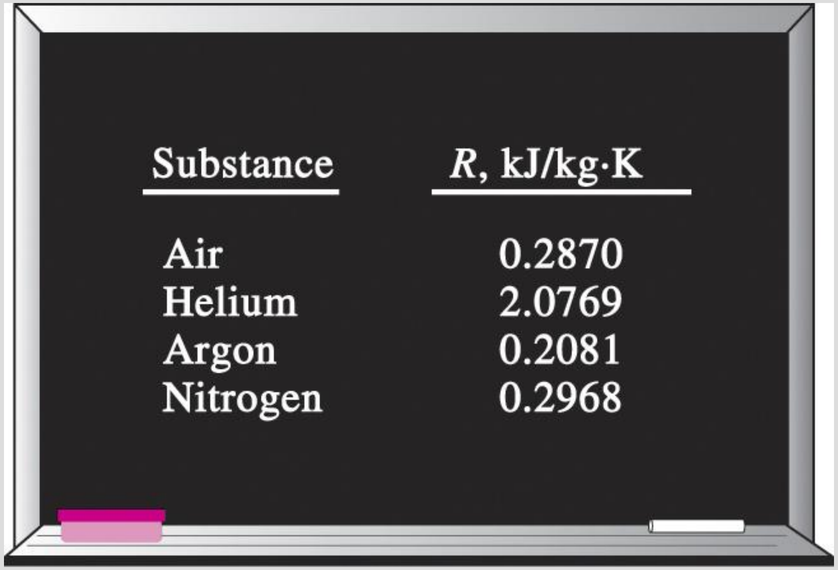
$$Pv = RT$$

Ideal gas equation of state

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

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 × Mole number

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

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

Ideal gas equation at two states for a fixed mass

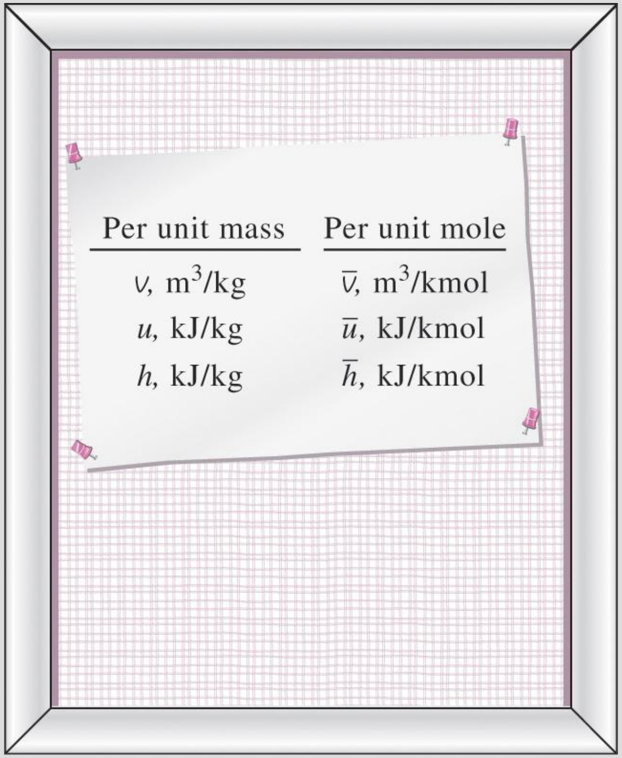
$$V = m\text{v} \longrightarrow PV = mRT$$

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

$$V = N\bar{\text{v}} \longrightarrow P\bar{\text{v}} = R_uT$$

Various expressions of ideal gas equation

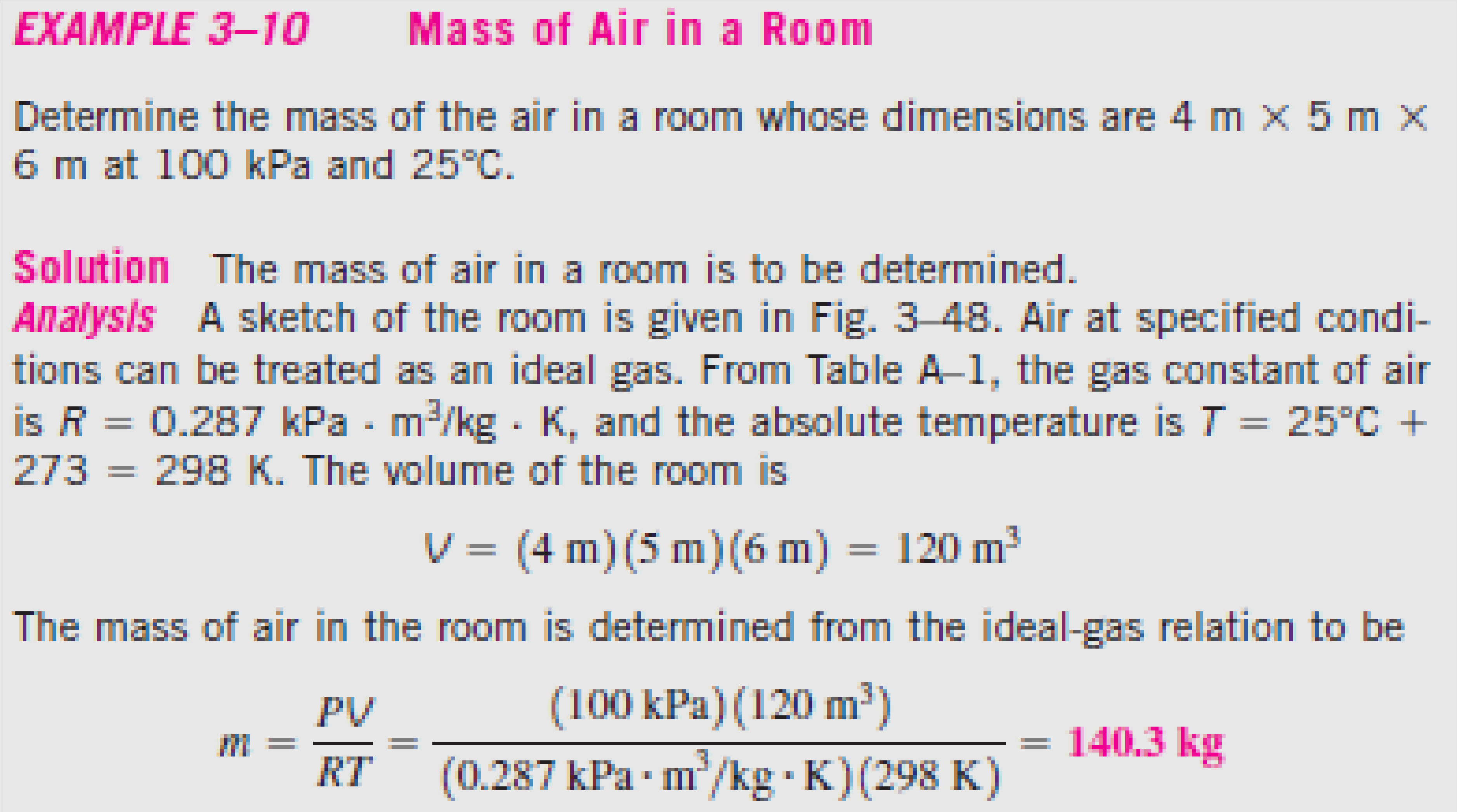
Real gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).



