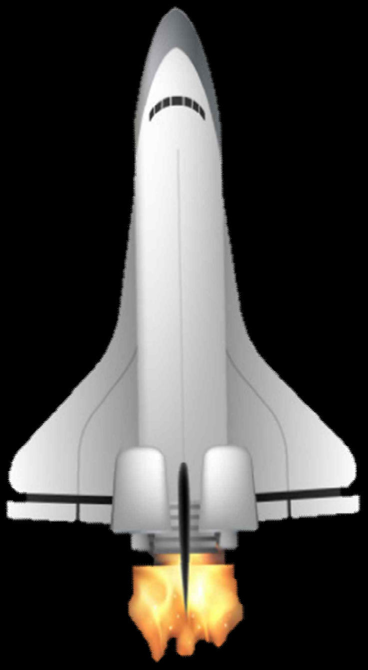
CHAPTER
3

Properties of Pure Substances



2022 Spring semester

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.

3-1 PURE SUBSTANCE

Pure substance: A substance that has a fixed chemical composition throughout.

Air is a mixture of several gases, but it is considered to be a pure substance.

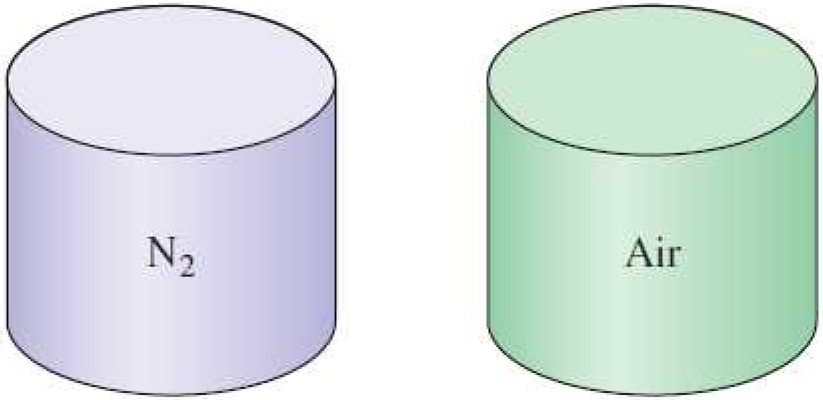
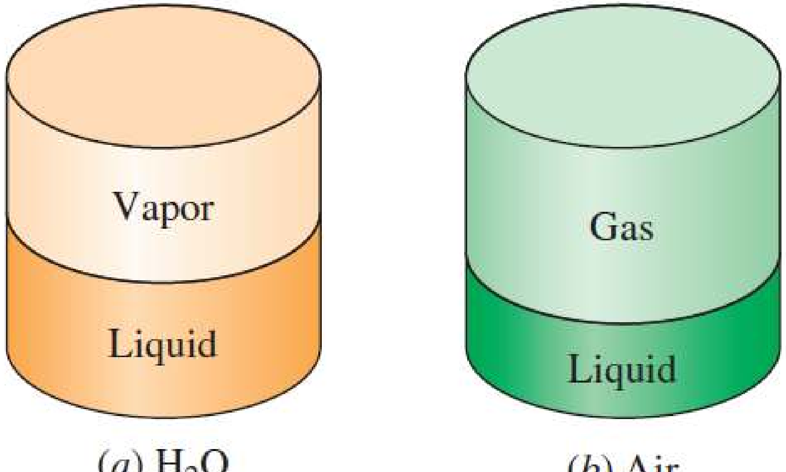


FIGURE 3–1
Nitrogen and gaseous air are pure substances.

