Chapter 3

PROPERTIES OF PURE SUBSTANCES

Thermodynamics: An Engineering Approach
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McGraw-Hill

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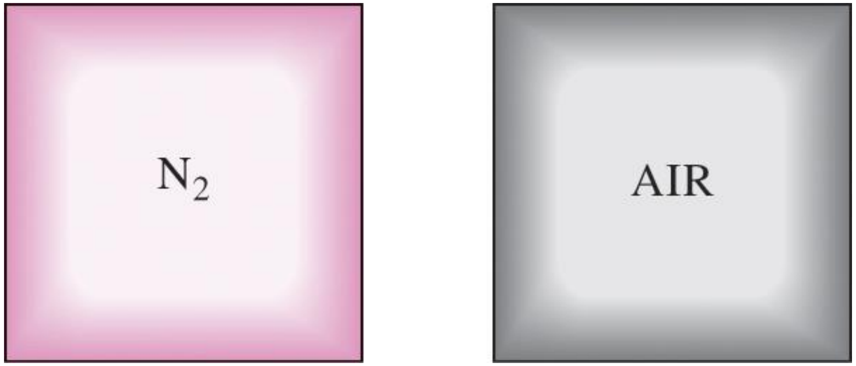
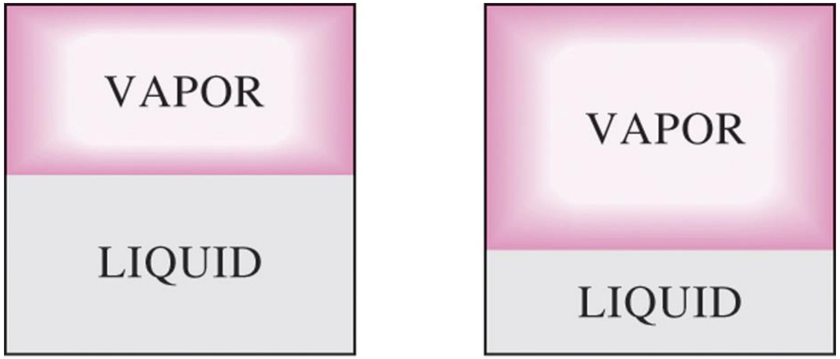
PURE SUBSTANCE

- **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.



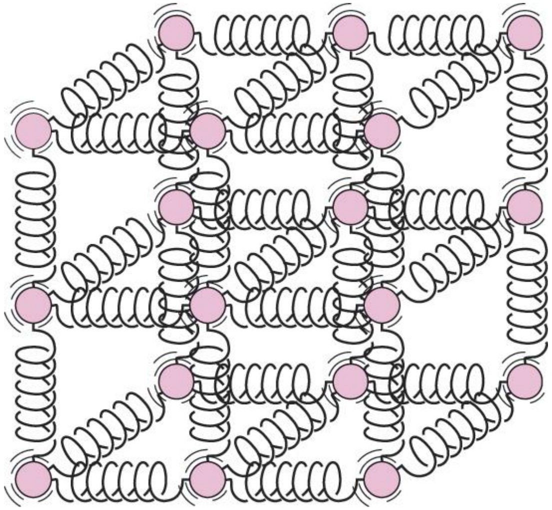
Nitrogen and gaseous air are pure substances.



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

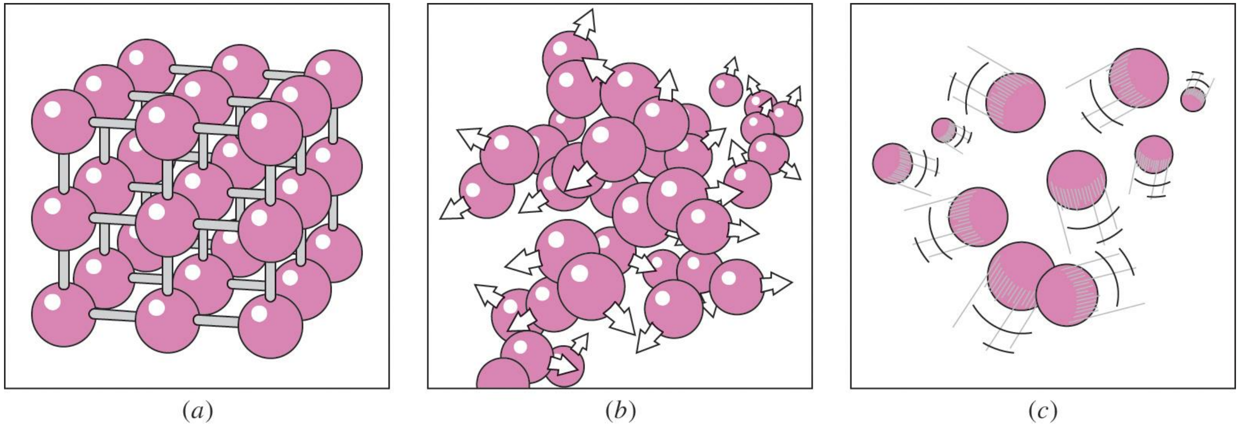
- **A mixture of liquid and gaseous water is a pure substance, but**
- **A mixture of liquid and gaseous air is not.**

PHASES OF A PURE SUBSTANCE



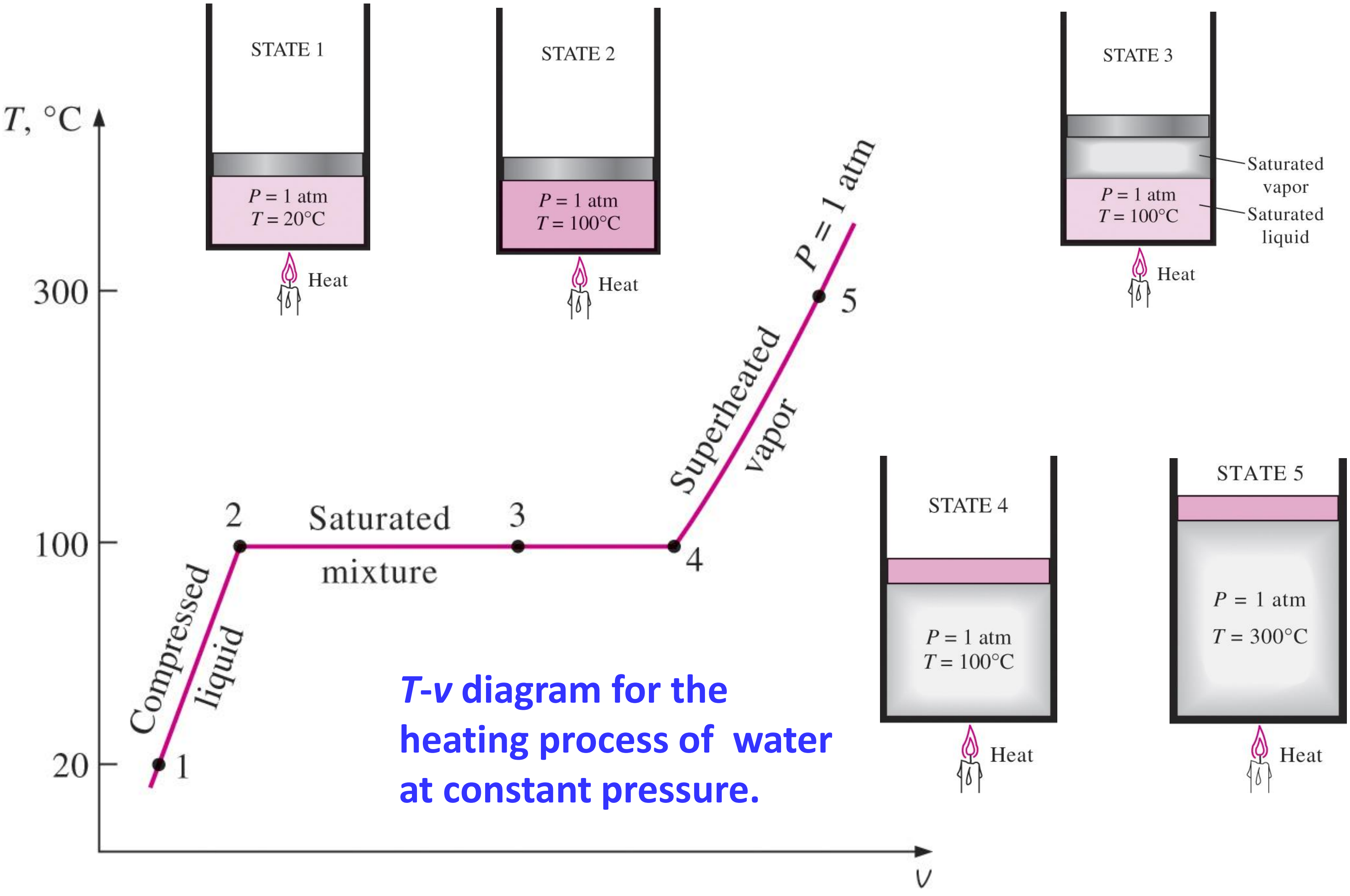
The molecules in a solid are kept at their positions by the large springlike intermolecular forces.

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.

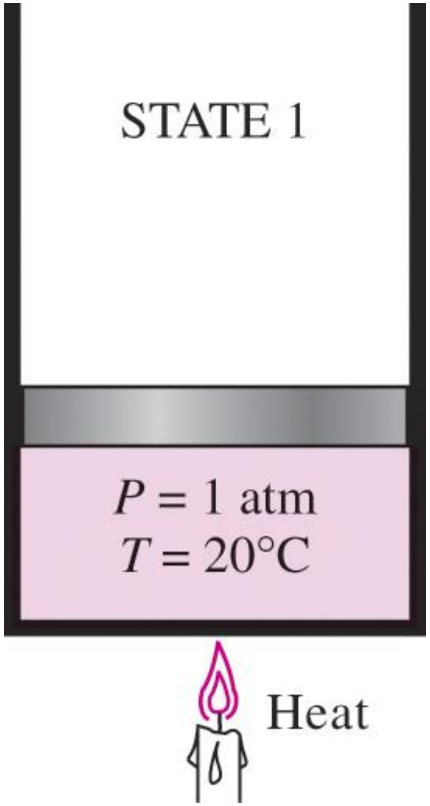
PHASE-CHANGE PROCESSES OF PURE SUBSTANCES



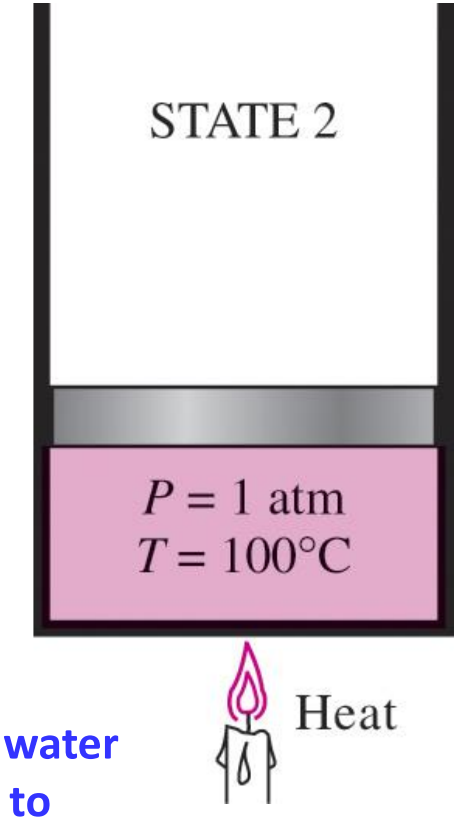
***T-v* diagram for the heating process of water at constant pressure.**

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.*

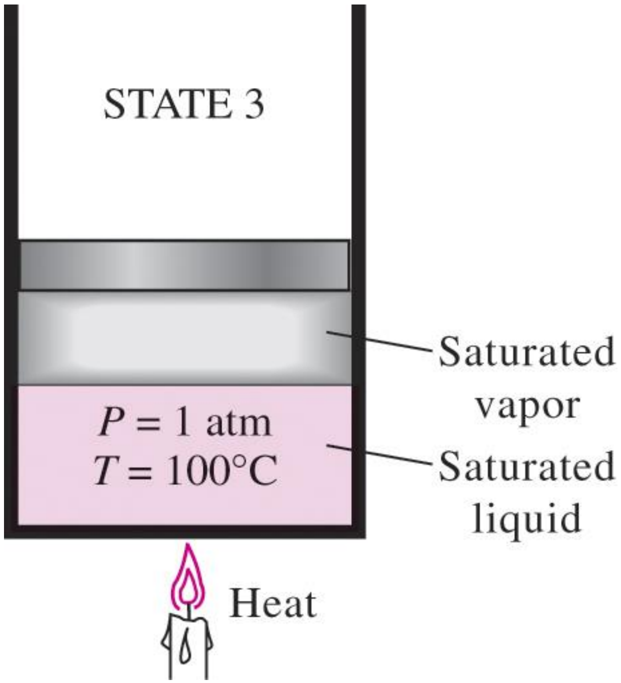


At 1 atm and 20°C, water exists in the liquid phase (*compressed liquid*).

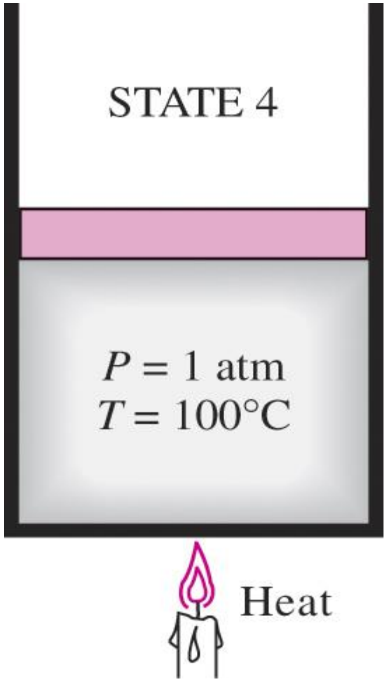


At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (*saturated liquid*).

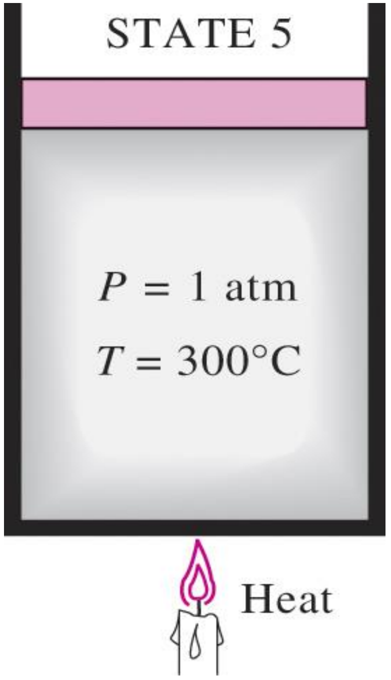
- **Saturated vapor**: A vapor that is *about to condense.*
- **Saturated liquid–vapor mixture**: The state at which the *liquid and vapor phases coexist* in equilibrium.
- **Superheated vapor**: A vapor that is *not about to condense* (i.e., not a saturated vapor).