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

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

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



EXAMPLE 3–10 Mass of Air in a Room

Determine the mass of the air in a room whose dimensions are 4 m × 5 m × 6 m at 100 kPa and 25°C.

Solution The mass of air in a room is to be determined.

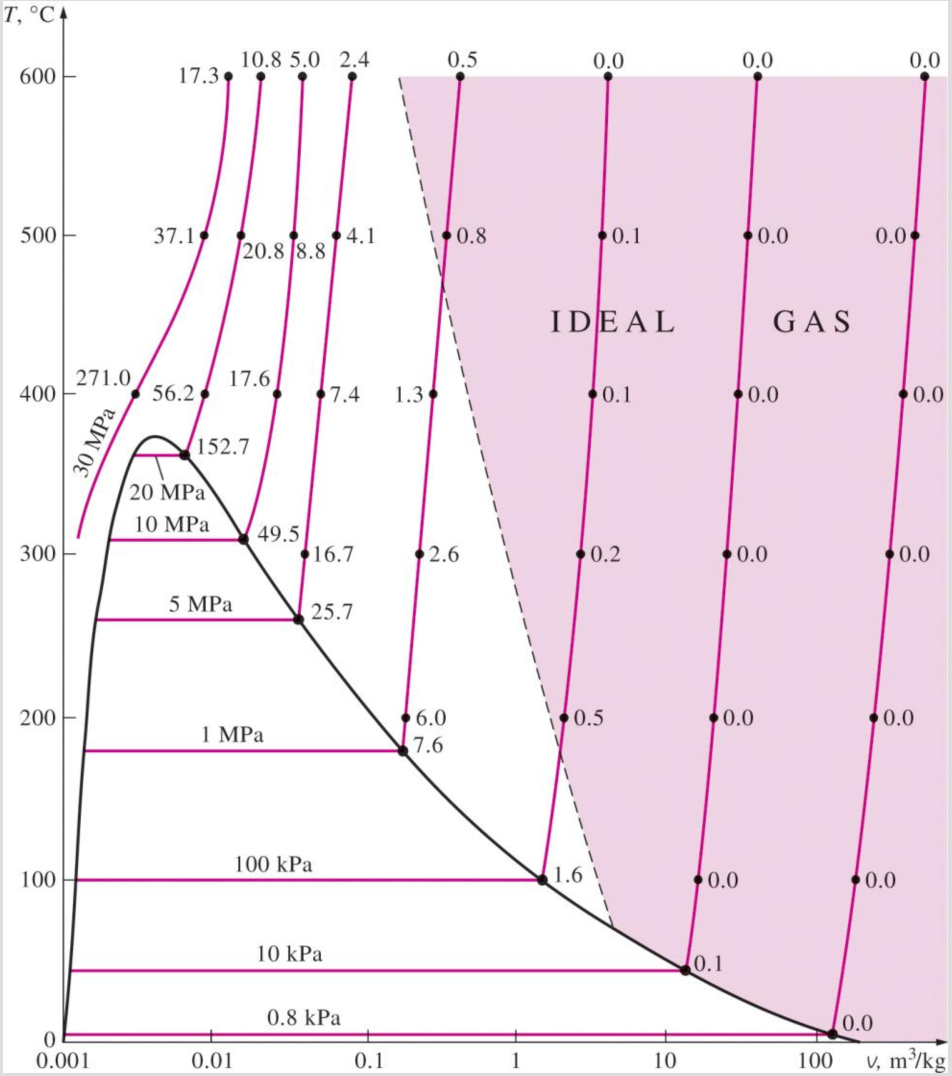
Analysis A sketch of the room is given in Fig. 3–48. Air at specified conditions can be treated as an ideal gas. From Table A–1, the gas constant of air is $R = 0.287\ \text{kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}$, and the absolute temperature is $T = 25°\text{C} + 273 = 298\ \text{K}$. The volume of the room is

$$V = (4\ \text{m})(5\ \text{m})(6\ \text{m}) = 120\ \text{m}^3$$

The mass of air in the room is determined from the ideal-gas relation to be

$$m = \frac{PV}{RT} = \frac{(100\ \text{kPa})(120\ \text{m}^3)}{(0.287\ \text{kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(298\ \text{K})} = \mathbf{140.3\ kg}$$

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 ($[|v_{\text{table}} - v_{\text{ideal}}|/v_{\text{table}}] \times 100$) 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.