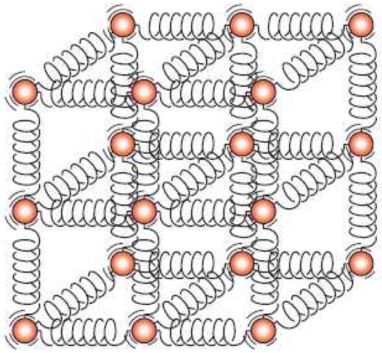


(*a*) H_2O (*b*) Air

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

3-2. PHASES OF A PURE SUBSTANCE

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



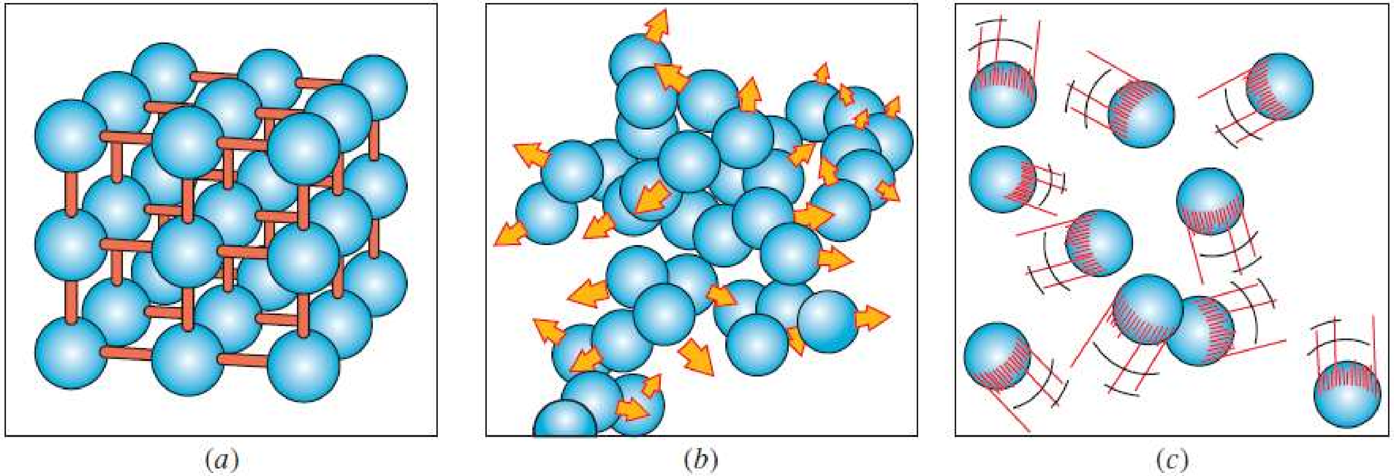


FIGURE 3–4

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

3-3. PHASE-CHANGE PROCESSES

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

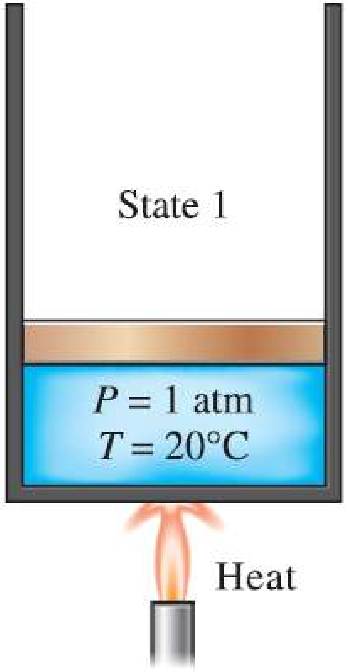


FIGURE 3–5
At 1 atm and 20°C, water exists in the liquid phase (*compressed liquid*).

3-3. PHASE-CHANGE PROCESSES

Saturated liquid:
A liquid that is
about to vaporize

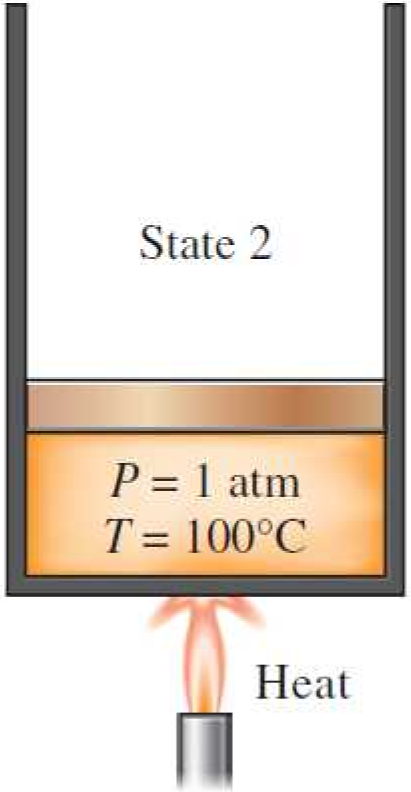


FIGURE 3–6
At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (*saturated liquid*).