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



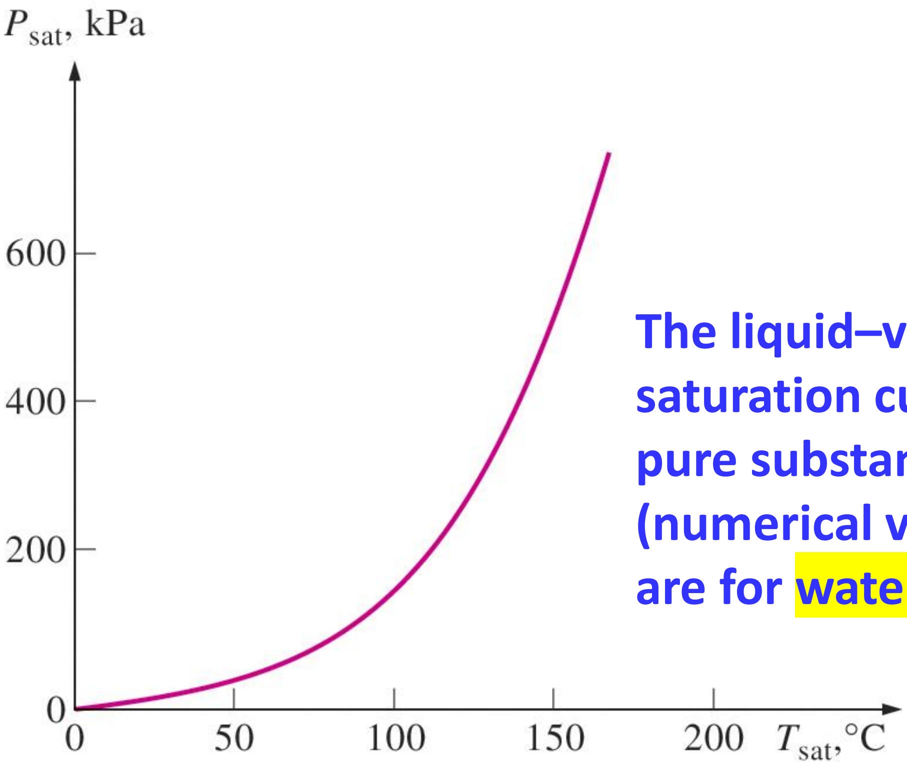
At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (*saturated vapor*).



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

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).

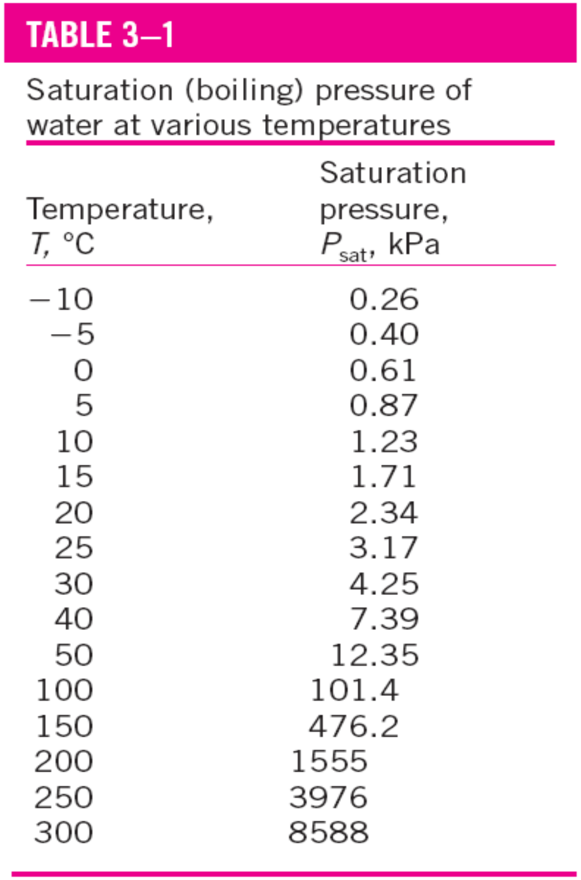


TABLE 3–1

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.

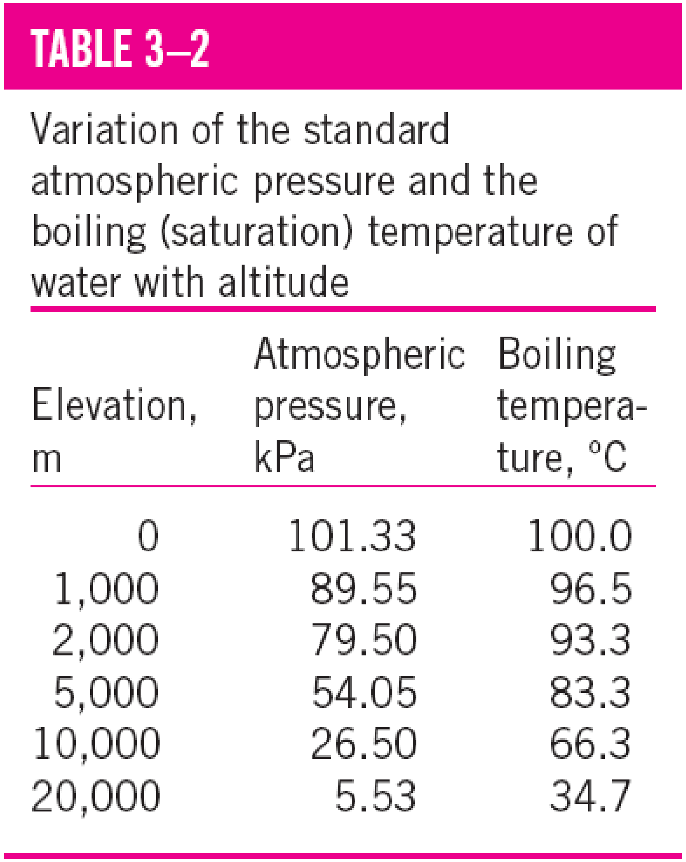


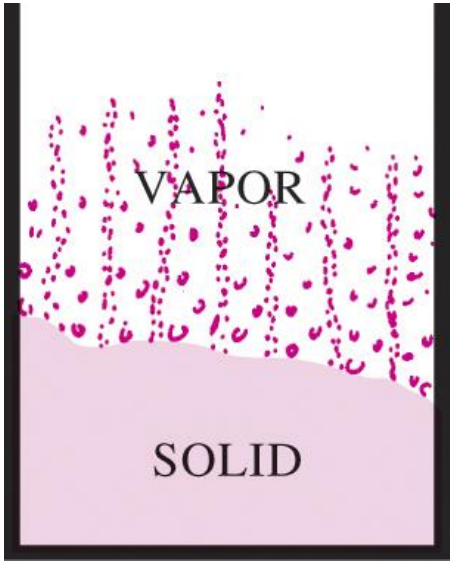
TABLE 3–2

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

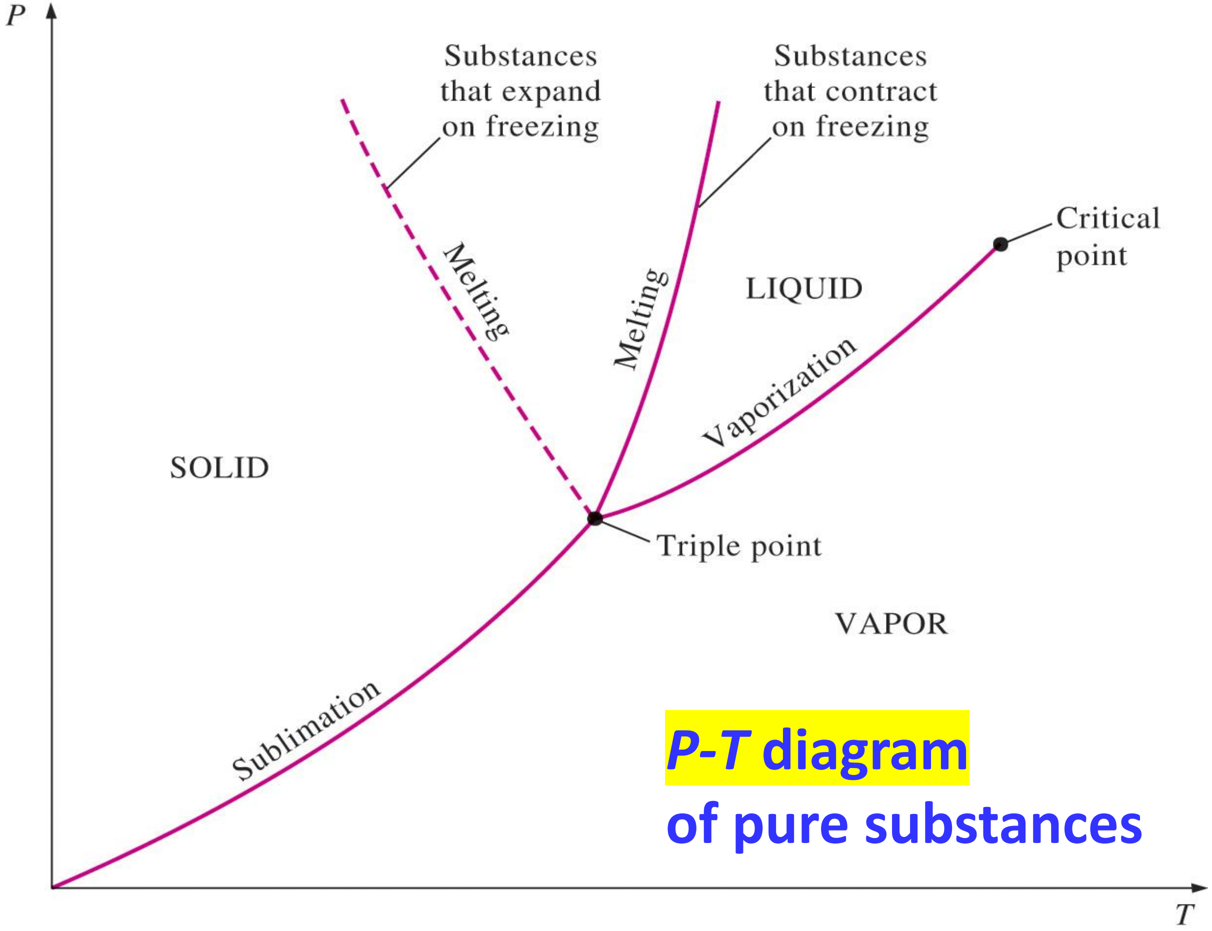
Elevation, m	Atmospheric pressure, kPa	Boiling temperature, °C
0	101.33	100.0
1,000	89.55	96.5
2,000	79.50	93.3
5,000	54.05	83.3
10,000	26.50	66.3
20,000	5.53	34.7

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 ***P-T, T-v and P-v*** diagrams for pure substances.



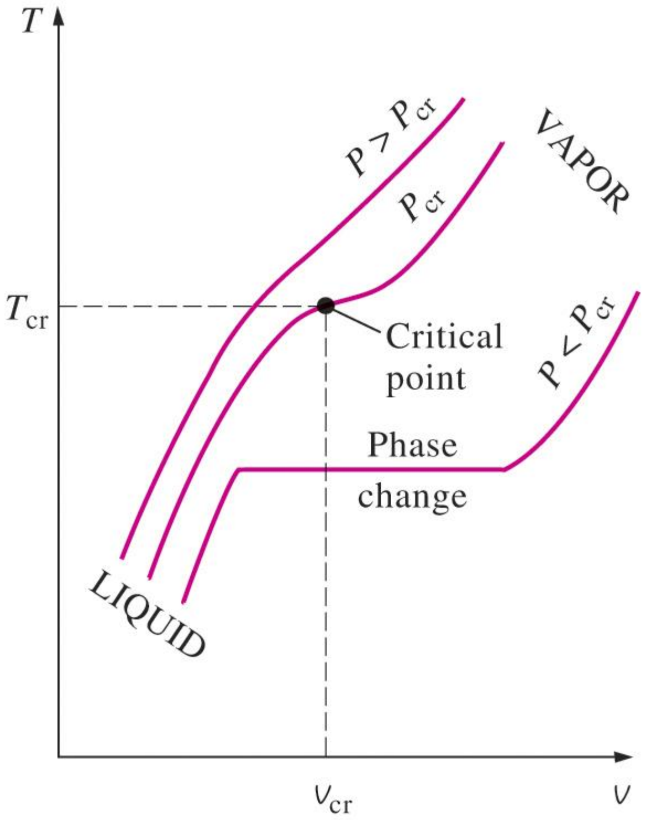
Sublimation: Passing from the solid phase directly into the vapor phase.