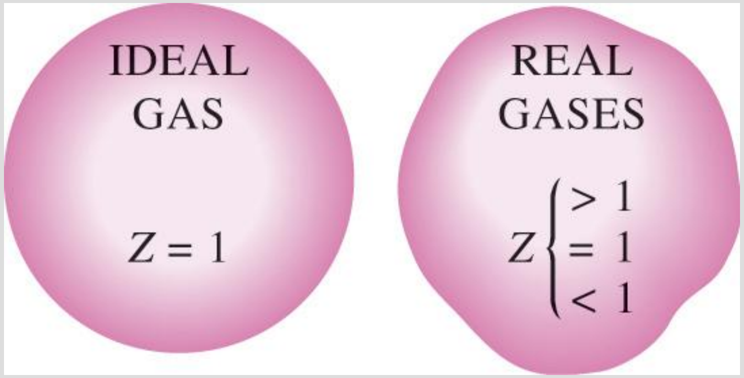
COMPRESSIBILITY FACTOR—A MEASURE OF DEVIATION FROM IDEAL-GAS BEHAVIOR

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

$$Pv = ZRT$$

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

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



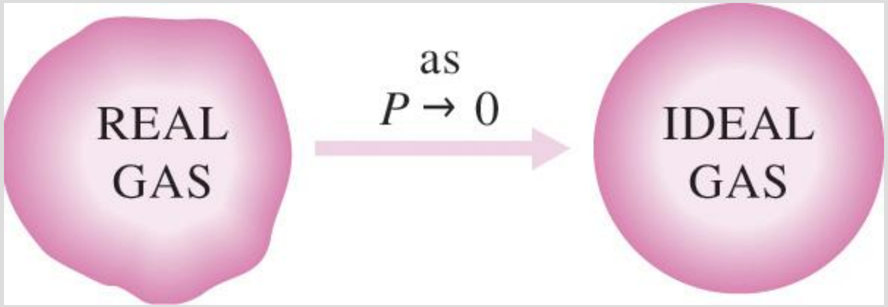
The compressibility factor is unity for ideal gases.

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.



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

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

Reduced pressure

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

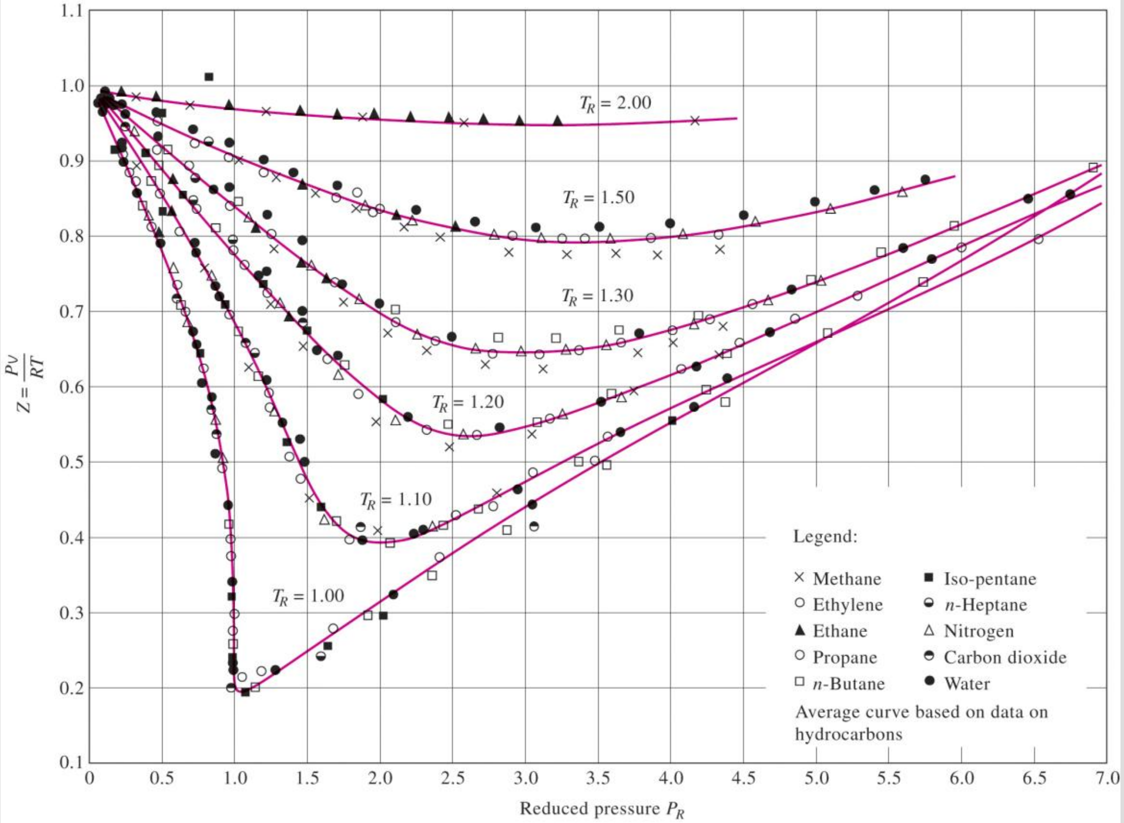
Reduced temperature

$$v_R = \frac{v_{actual}}{RT_{cr}/P_{cr}}$$

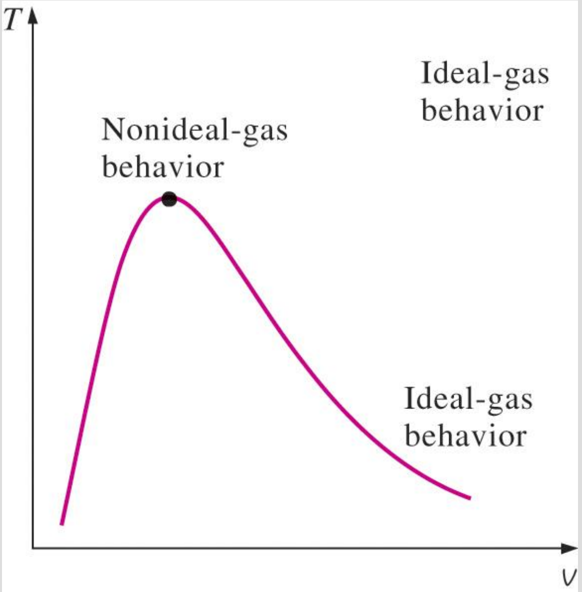
Pseudo-reduced specific volume

$$\left.\begin{array}{r} P_R = \dfrac{P}{P_{cr}} \\[2ex] v_R = \dfrac{v}{RT_{cr}/P_{cr}} \end{array}\right\} \begin{array}{l} Z = \ldots \\ \text{(Fig. A–15)} \end{array}$$

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



Comparison of *Z* factors for various gases.