3-3. PHASE-CHANGE PROCESSES

Saturated liquid–vapor mixture: The state at which the *liquid and vapor phases coexist* in equilibrium.

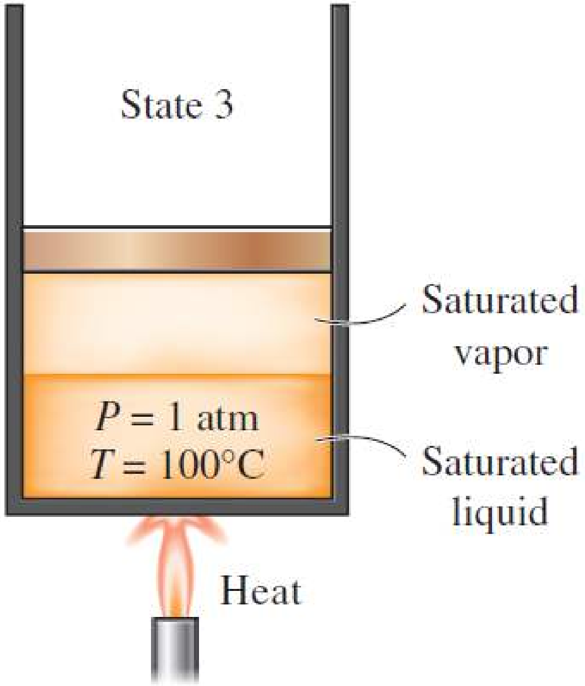


FIGURE 3–7

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

3-3. PHASE-CHANGE PROCESSES

Saturated vapor: A vapor that is *about to condense.*

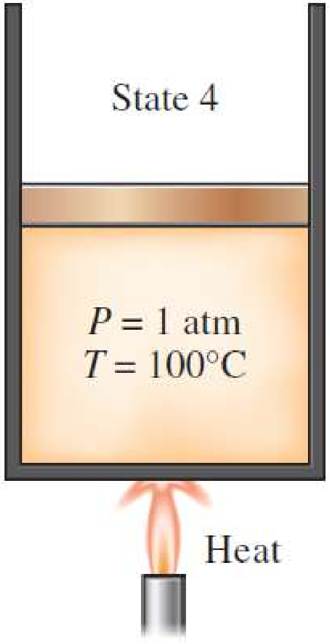


FIGURE 3–8

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

3-3. PHASE-CHANGE PROCESSES

Superheated vapor: A vapor that is *not about to condense* (i.e., not a saturated vapor).