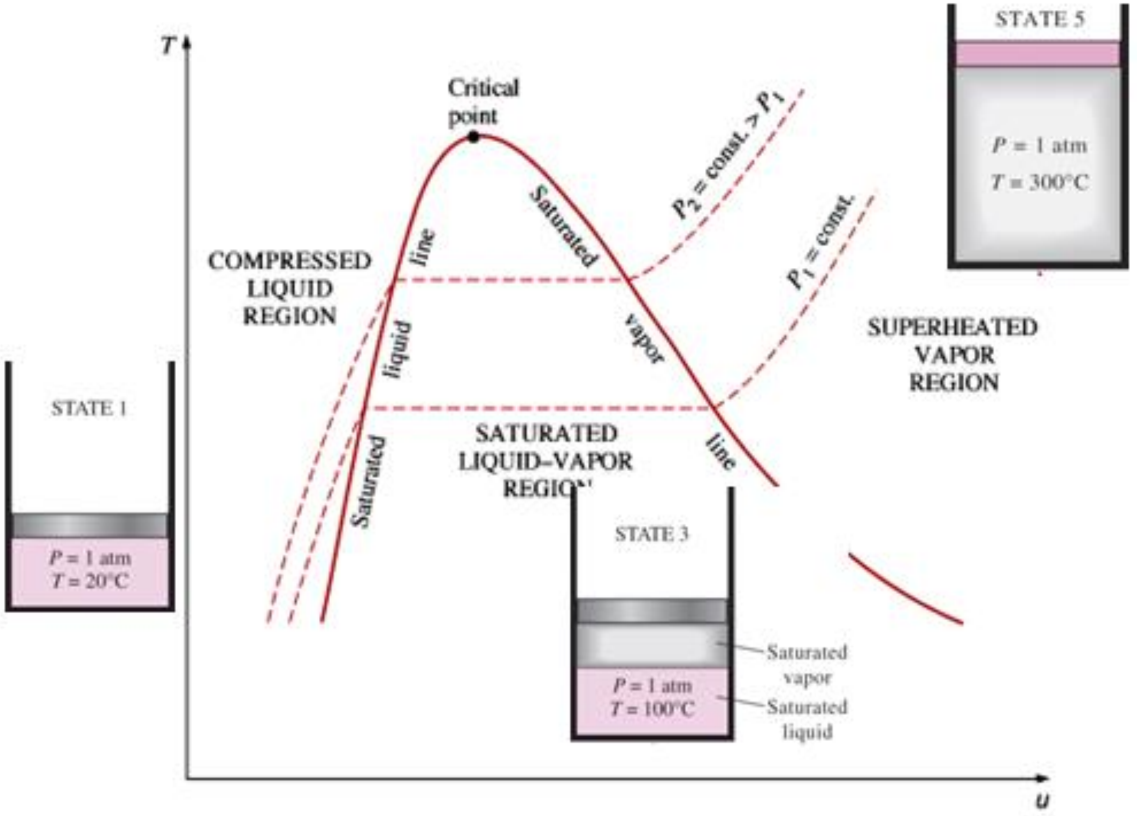


***P-T* diagram of pure substances**

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

T-v diagram of a pure substance





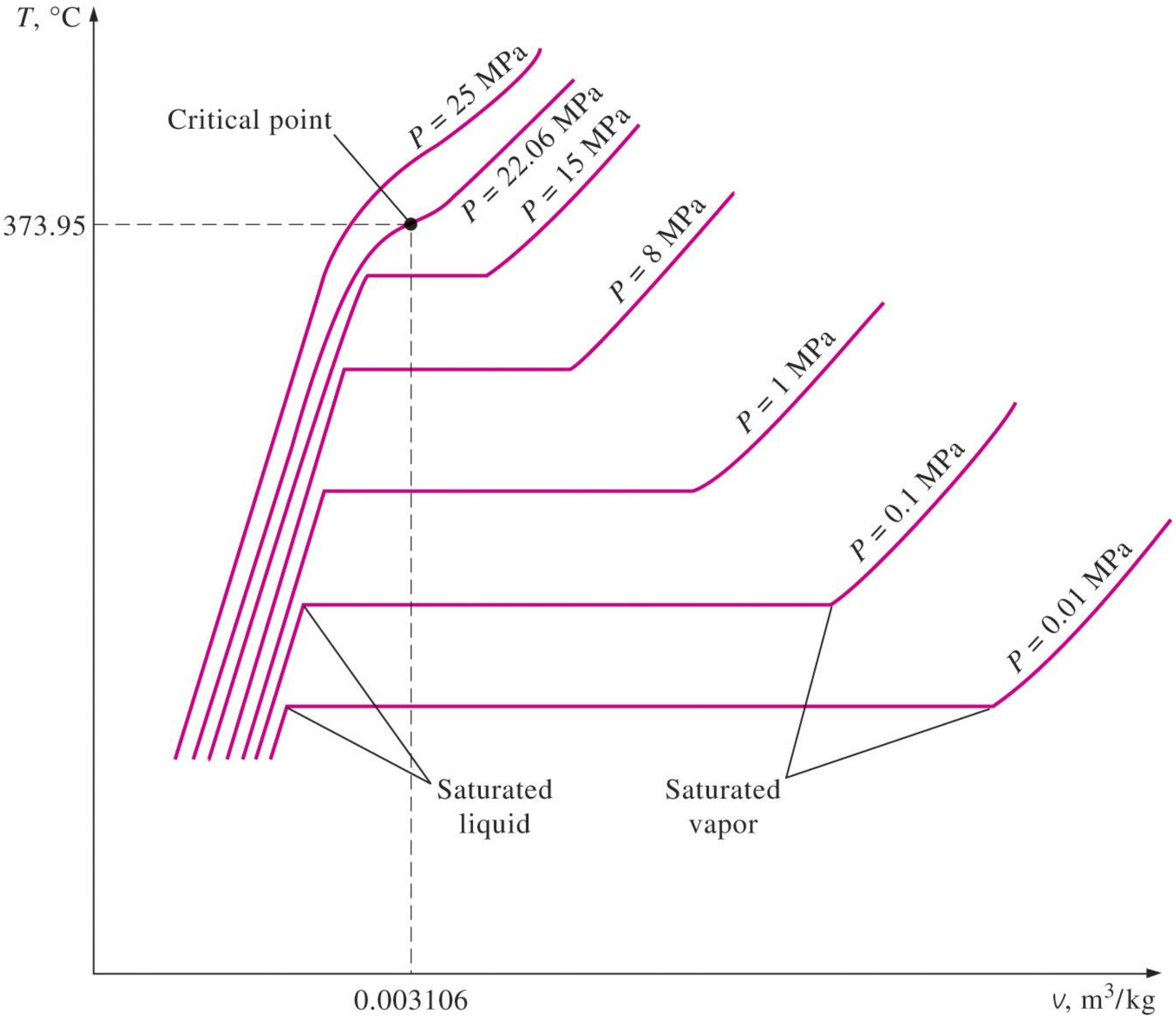
❑ **Critical point**:
The point at which the saturated liquid and saturated vapor states are **identical.**

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

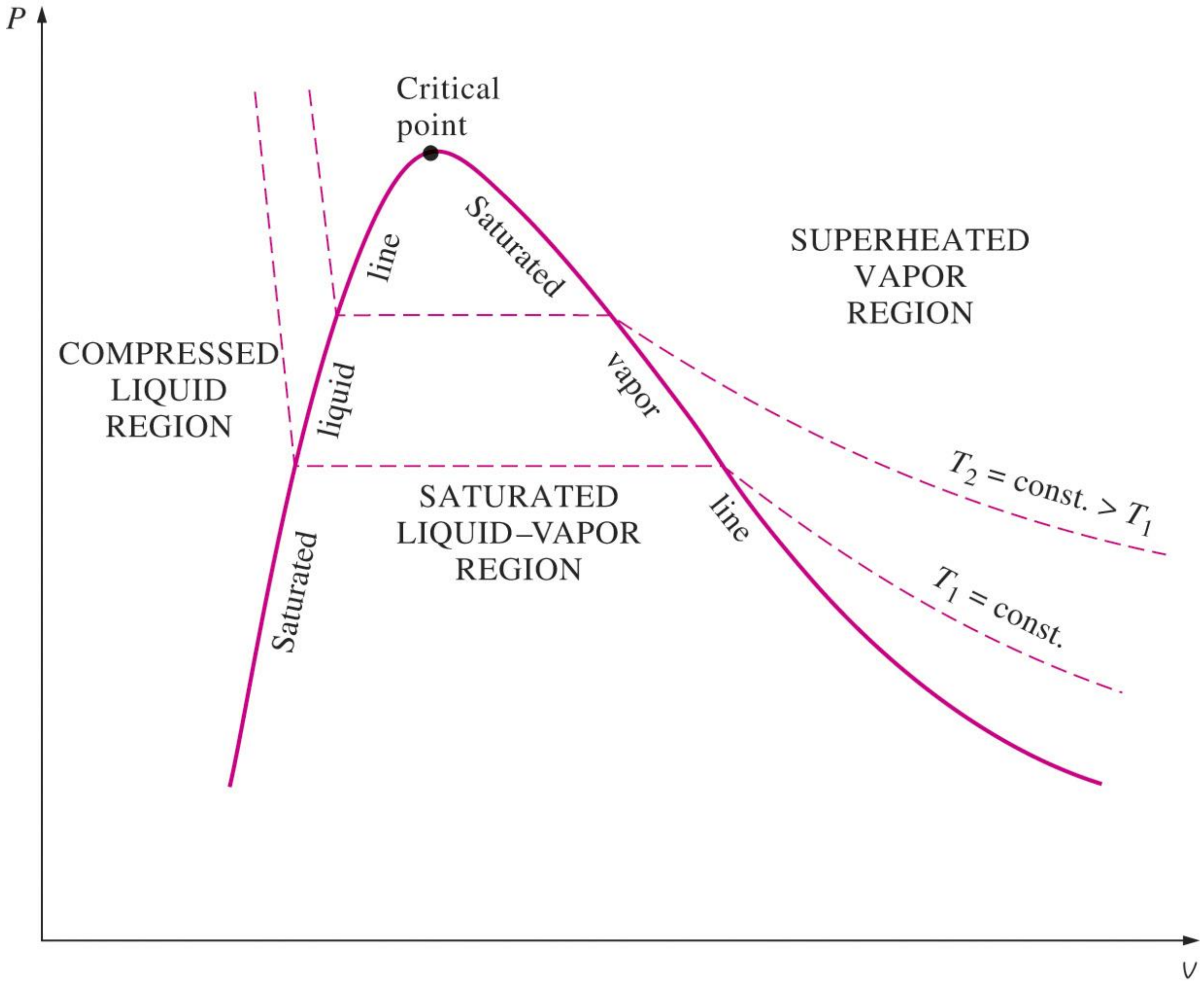
❑ **For water,**
T_c = 374°C
P_c = 22.06 MPa

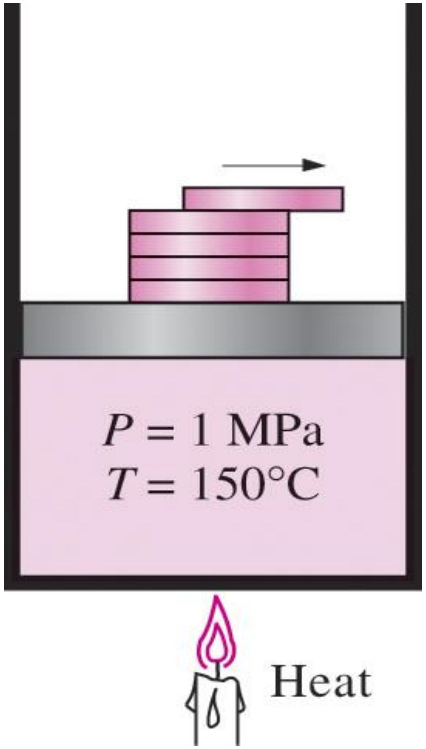
T-v diagram

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



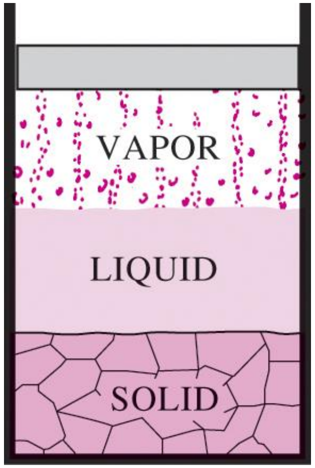
P-v diagram of a pure substance.





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

Extending Diagrams to Include Solid Phase

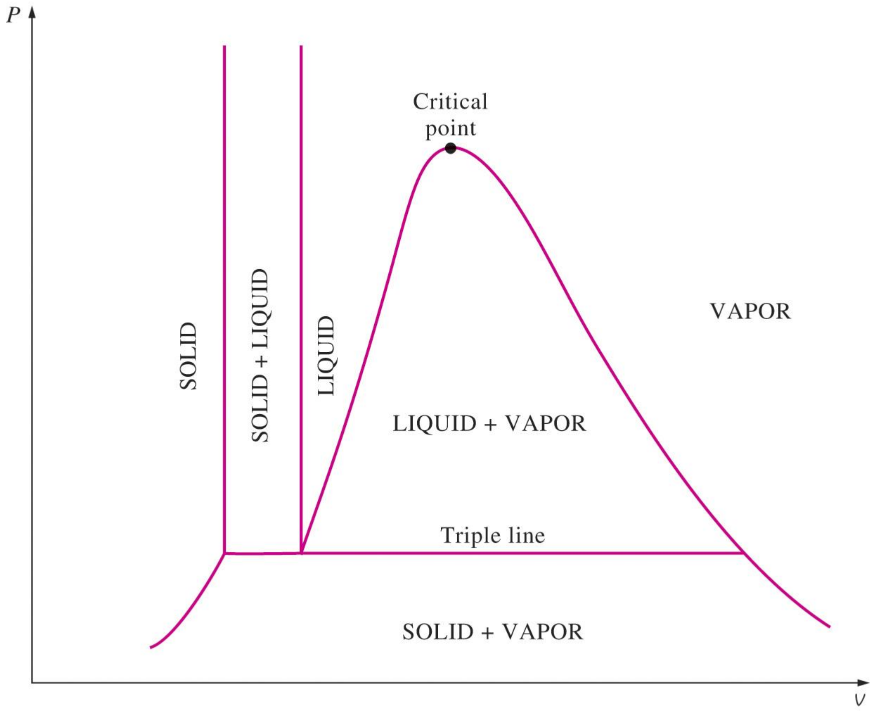


- ❑ ***At triple-point pressure and temperature, a substance exists in three phases in equilibrium.***