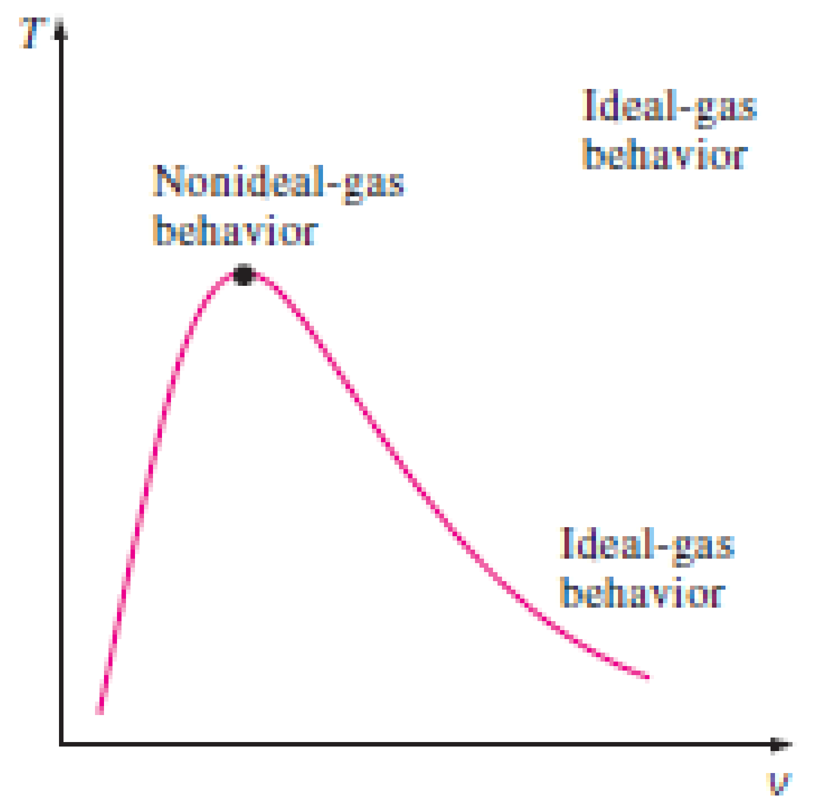


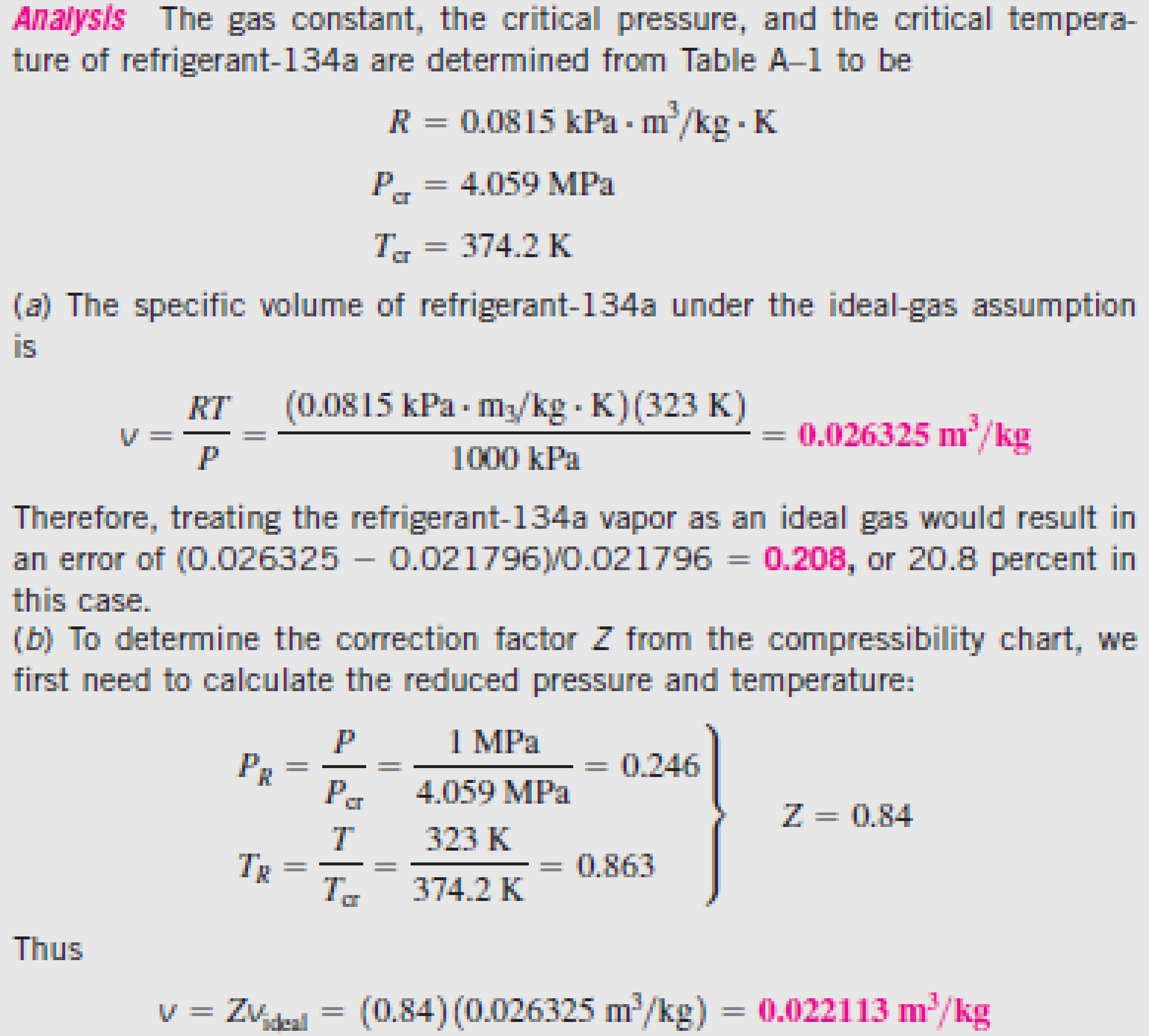
Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