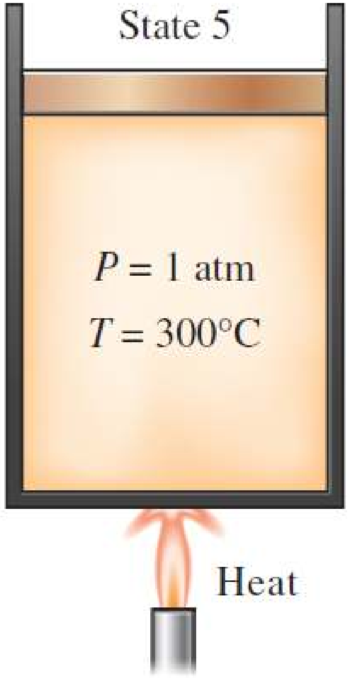
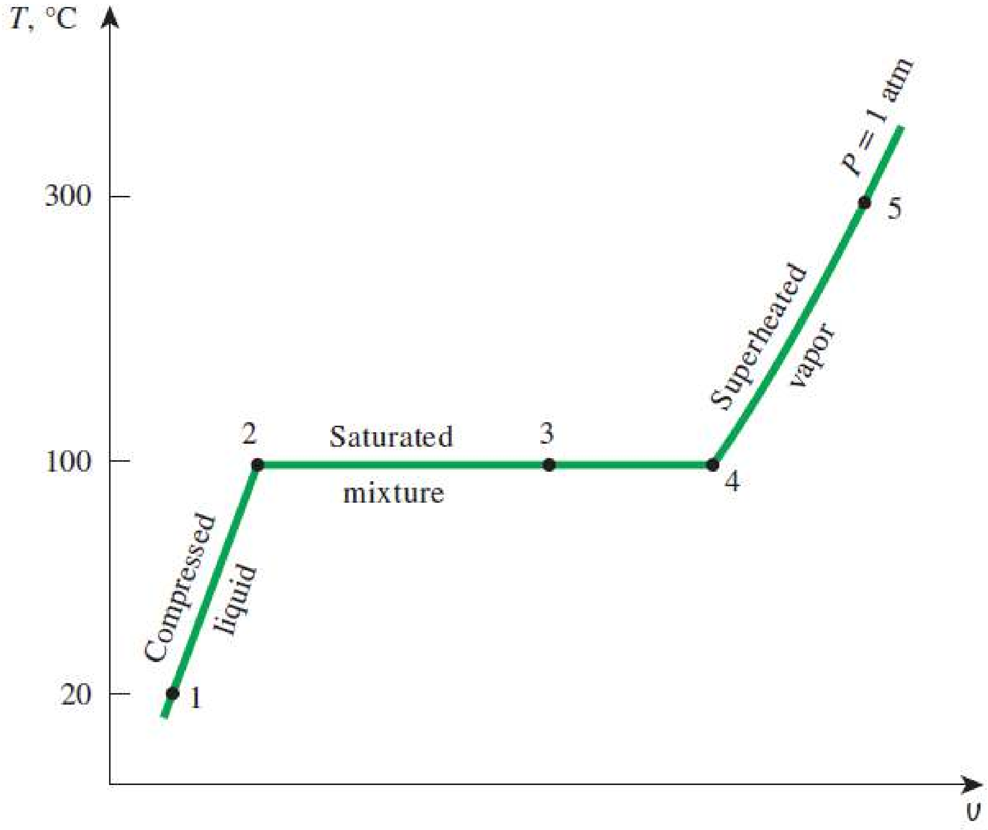


FIGURE 3–9

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

3-3. PHASE-CHANGE PROCESSES

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



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

3-3. PHASE-CHANGE PROCESSES

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.

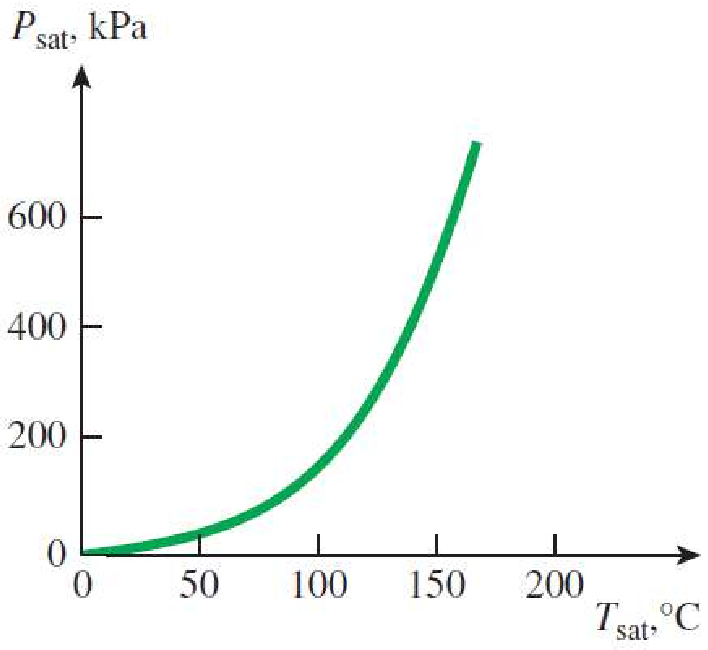


FIGURE 3–11
The liquid–vapor saturation curve of a pure substance (numerical values are for water).