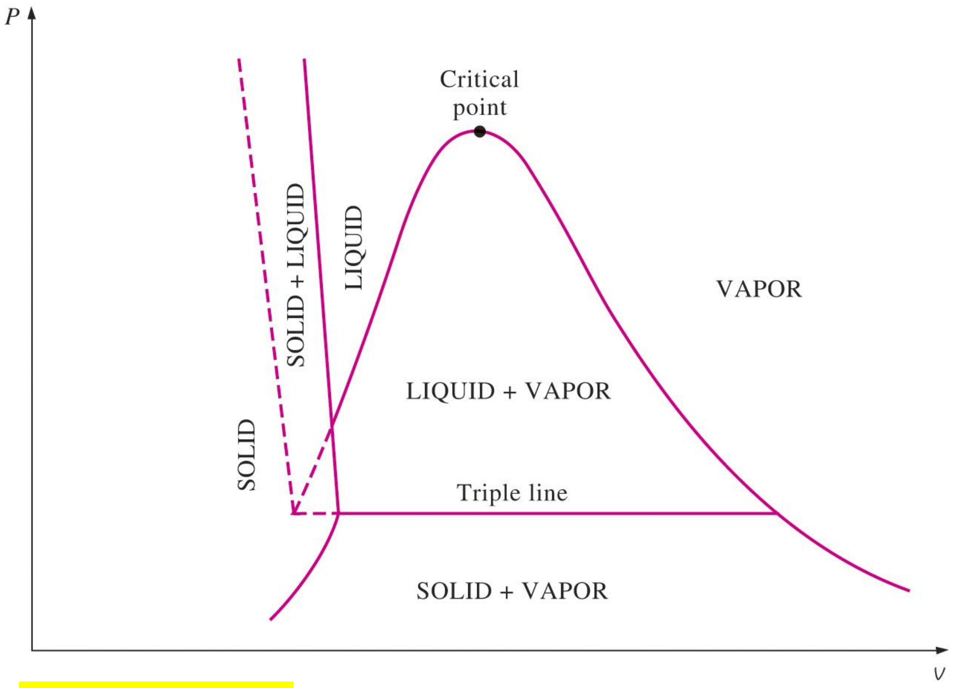
❑ **<u>For water,</u>**

T_{tp} **= 0.01°C**

P_{tp} **= 0.6117 kPa**



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



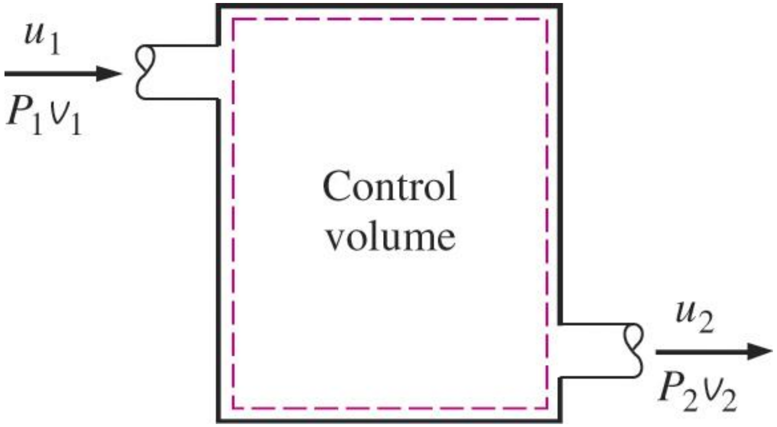
P-v **diagram of a substance that expands on freezing (such as water).**

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.

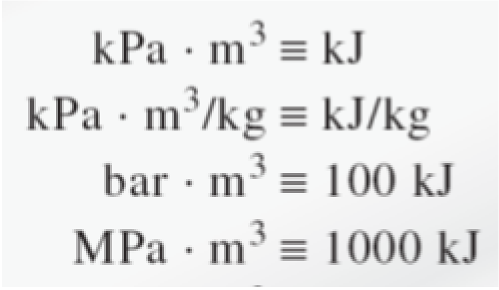
Enthalpy—A Combination Property

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



The combination *u + Pv* is frequently encountered in the analysis of *control volumes* (chapter 5)

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

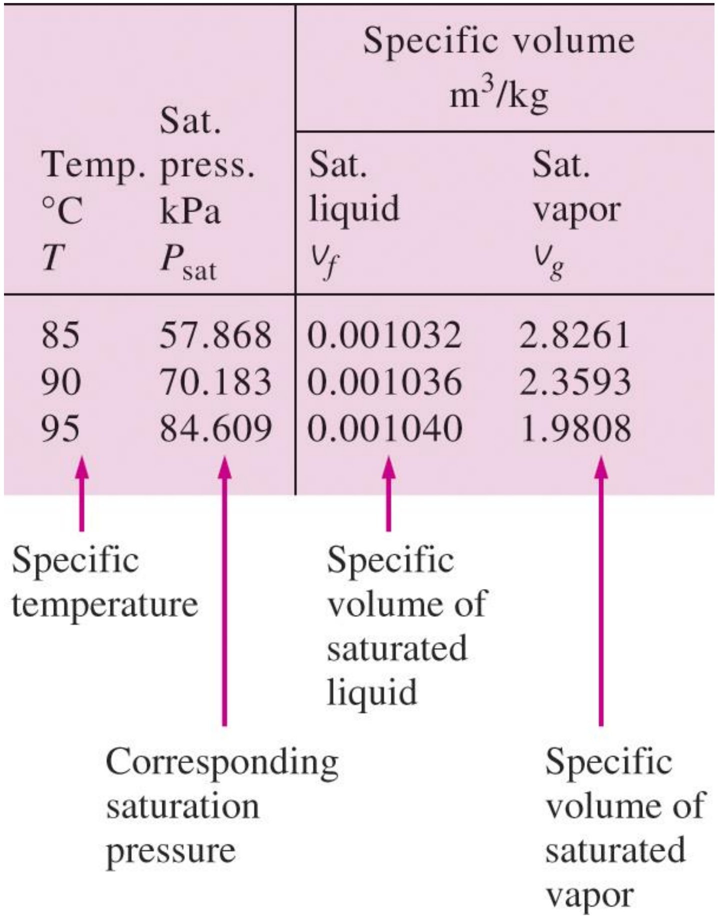


$$\text{kPa}\cdot\text{m}^3 \equiv \text{kJ}$$
$$\text{kPa}\cdot\text{m}^3/\text{kg} \equiv \text{kJ/kg}$$
$$\text{bar}\cdot\text{m}^3 \equiv 100\ \text{kJ}$$
$$\text{MPa}\cdot\text{m}^3 \equiv 1000\ \text{kJ}$$

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 m³/kg: Sat. liquid v_f	Specific volume m³/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

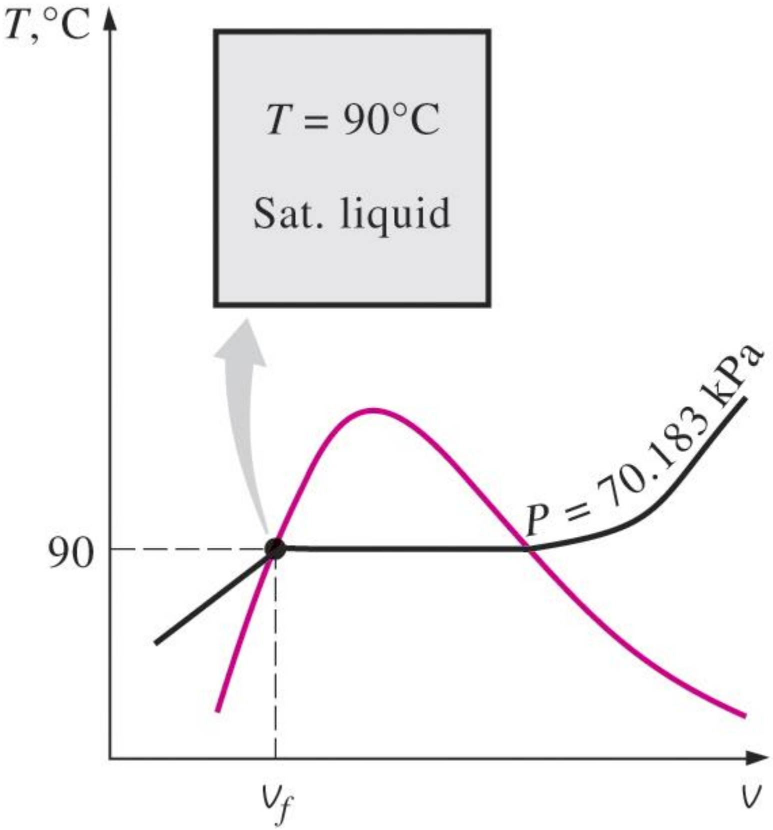
v_{fg} = difference between v_g and v_f (that is, $v_{fg} = v_g - v_f$)

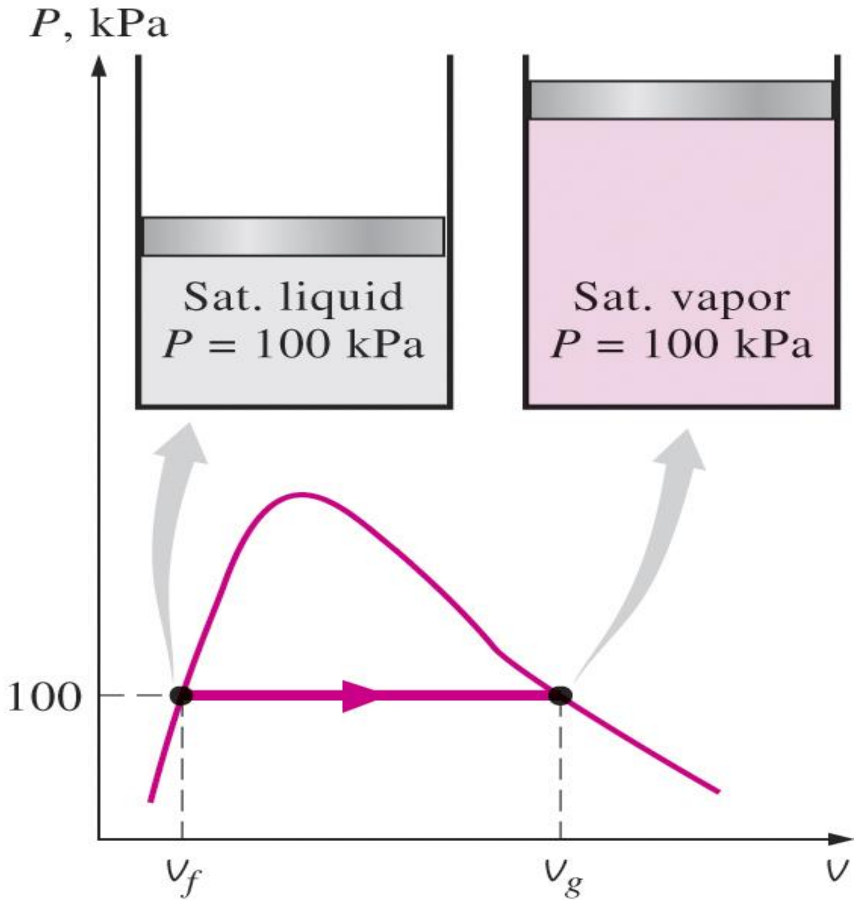
Enthalpy of vaporization, *h_{fg}*

(Latent heat of vaporization):

The amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure.

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.

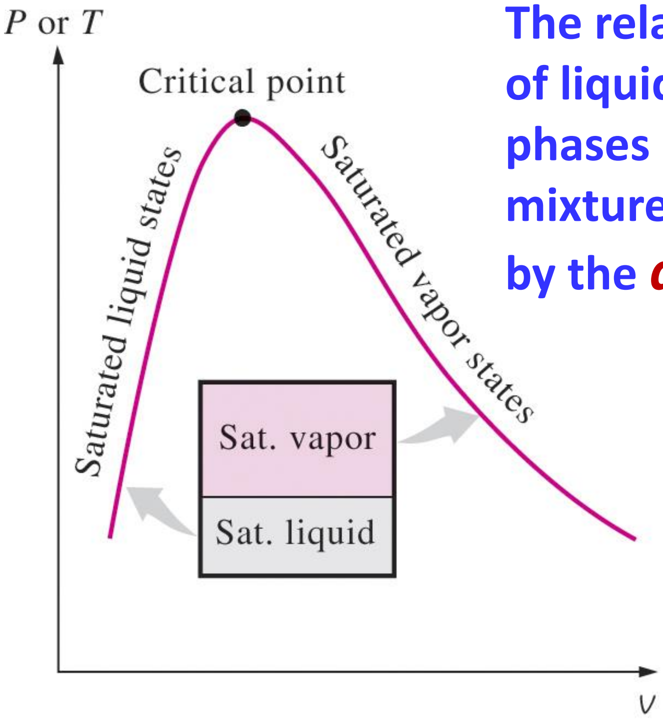
Quality is between 0 and 1 **0: sat. liquid, 1: sat. vapor.**

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

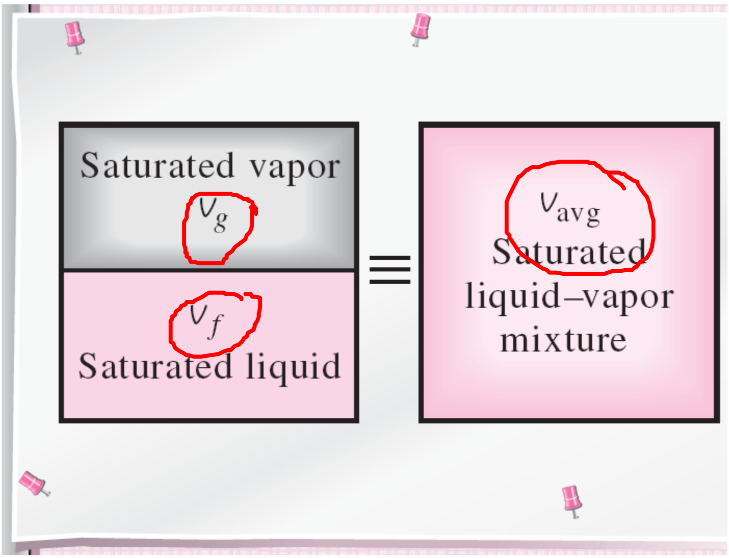
$$\boxed{x = \frac{m_{\text{vapor}}}{m_{\text{total}}}}$$

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

T and P 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.