EXAMPLE 3–11 The Use of Generalized Charts

Determine the specific volume of refrigerant-134a at 1 MPa and 50°C, using (*a*) the ideal-gas equation of state and (*b*) the generalized compressibility chart. Compare the values obtained to the actual value of 0.021796 m^3/kg and determine the error involved in each case.

Solution The specific volume of refrigerant-134a is to be determined assuming ideal- and nonideal-gas behavior.





Analysis The gas constant, the critical pressure, and the critical temperature of refrigerant-134a are determined from Table A–1 to be

$$R = 0.0815\ \mathrm{kPa \cdot m^3/kg \cdot K}$$

$$P_{cr} = 4.059\ \mathrm{MPa}$$

$$T_{cr} = 374.2\ \mathrm{K}$$

(*a*) The specific volume of refrigerant-134a under the ideal-gas assumption is

$$v = \frac{RT}{P} = \frac{(0.0815\ \mathrm{kPa \cdot m_3/kg \cdot K})(323\ \mathrm{K})}{1000\ \mathrm{kPa}} = \mathbf{0.026325\ m^3/kg}$$

Therefore, treating the refrigerant-134a vapor as an ideal gas would result in an error of (0.026325 − 0.021796)/0.021796 = **0.208**, or 20.8 percent in this case.

(*b*) To determine the correction factor *Z* from the compressibility chart, we first need to calculate the reduced pressure and temperature:

$$\left.\begin{aligned} P_R &= \frac{P}{P_{cr}} = \frac{1\ \mathrm{MPa}}{4.059\ \mathrm{MPa}} = 0.246 \\ T_R &= \frac{T}{T_{cr}} = \frac{323\ \mathrm{K}}{374.2\ \mathrm{K}} = 0.863 \end{aligned}\right\} \quad Z = 0.84$$

Thus

$$v = Zv_{\mathrm{ideal}} = (0.84)(0.026325\ \mathrm{m^3/kg}) = \mathbf{0.022113\ m^3/kg}$$

EXAMPLE 3–12 Using Generalized Charts to Determine Pressure

Determine the pressure of water vapor at 600°F and 0.51431 ft^3/lbm, using (*a*) the steam tables, (*b*) the ideal-gas equation, and (*c*) the generalized compressibility chart.

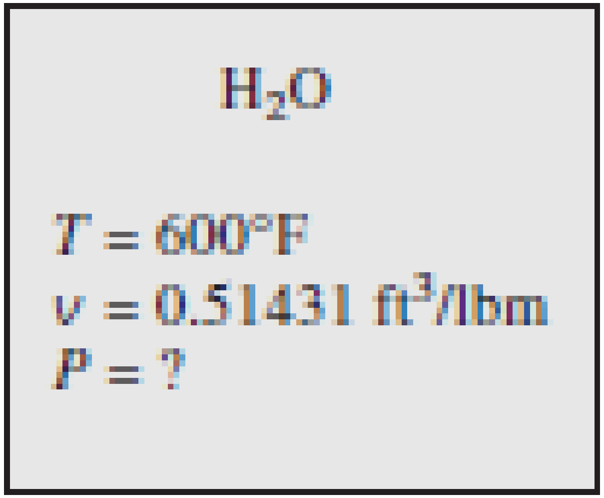
Solution The pressure of water vapor is to be determined in three different ways.