3-3. PHASE-CHANGE PROCESSES

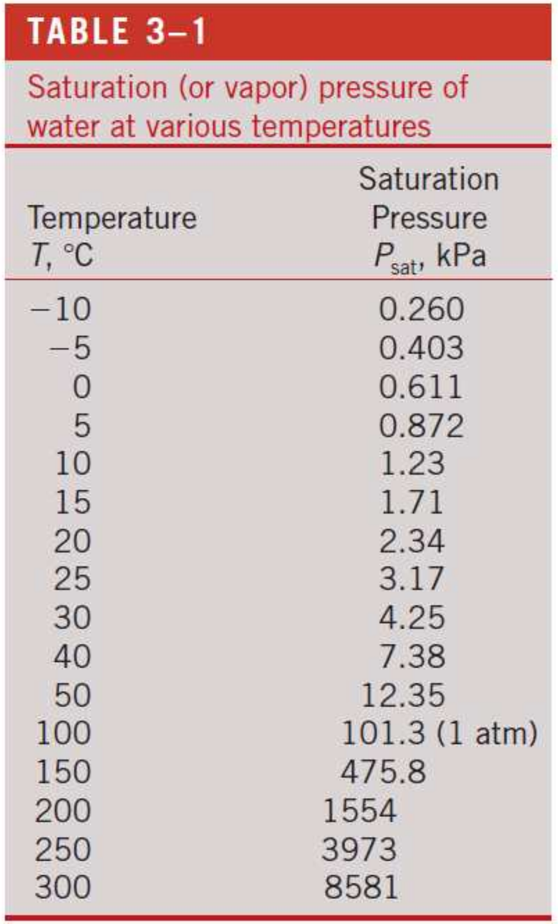


TABLE 3–1

Saturation (or vapor) pressure of water at various temperatures

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

3-3. PHASE-CHANGE PROCESSES

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 334 kJ/kg and the latent heat of vaporization is 2257 kJ/kg.

The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation.

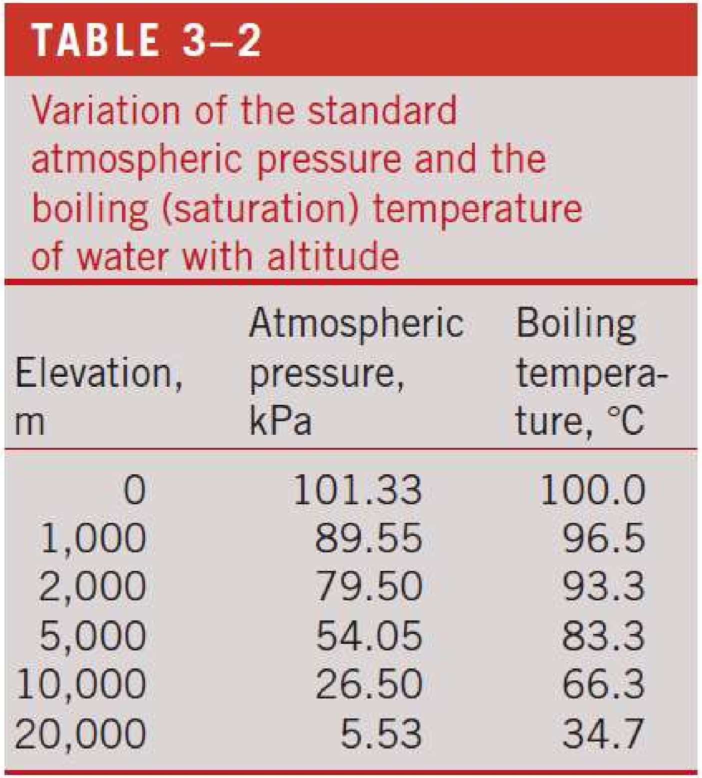
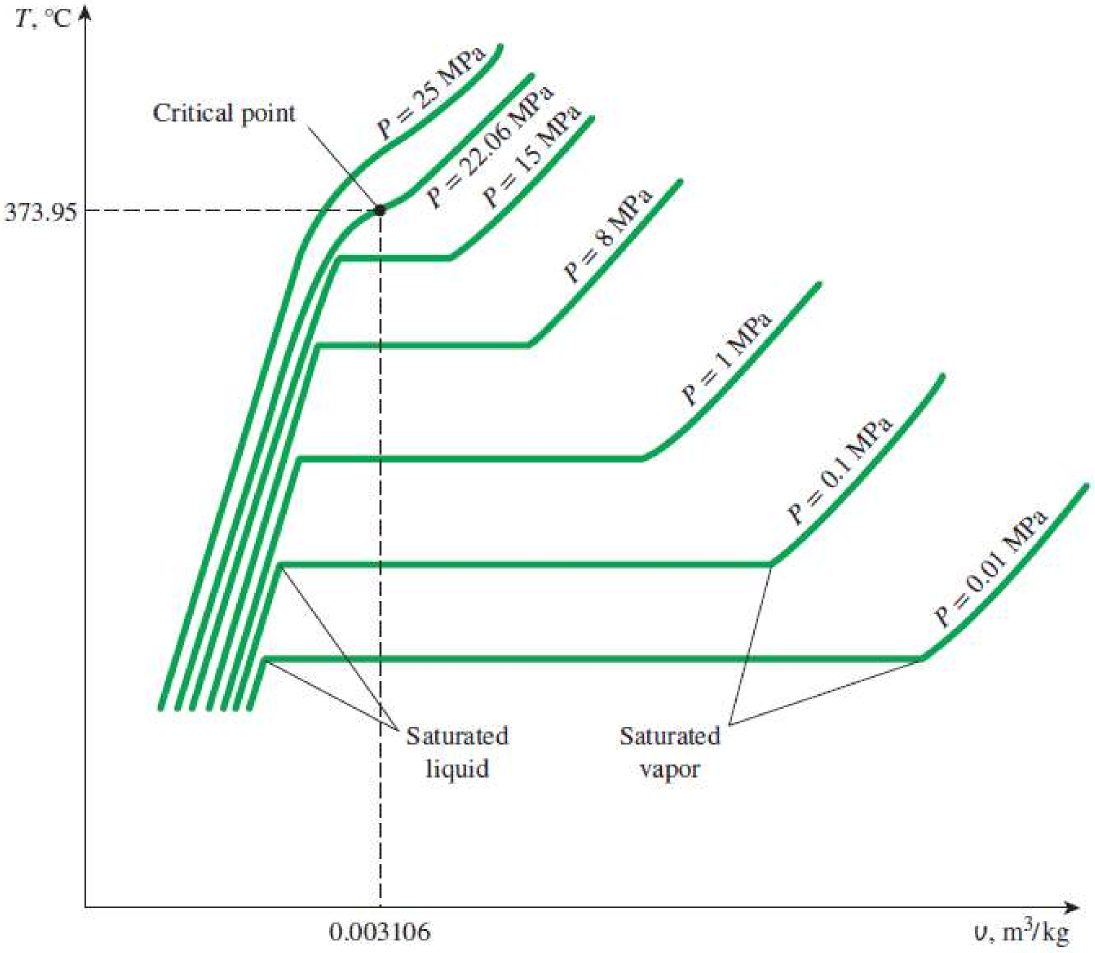