Quality:

$$\boxed{x = m_g / m_t}$$

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

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

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

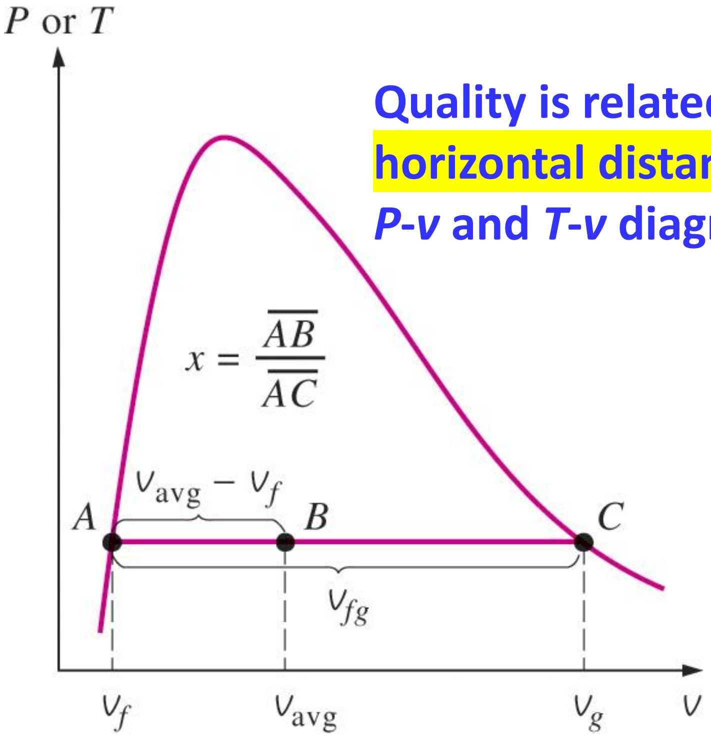
$$h_{\text{avg}} = h_f + x h_{fg} \qquad (\text{kJ/kg})$$

In General:

***y* designates v, u, h or S.**

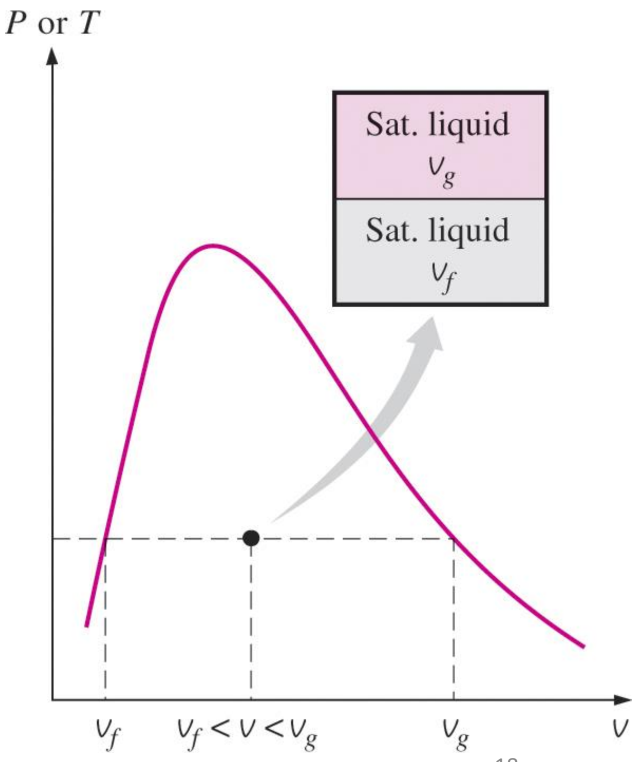
$$y_{\text{avg}} = y_f + x y_{fg}$$

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



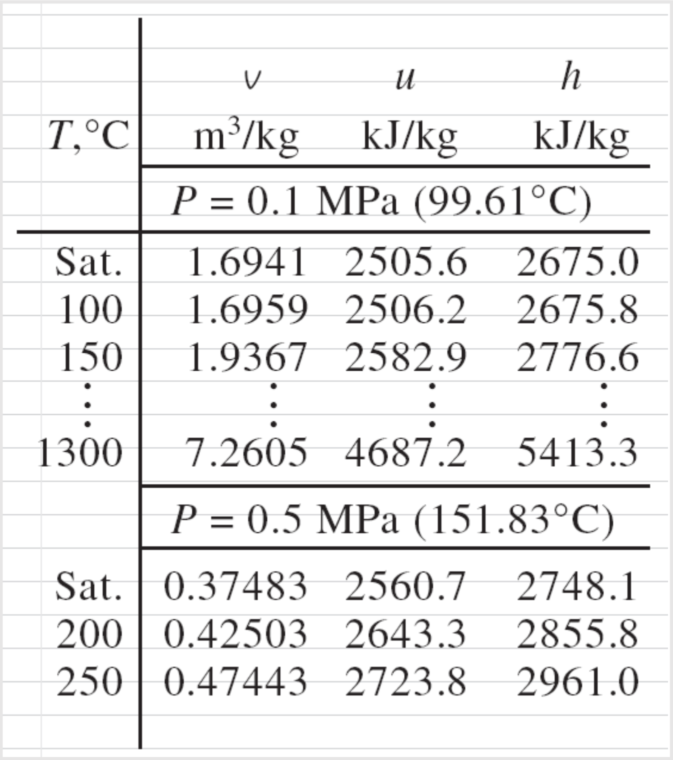
Quality is related to the horizontal distances on *P*-*v* and *T*-*v* diagrams.

The ***v*** value (specific volume) of a saturated liquid–vapor mixture lies between the v_f and v_g values at the specified *T* or *P*.



Superheated Vapor

- **In the region to the right of the saturated vapor line and at temperatures above the critical point Temp., a substance exists as super-heated vapor.**
- **In this region, temperature and pressure are independent properties.**



T,°C	v 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 ($P < P_{\text{sat}}$ at a given T)

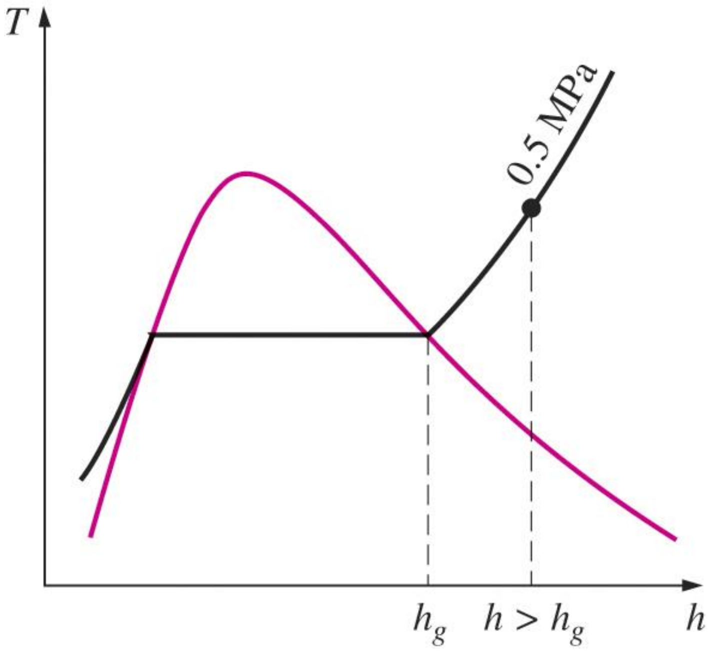
Higher tempreatures ($T > T_{\text{sat}}$ at a given P)

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.

Compressed Liquid

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

$$\boxed{y \cong y_{f\,@\,T}}$$

$y \rightarrow v, u,$ or h

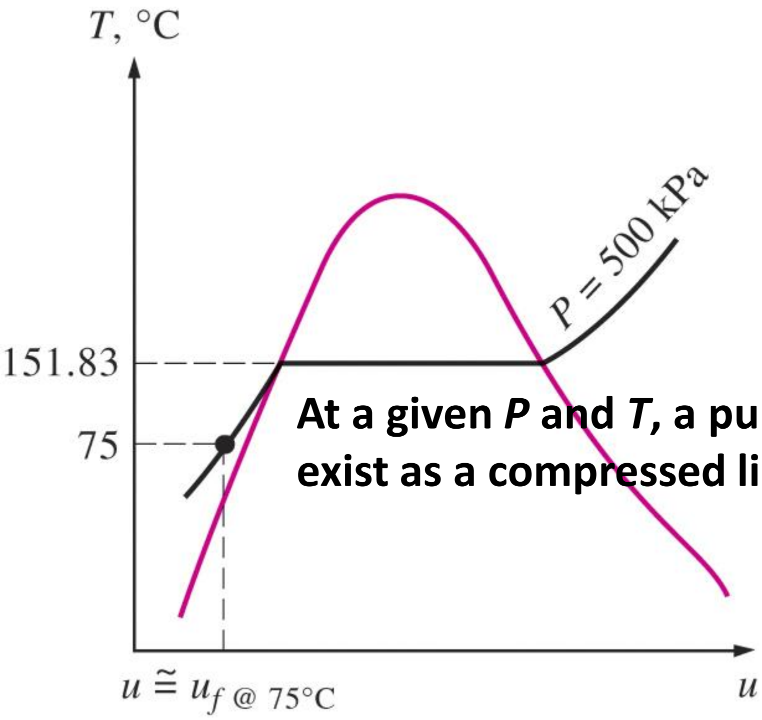
Given: P and T

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

A compressed liquid *may be approximated as* a saturated liquid at the given temperature. (Table A-7)

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)



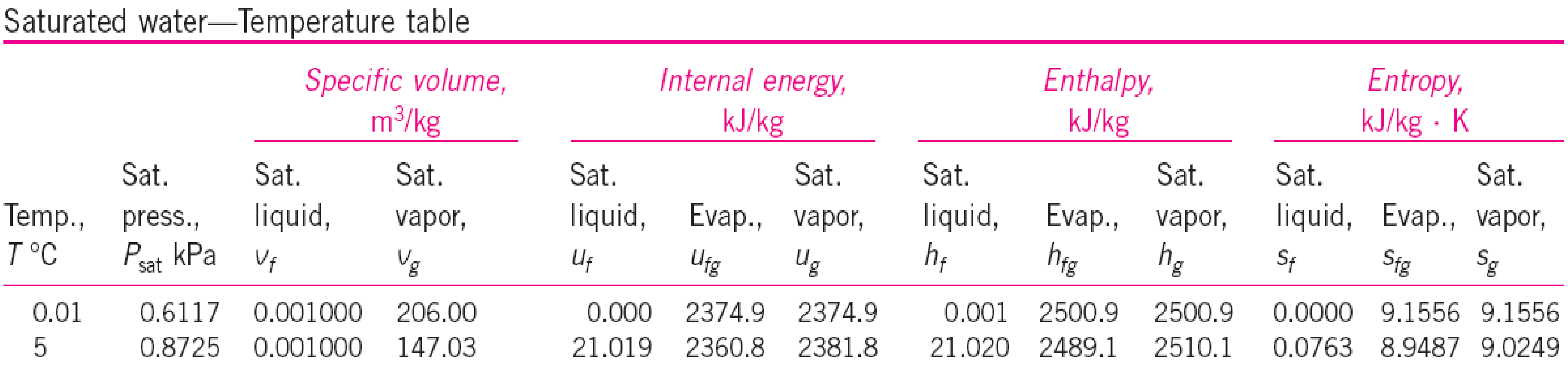
At a given *P* and *T*, a pure substance will exist as a compressed liquid if:

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

Reference State and Reference Values

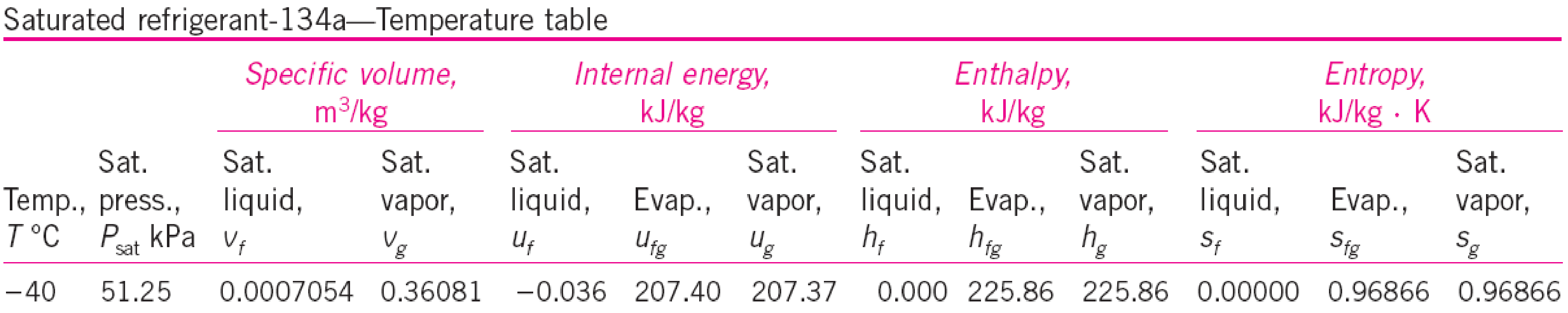
- ❑The values **of *u*, *h*,** and ***s*** cannot be measured directly, and they are *calculated from measurable properties* using the **Relations** between properties.
- ❑Those relations give the ***changes* in properties**, not the (absolute) values of properties at specified states.
- ❑We need to 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°C** and for R-134a is **-40°C (see tables).**
- ❑However, in thermodynamics, we are concerned with the ***changes* in properties,** and thus the reference state chosen is of no consequence in calculations.

Reference State and Reference Values



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

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.

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

Ideal gas equation of state

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

***R*: gas constant**

***M*: molar mass (kg/kmol)**

R_u: universal gas constant

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

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

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

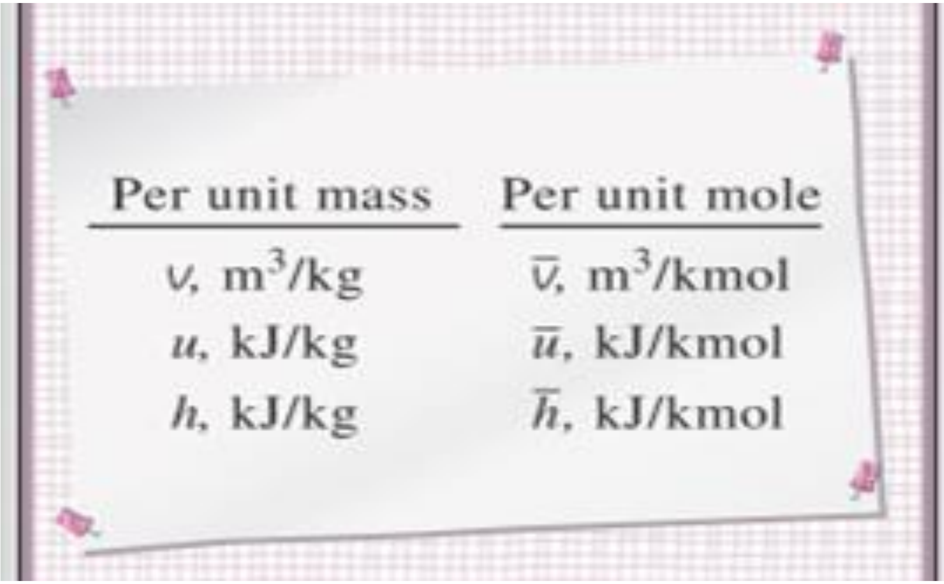
Ideal gas equation at two states for a fixed mass