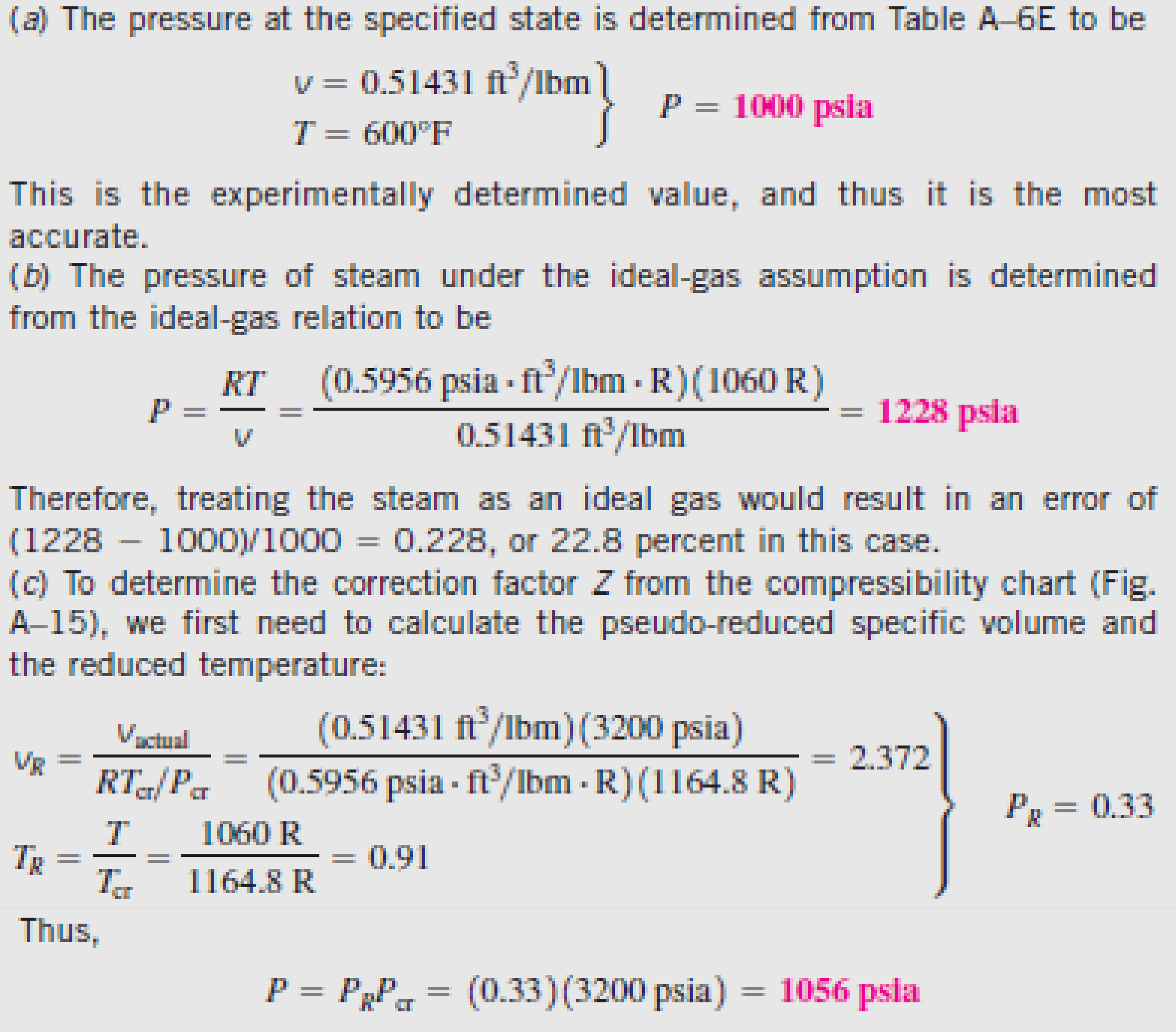
Analysis A sketch of the system is given in Fig. 3–55. The gas constant, the critical pressure, and the critical temperature of steam are determined from Table A–1E to be

$$R = 0.5956 \text{ psia} \cdot \text{ft}^3/\text{lbm} \cdot \text{R}$$

$$P_{cr} = 3200 \text{ psia}$$

$$T_{cr} = 1164.8 \text{ R}$$





(*a*) The pressure at the specified state is determined from Table A–6E to be

$$\left.\begin{aligned} v &= 0.51431\ \text{ft}^3/\text{lbm} \\ T &= 600°\text{F} \end{aligned}\right\} \quad P = \mathbf{1000\ psia}$$

This is the experimentally determined value, and thus it is the most accurate.

(*b*) The pressure of steam under the ideal-gas assumption is determined from the ideal-gas relation to be

$$P = \frac{RT}{v} = \frac{(0.5956\ \text{psia}\cdot\text{ft}^3/\text{lbm}\cdot\text{R})(1060\ \text{R})}{0.51431\ \text{ft}^3/\text{lbm}} = \mathbf{1228\ psia}$$

Therefore, treating the steam as an ideal gas would result in an error of (1228 − 1000)/1000 = 0.228, or 22.8 percent in this case.

(*c*) To determine the correction factor *Z* from the compressibility chart (Fig. A–15), we first need to calculate the pseudo-reduced specific volume and the reduced temperature:

$$\left.\begin{aligned} v_R &= \frac{v_{\text{actual}}}{RT_{\text{cr}}/P_{\text{cr}}} = \frac{(0.51431\ \text{ft}^3/\text{lbm})(3200\ \text{psia})}{(0.5956\ \text{psia}\cdot\text{ft}^3/\text{lbm}\cdot\text{R})(1164.8\ \text{R})} = 2.372 \\ T_R &= \frac{T}{T_{\text{cr}}} = \frac{1060\ \text{R}}{1164.8\ \text{R}} = 0.91 \end{aligned}\right\} \quad P_R = 0.33$$

Thus,

$$P = P_R P_{\text{cr}} = (0.33)(3200\ \text{psia}) = \mathbf{1056\ psia}$$

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
Berthelet
Redlich-Kwang
Beattie-Bridgeman
Benedict-Webb-Rubin
Strobridge
Virial

Van der Waals Equation of State

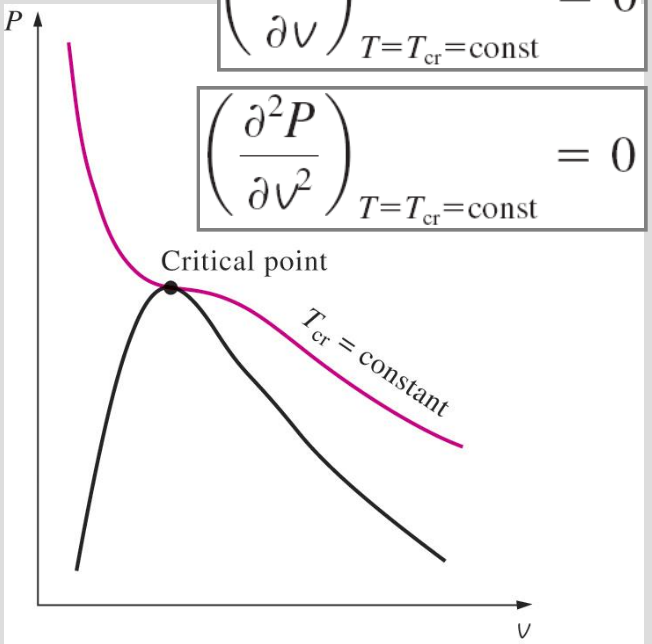
$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

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

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

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_{\mathrm{cr}}=\mathrm{const}} = 0$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_{\mathrm{cr}}=\mathrm{const}} = 0$$



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.