TABLE 3–2

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

3-4. 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).

3-4. PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

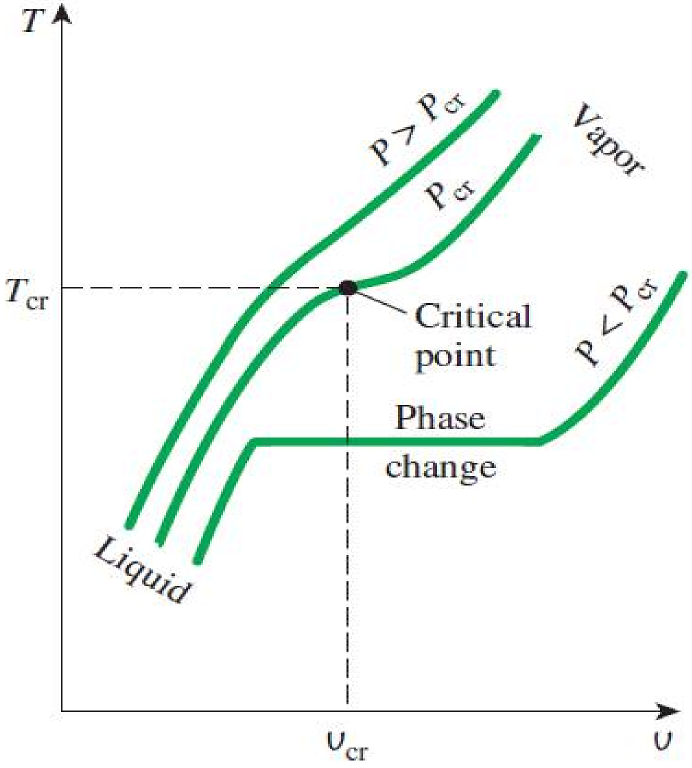


FIGURE 3–16

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.