$$V = mv \longrightarrow \boxed{PV = mRT}$$

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

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

Various expressions of ideal gas equation

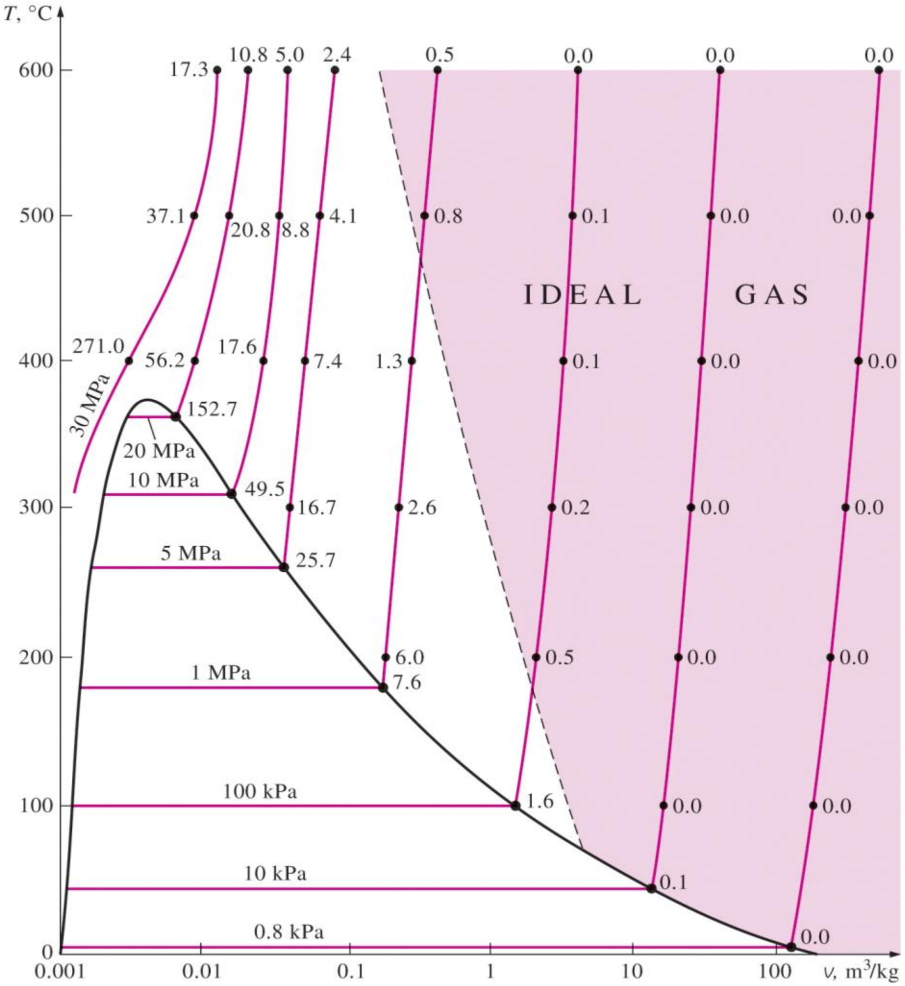


Per unit mass	Per unit mole
v, m^3/kg	$\bar{v}$, m^3/kmol
u, kJ/kg	$\bar{u}$, kJ/kmol
h, kJ/kg	$\bar{h}$, kJ/kmol

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

- **Real gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).**
- **The ideal-gas relation often is not applicable to real gases.**

Is Water Vapor an Ideal Gas?



1) 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).
2) At higher pressures, however, the ideal gas assumption yields **unacceptable err**ors, particularly in the vicinity of the critical point and the saturated vapor line.
3) In air-conditioning applications, the water vapor in the air can be treated as an ideal gas. Why?
4) In **steam power plant** applications, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.

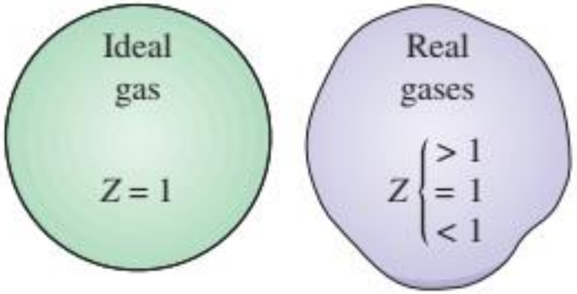
Percentage of error ([|v_{table} - v_{ideal}|/v_{table}] ×100) involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with *less than 1 percent error.*

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.

$$Pv = ZRT$$

$$Z = \frac{Pv}{RT} \quad \& \quad Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}}$$

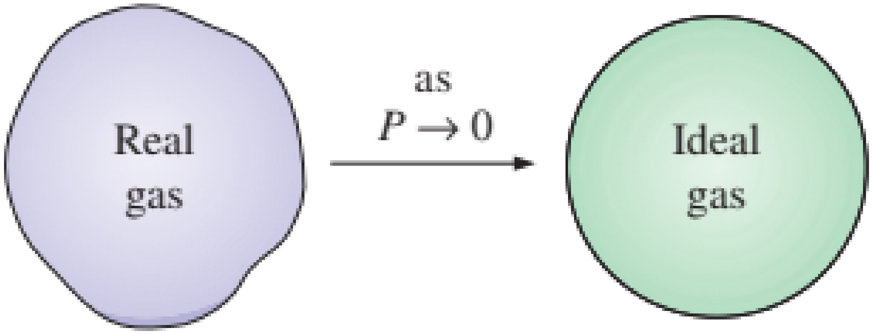


The compressibility factor is unity for ideal gases.

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

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

A: *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).

Reduced Properties

- The Z factor is approximately the same for all gases at the same *reduced temperature* and *reduced pressure*, which are defined as

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

where P_{cr} and T_{cr} are the critical pressure and temperature, respectively.

- This is known as the ***principle of corresponding states.***

Reduced pressure

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

Reduced temperature

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

Pseudo-reduced specific volume

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

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

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

Comparison of Z Factors for Various Gases

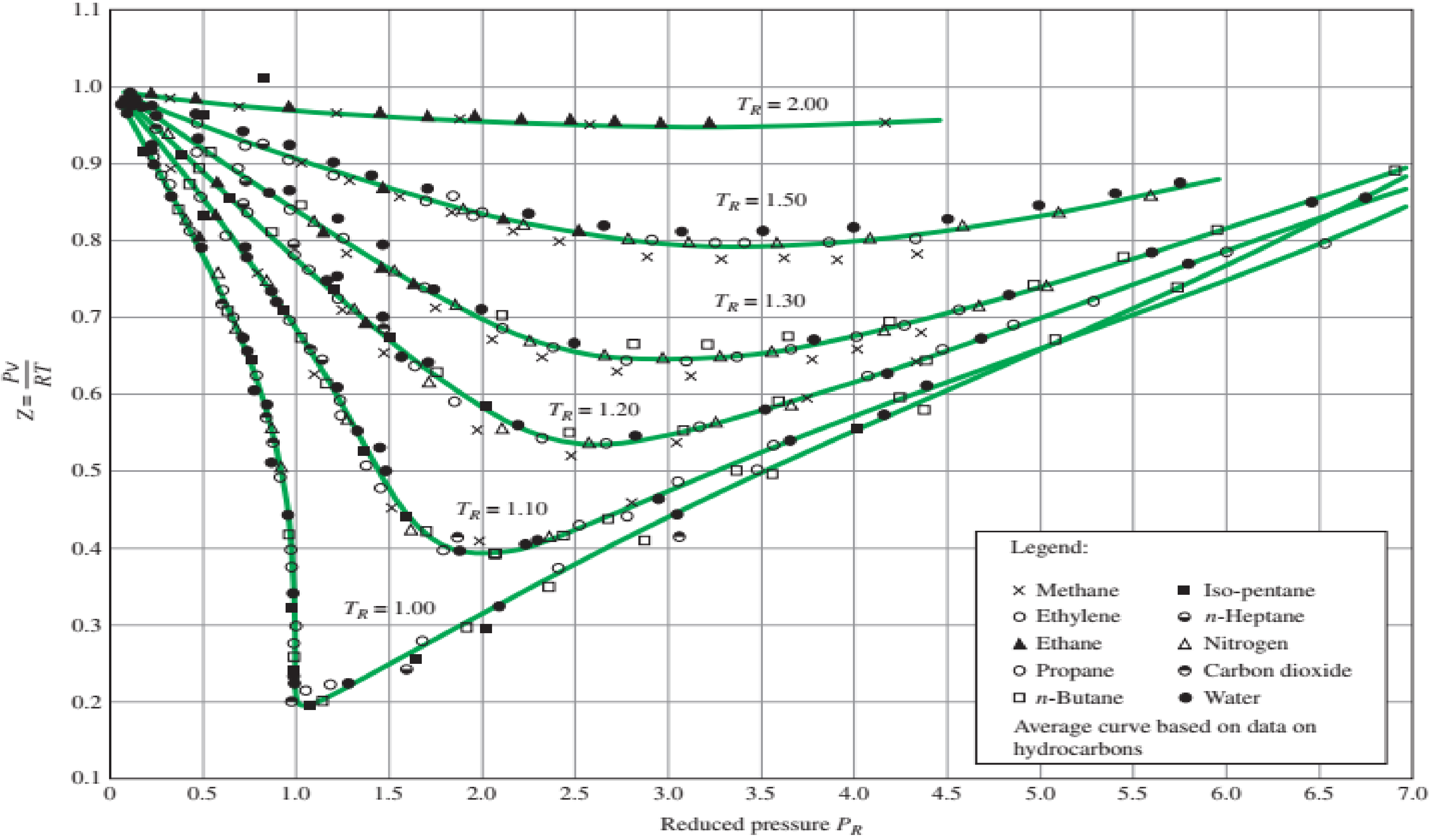


FIGURE 3–47

Comparison of *Z* factors for various gases.

Source: Gour-Jen Su, "Modified Law of Corresponding States," *Ind. Eng. Chem. (international ed.)* 38 (1946), p. 803.

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

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

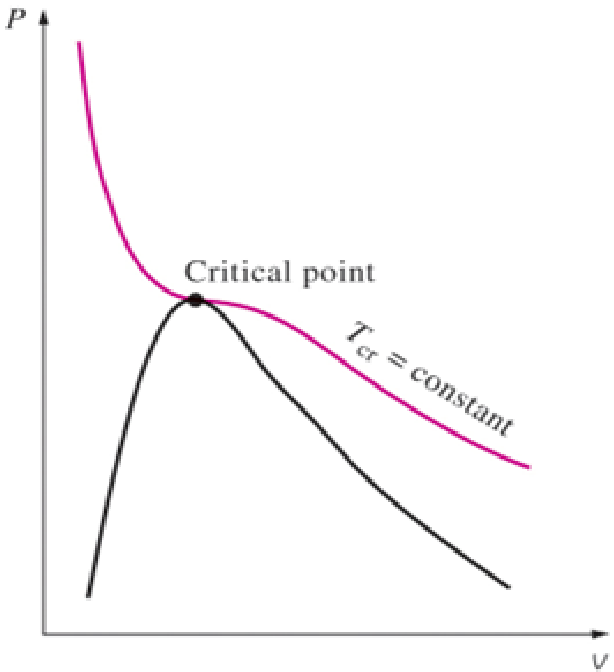
$$a = \frac{27R^2T_{\text{cr}}^2}{64P_{\text{cr}}} \qquad b = \frac{RT_{\text{cr}}}{8P_{\text{cr}}}$$

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

❑ ***Isotherm of a pure substance has an inflection point at the critical point.***

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

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



Beattie-Bridgeman Equation of State

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

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

- 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

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

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

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. 3–28. Since saturation conditions exist in the tank, the pressure must be the saturation pressure at 90°C:

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

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

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

Then the total volume of the tank becomes

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

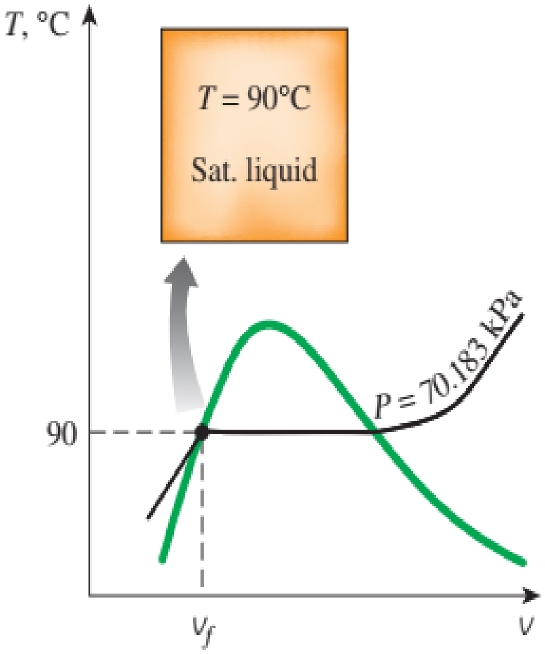


FIGURE 3–28
Schematic and *T-v* diagram for Example 3–1.

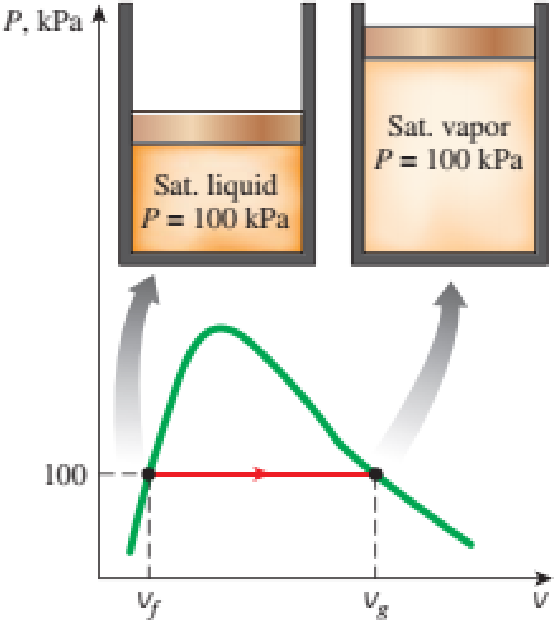


FIGURE 3–30
Schematic and P-v diagram for Example 3–3.

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.