Beattie-Bridgeman Equation of State

$$P = \frac{R_u T}{\bar{v}^2}\left(1 - \frac{c}{\bar{v} T^3}\right)(\bar{v} + B) - \frac{A}{\bar{v}^2}$$

$$A = A_0\left(1 - \frac{a}{\bar{v}}\right) \qquad B = B_0\left(1 - \frac{b}{\bar{v}}\right)$$

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

Benedict-Webb-Rubin Equation of State

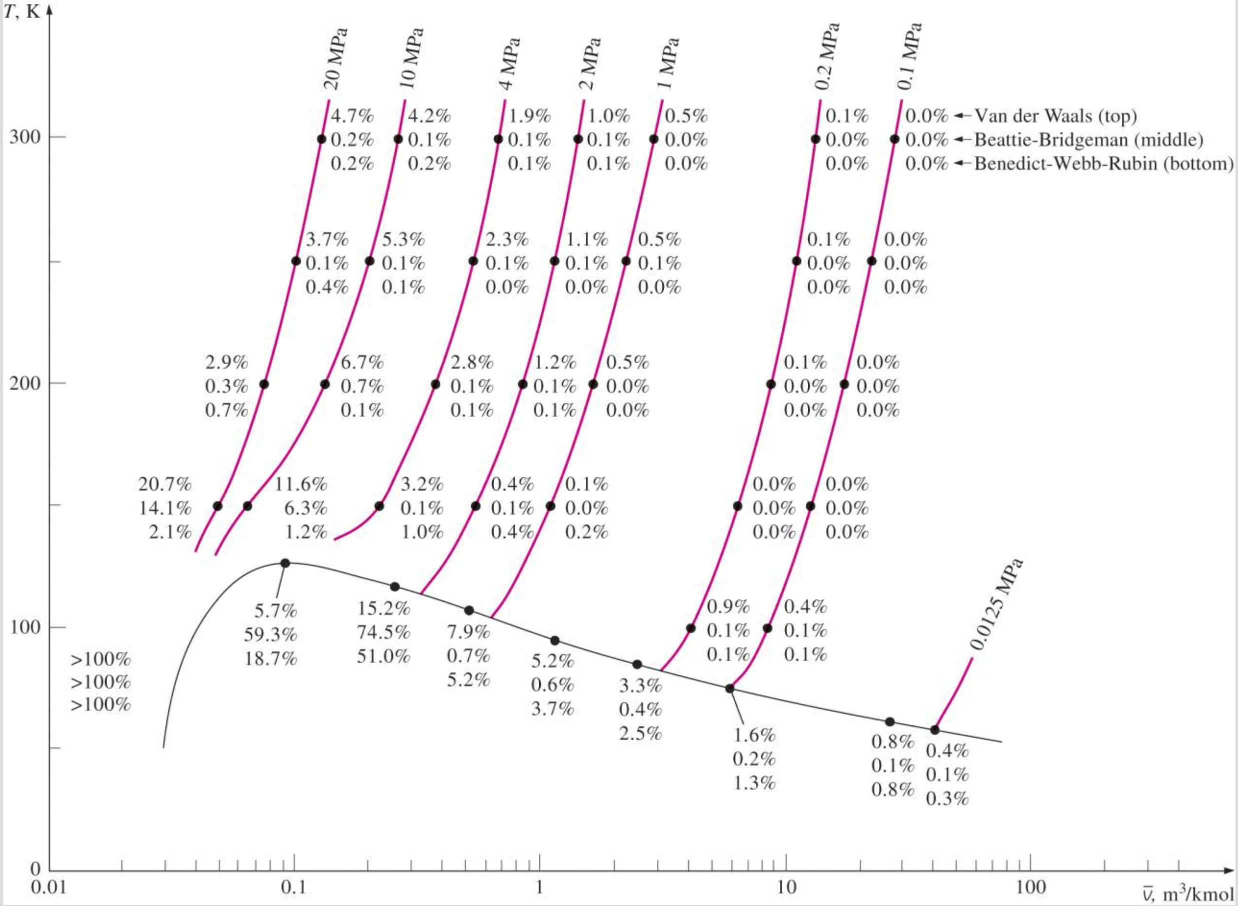
$$P = \frac{R_u T}{\bar{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2}\right)\frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2}\left(1 + \frac{\gamma}{\bar{v}^2}\right)e^{-\gamma/\bar{v}^2}$$

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

Virial Equation of State

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

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



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

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.

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

EXAMPLE 3–13 Different Methods of Evaluating Gas Pressure

Predict the pressure of nitrogen gas at $T = 175$ K and $v = 0.00375$ m^3/kg on the basis of (*a*) the ideal-gas equation of state, (*b*) the van der Waals equation of state, (*c*) the Beattie-Bridgeman equation of state, and (*d*) the Benedict-Webb-Rubin equation of state. Compare the values obtained to the experimentally determined value of 10,000 kPa.

Solution The pressure of nitrogen gas is to be determined using four different equations of state.

Properties The gas constant of nitrogen gas is 0.2968 kPa · m^3/kg · K (Table A–1).

Analysis (*a*) Using the ideal-gas equation of state, the pressure is found to be

$$P = \frac{RT}{v} = \frac{(0.2968\ \text{kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})(175\ \text{K})}{0.00375\ \text{m}^3/\text{kg}} = \mathbf{13{,}851\ kPa}$$

which is in error by 38.5 percent.

(*b*) The van der Waals constants for nitrogen are determined from Eq. 3–23 to be

$$a = 0.175\ \text{m}^6\cdot\text{kPa/kg}^2$$

$$b = 0.00138\ \text{m}^3/\text{kg}$$

From Eq. 3–22,

$$P = \frac{RT}{v - b} - \frac{a}{v^2} = \mathbf{9471\ kPa}$$

which is in error by 5.3 percent.

(*c*) The constants in the Beattie-Bridgeman equation are determined from Table 3–4 to be

$$A = 102.29$$

$$B = 0.05378$$

$$c = 4.2 \times 10^4$$

Also, $\bar{v} = Mv$ = (28.013 kg/mol)(0.00375 m^3/kg) = 0.10505 m^3/kmol. Substituting these values into Eq. 3–24, we obtain

$$P = \frac{R_uT}{\bar{v}^2}\left(1 - \frac{c}{\bar{v}T^3}\right)(\bar{v} + B) - \frac{A}{\bar{v}^2} = \mathbf{10{,}110\ kPa}$$

which is in error by 1.1 percent.

(*d*) The constants in the Benedict-Webb-Rubin equation are determined from Table 3–4 to be

$$\begin{array}{ll} a = 2.54 & A_0 = 106.73 \\ b = 0.002328 & B_0 = 0.04074 \\ c = 7.379 \times 10^4 & C_0 = 8.164 \times 10^5 \\ \alpha = 1.272 \times 10^{-4} & \gamma = 0.0053 \end{array}$$

Substituting these values into Eq. 3–26 gives

$$P = \frac{R_uT}{\bar{v}} + \left(B_0R_uT - A_0 - \frac{C_0}{T^2}\right)\frac{1}{\bar{v}^2} + \frac{bR_uT - a}{\bar{v}^3}$$

$$+ \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3T^2}\left(1 + \frac{\gamma}{\bar{v}^2}\right)e^{-\gamma/\bar{v}^2}$$

$$= \mathbf{10{,}009\ kPa}$$

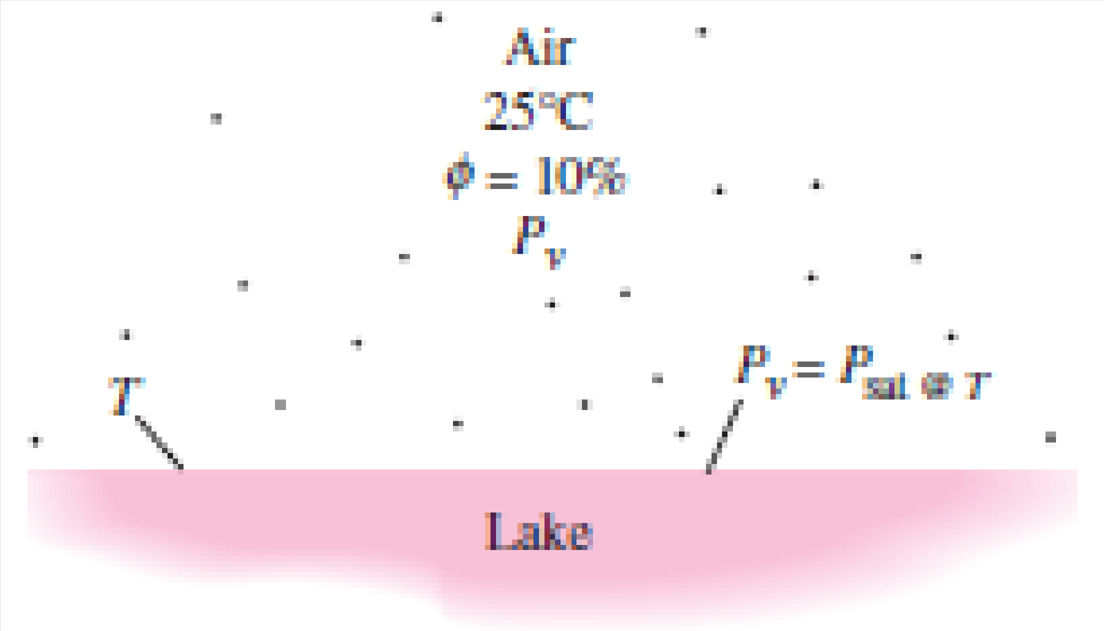
which is in error by only 0.09 percent. Thus, the accuracy of the Benedict-Webb-Rubin equation of state is rather impressive in this case.

EXAMPLE 3–14 Temperature Drop of a Lake Due to Evaporation

On a summer day, the air temperature over a lake is measured to be 25°C. Determine water temperature of the lake when phase equilibrium conditions are established between the water in the lake and the vapor in the air for relative humidities of 10, 80, and 100 percent for the air (Fig. 3–65).

Solution Air at a specified temperature is blowing over a lake. The equilibrium temperatures of water for three different cases are to be determined.

Analysis The saturation pressure of water at 25°C, from Table 3–1, is 3.17 kPa. Then the vapor pressures at relative humidities of 10, 80, and 100 percent are determined from Eq. 3–29 to be



Solution Air at a specified temperature is blowing over a lake. The equilibrium temperatures of water for three different cases are to be determined.

Analysis The saturation pressure of water at 25°C, from Table 3–1, is 3.17 kPa. Then the vapor pressures at relative humidities of 10, 80, and 100 percent are determined from Eq. 3–29 to be

$$\text{Relative humidity} = 10\%: \qquad P_{v1} = \phi_1 P_{\text{sat @ 25°C}} = 0.1 \times (3.17\text{ kPa}) = 0.317\text{ kPa}$$

$$\text{Relative humidity} = 80\%: \qquad P_{v2} = \phi_2 P_{\text{sat @ 25°C}} = 0.8 \times (3.17\text{ kPa}) = 2.536\text{ kPa}$$

$$\text{Relative humidity} = 100\%: \qquad P_{v3} = \phi_3 P_{\text{sat @25°C}} = 1.0 \times (3.17\text{ kPa}) = 3.17\text{ kPa}$$

The saturation temperatures corresponding to these pressures are determined from Table 3–1 (or Table A–5) by interpolation to be

$$T_1 = -8.0°\text{C} \quad T_2 = 21.2°\text{C} \quad \text{and} \quad T_3 = 25°\text{C}$$

Therefore, water will freeze in the first case even though the surrounding air is hot. In the last case the water temperature will be the same as the surrounding air temperature.

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