Analysis (*a*) The process described is illustrated on a P-v diagram in Fig. 3–30. The volume change per unit mass during a vaporization process is v_{fg}, which is the difference between v_g and v_f. Reading these values from Table A–5 at 100 kPa and substituting yield

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

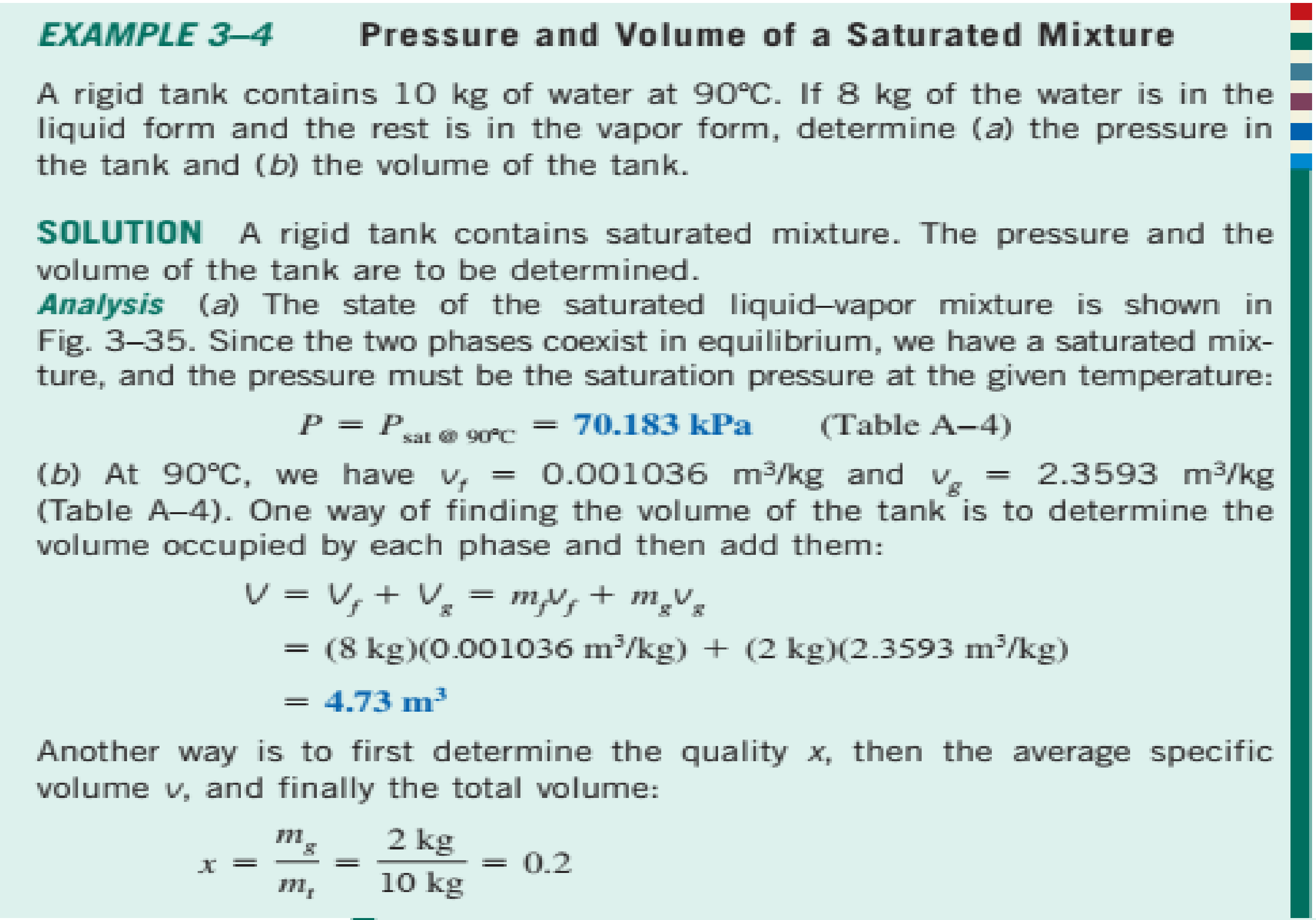
Thus,

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

(*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

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

Discussion Note that we have considered the first four decimal digits of v_{fg} and disregarded the rest. This is because v_g has significant numbers to the first four decimal places only, and we do not know the numbers in the other decimal places. Copying all the digits from the calculator would mean that we are assuming $v_g = 1.694100$, which is not necessarily the case. It could very well be that $v_g = 1.694138$ since this number, too, would truncate to 1.6941. All the digits in our result (1.6931) are significant. But if we did not truncate the result, we would obtain $v_{fg} = 1.693057$, which falsely implies that our result is accurate to the sixth decimal place.



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. 3–35. Since the two phases coexist in equilibrium, we have a saturated mixture, and the pressure must be the saturation pressure at the given temperature:

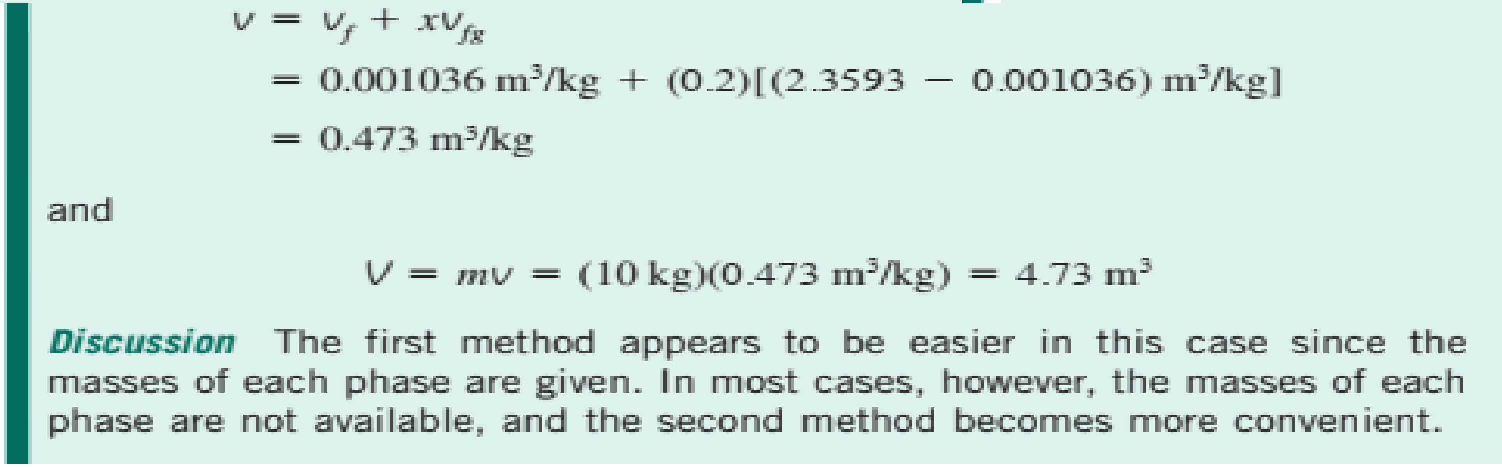
$$P = P_{\text{sat @ 90°C}} = \mathbf{70.183\ kPa} \qquad \text{(Table A–4)}$$

(*b*) At 90°C, we have $v_f = 0.001036\ \text{m}^3/\text{kg}$ and $v_g = 2.3593\ \text{m}^3/\text{kg}$ (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:

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

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

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



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

and

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

Discussion The first method appears to be easier in this case since the masses of each phase are given. In most cases, however, the masses of each phase are not available, and the second method becomes more convenient.

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.

Analysis (*a*) The state of the saturated liquid–vapor mixture is shown in Fig. 3–36. At this point we do not know whether the refrigerant is in the compressed liquid, superheated vapor, or saturated mixture region. This can be determined by comparing a suitable property to the saturated liquid and saturated vapor values. From the information given, we can determine the specific volume:

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

At 160 kPa, we read

$$v_f = 0.0007435\ \text{m}^3/\text{kg}$$

$$v_g = 0.12355\ \text{m}^3/\text{kg} \qquad \text{(Table A–12)}$$

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:

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

(*b*) Quality can be determined from

$$x = \frac{v - v_f}{v_{fg}} = \frac{0.02 - 0.0007435}{0.12355 - 0.0007435} = \mathbf{0.157}$$

(*c*) At 160 kPa, we also read from Table A–12 that $h_f = 31.18$ kJ/kg and $h_{fg} = 209.96$ kJ/kg. Then,

$$\begin{aligned} h &= h_f + xh_{fg} \\ &= 31.18 \text{ kJ/kg} + (0.157)(209.96 \text{ kJ/kg}) \\ &= \mathbf{64.1 \text{ kJ/kg}} \end{aligned}$$

(*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

$$V_g = m_g v_g = (0.628 \text{ kg})(0.12355 \text{ m}^3\text{/kg}) = \mathbf{0.0776 \text{ m}^3} \text{ (or 77.6 L)}$$

The rest of the volume (2.4 L) is occupied by the liquid.

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. 3–38, 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

$$T = \mathbf{216.3°C}$$

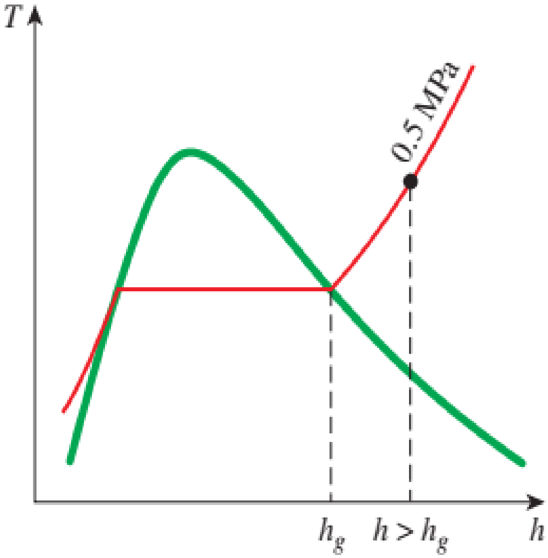


FIGURE 3–38

At a specified P, superheated vapor exists at a higher h than the saturated vapor (Example 3–7).

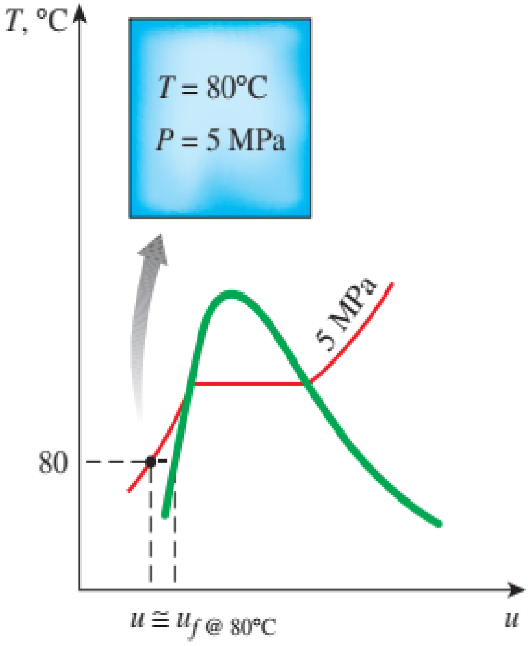


FIGURE 3–40

Schematic and *T*-*u* diagram for Example 3–8.

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. 3–40.

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

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

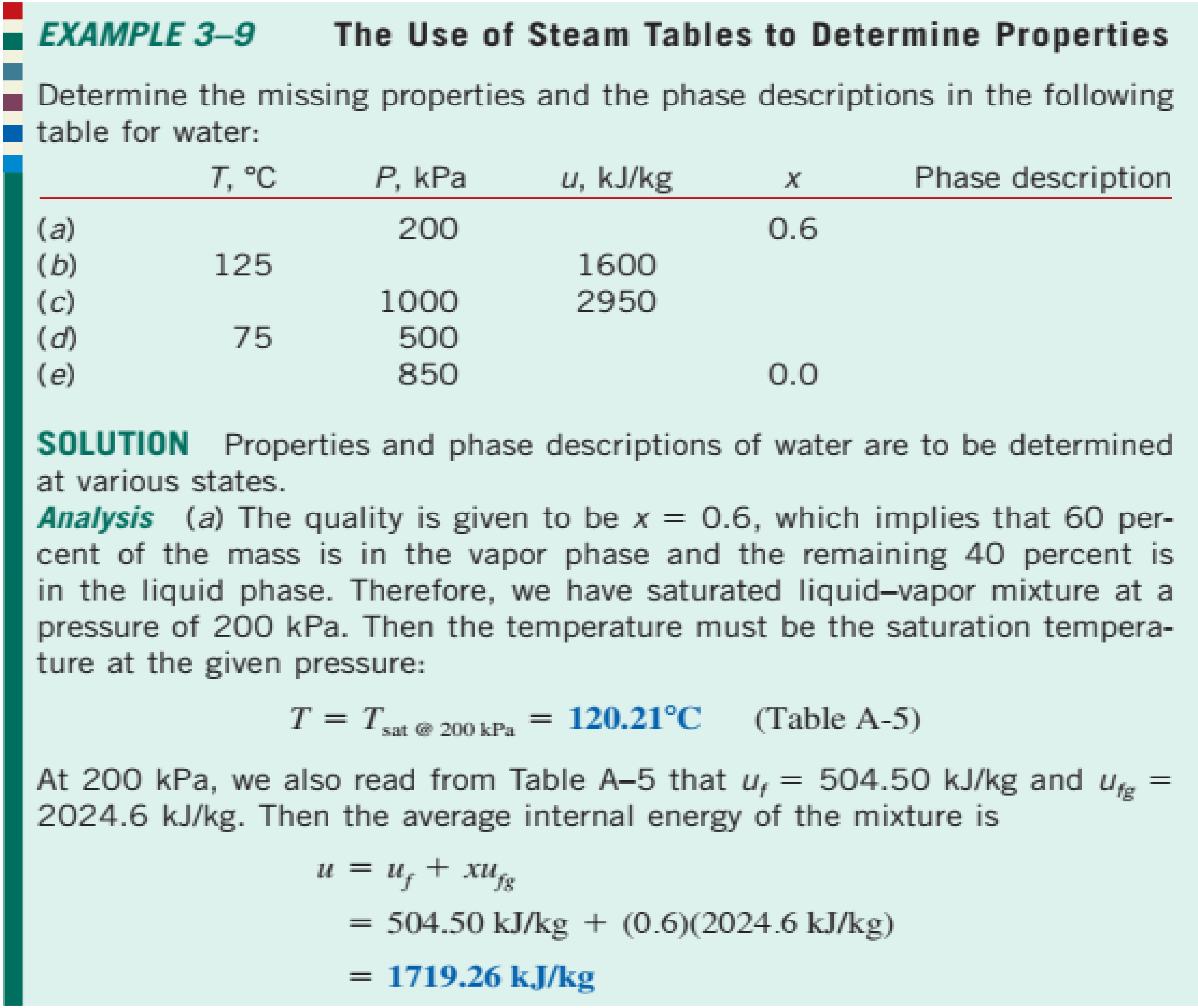
(*b*) From the saturation table (Table A–4), we read

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

The error involved is

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

which is less than 1 percent.



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	

SOLUTION Properties and phase descriptions of water are to be determined at various states.

Analysis (*a*) The quality is given to be $x = 0.6$, which implies that 60 percent of the mass is in the vapor phase and the remaining 40 percent is in the liquid phase. Therefore, we have saturated liquid–vapor mixture at a pressure of 200 kPa. Then the temperature must be the saturation temperature at the given pressure:

$$T = T_{\text{sat @ 200 kPa}} = \mathbf{120.21^\circ C} \qquad \text{(Table A-5)}$$

At 200 kPa, we also read from Table A–5 that $u_f = 504.50$ kJ/kg and $u_{fg} = 2024.6$ kJ/kg. Then the average internal energy of the mixture is

$$\begin{aligned} u &= u_f + xu_{fg} \\ &= 504.50 \text{ kJ/kg} + (0.6)(2024.6 \text{ kJ/kg}) \\ &= \mathbf{1719.26 \text{ kJ/kg}} \end{aligned}$$

(*b*) This time the temperature and the internal energy are given, but we do not know which table to use to determine the missing properties because we have no clue as to whether we have saturated mixture, compressed liquid, or superheated vapor. To determine the region we are in, we first go to the saturation table (Table A–4) and determine the u_f and u_g values at the given temperature. At 125°C, we read $u_f = 524.83$ kJ/kg and $u_g = 2534.3$ kJ/kg. Next we compare the given u value to these u_f and u_g values, keeping in mind that

$$\begin{aligned} &\text{if} \quad u < u_f && \text{we have } \textit{compressed liquid} \\ &\text{if} \quad u_f \le u \le u_g && \text{we have } \textit{saturated mixture} \\ &\text{if} \quad u > u_g && \text{we have } \textit{superheated vapor} \end{aligned}$$

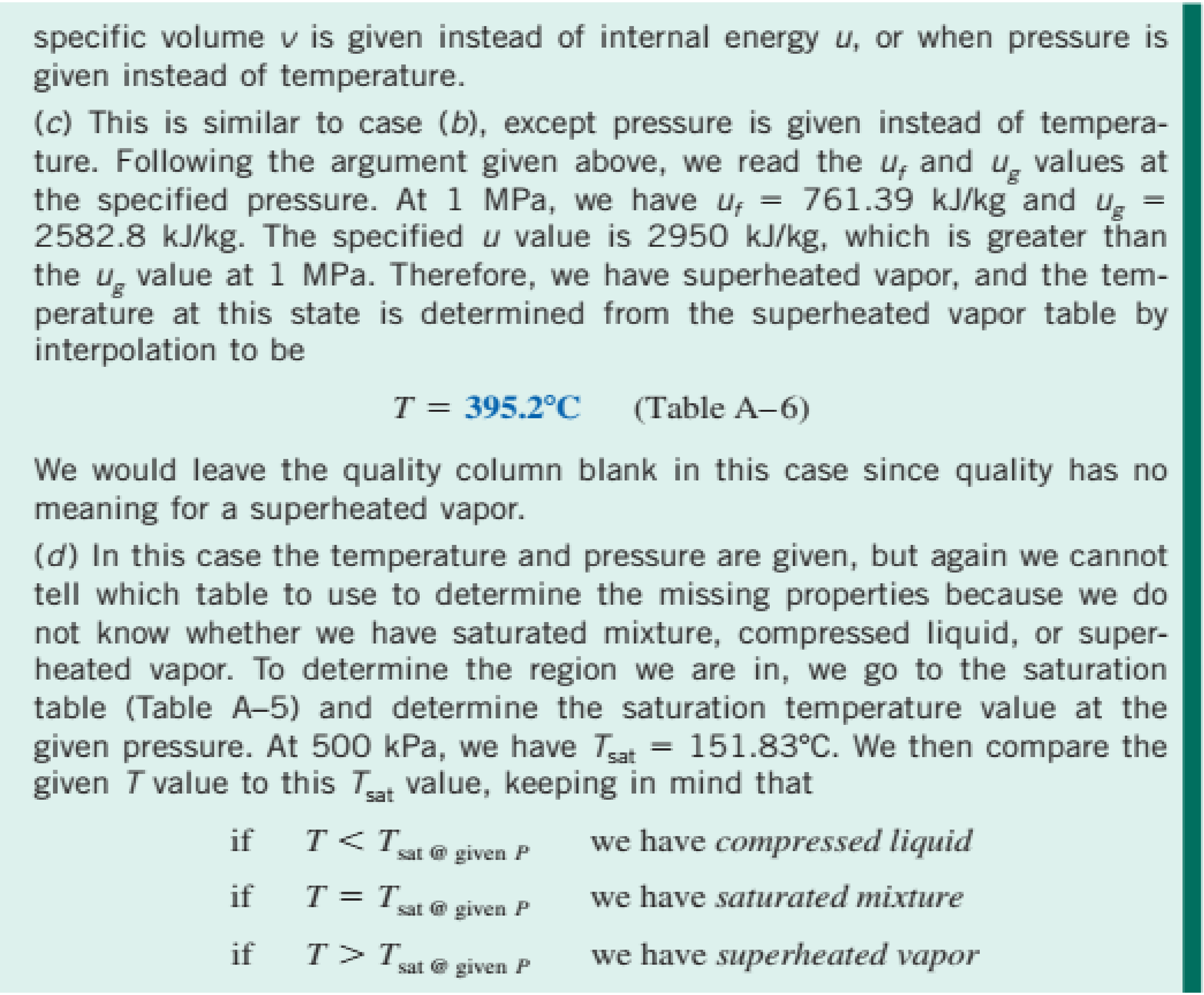
In our case the given u value is 1600, which falls between the u_f and u_g values at 125°C. Therefore, we have saturated liquid–vapor mixture. Then the pressure must be the saturation pressure at the given temperature:

$$P = P_{\text{sat @ } 125^\circ\text{C}} = \mathbf{232.23\ kPa} \qquad \text{(Table A–4)}$$

The quality is determined from

$$x = \frac{u - u_f}{u_{fg}} = \frac{1600 - 524.83}{2009.5} = \mathbf{0.535}$$

The criteria above for determining whether we have compressed liquid, saturated mixture, or superheated vapor can also be used when enthalpy *h* or



specific volume v is given instead of internal energy u, or when pressure is given instead of temperature.

(*c*) This is similar to case (*b*), except pressure is given instead of temperature. Following the argument given above, we read the u_f and u_g values at the specified pressure. At 1 MPa, we have $u_f = 761.39$ kJ/kg and $u_g = 2582.8$ kJ/kg. The specified u value is 2950 kJ/kg, which is greater than the u_g value at 1 MPa. Therefore, we have superheated vapor, and the temperature at this state is determined from the superheated vapor table by interpolation to be

$$T = \mathbf{395.2^\circ C} \qquad \text{(Table A–6)}$$

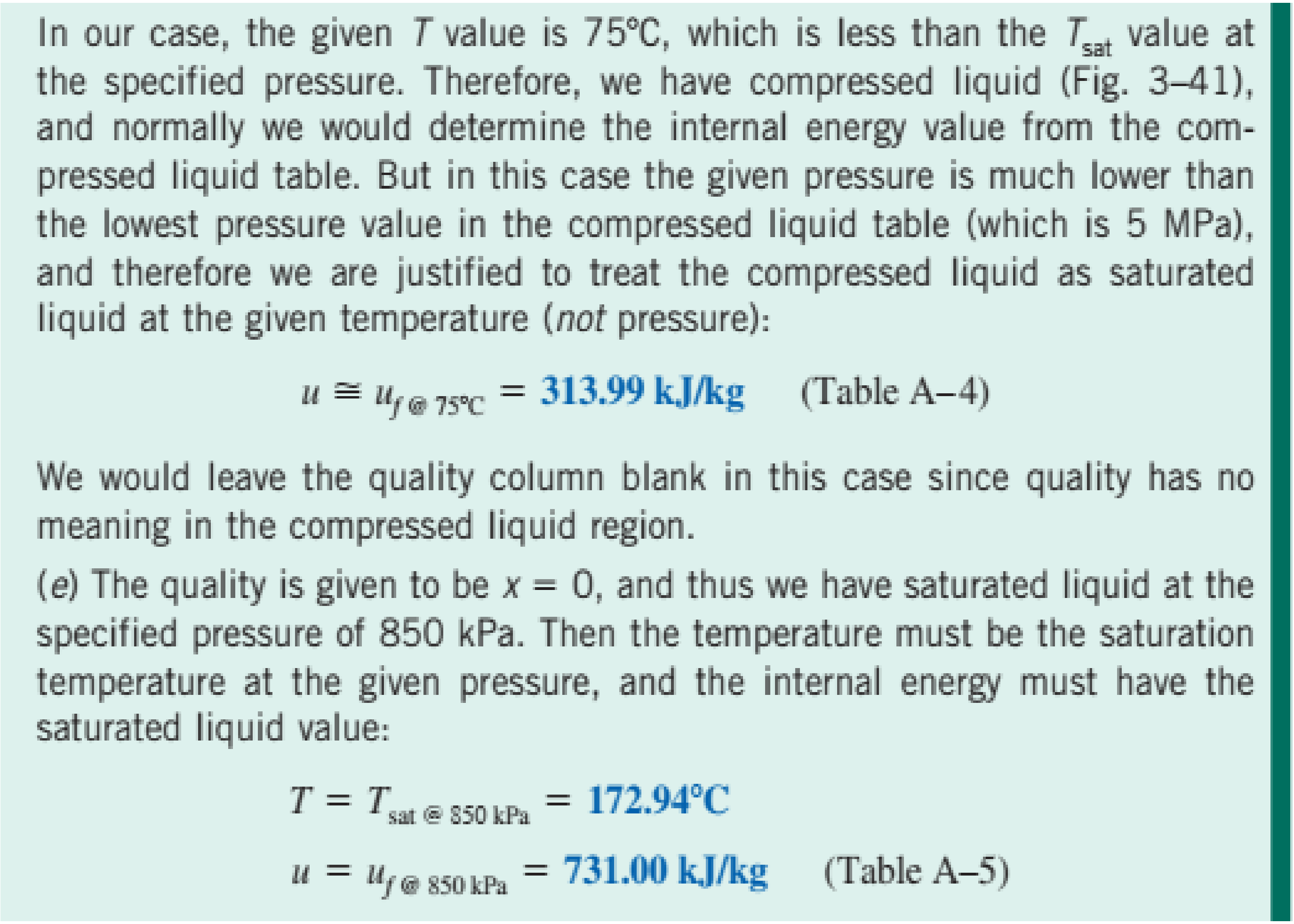
We would leave the quality column blank in this case since quality has no meaning for a superheated vapor.

(*d*) In this case the temperature and pressure are given, but again we cannot tell which table to use to determine the missing properties because we do not know whether we have saturated mixture, compressed liquid, or superheated vapor. To determine the region we are in, we go to the saturation table (Table A–5) and determine the saturation temperature value at the given pressure. At 500 kPa, we have $T_{sat} = 151.83$°C. We then compare the given T value to this T_{sat} value, keeping in mind that

if $T < T_{\text{sat @ given } P}$ we have *compressed liquid*

if $T = T_{\text{sat @ given } P}$ we have *saturated mixture*

if $T > T_{\text{sat @ given } P}$ we have *superheated vapor*



In our case, the given T value is 75°C, which is less than the T_{sat} value at the specified pressure. Therefore, we have compressed liquid (Fig. 3–41), and normally we would determine the internal energy value from the compressed liquid table. But in this case the given pressure is much lower than the lowest pressure value in the compressed liquid table (which is 5 MPa), and therefore we are justified to treat the compressed liquid as saturated liquid at the given temperature (*not* pressure):

$$u \cong u_{f\,@\,75^\circ\text{C}} = \mathbf{313.99\ kJ/kg} \qquad \text{(Table A–4)}$$

We would leave the quality column blank in this case since quality has no meaning in the compressed liquid region.

(*e*) The quality is given to be $x = 0$, and thus we have saturated liquid at the specified pressure of 850 kPa. Then the temperature must be the saturation temperature at the given pressure, and the internal energy must have the saturated liquid value:

$$T = T_{\text{sat}\,@\,850\text{ kPa}} = \mathbf{172.94^\circ C}$$

$$u = u_{f\,@\,850\text{ kPa}} = \mathbf{731.00\ kJ/kg} \qquad \text{(Table A–5)}$$

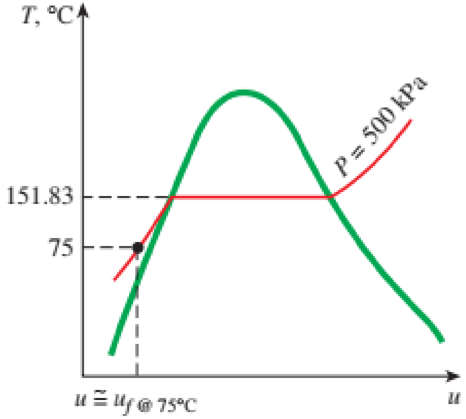


FIGURE 3–41

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

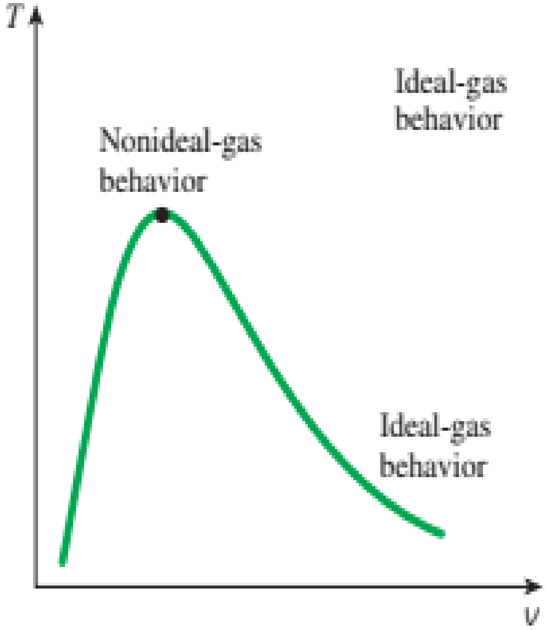


FIGURE 3–49
Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

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

$$R = 0.0815 \text{ kPa·m}^3\text{/kg·K}$$

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

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

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

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

Tetrafluoroethane (R−134a)	CF_3CH_2F	102.03	0.08149	374.2	4.059	0.1993

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:

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

Thus

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

Discussion The error in this result is less than **2 percent**. Therefore, in the absence of tabulated data, the generalized compressibility chart can be used with confidence.