3-4. PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

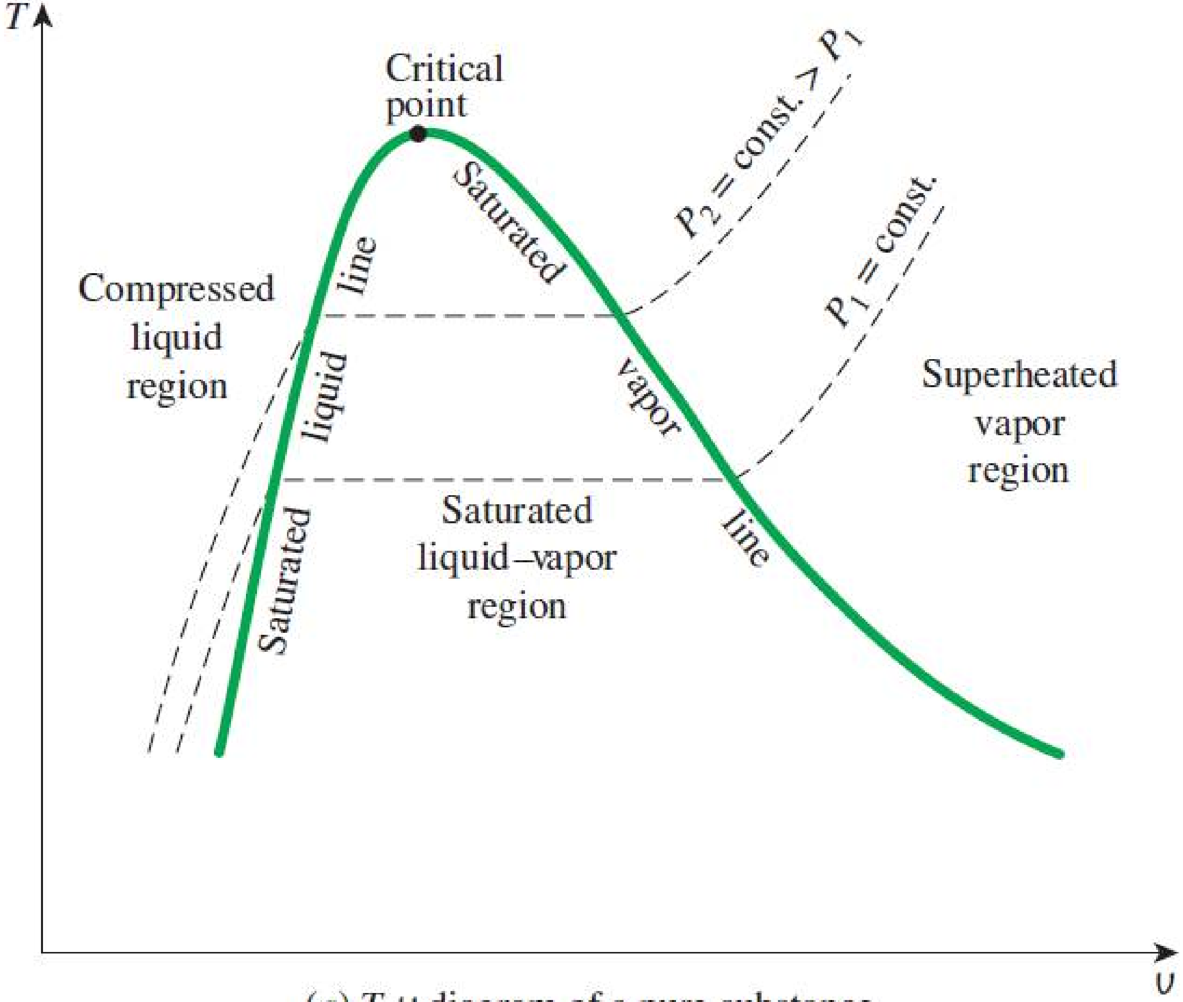
Saturated liquid line

Saturated vapor line

Compressed liquid region

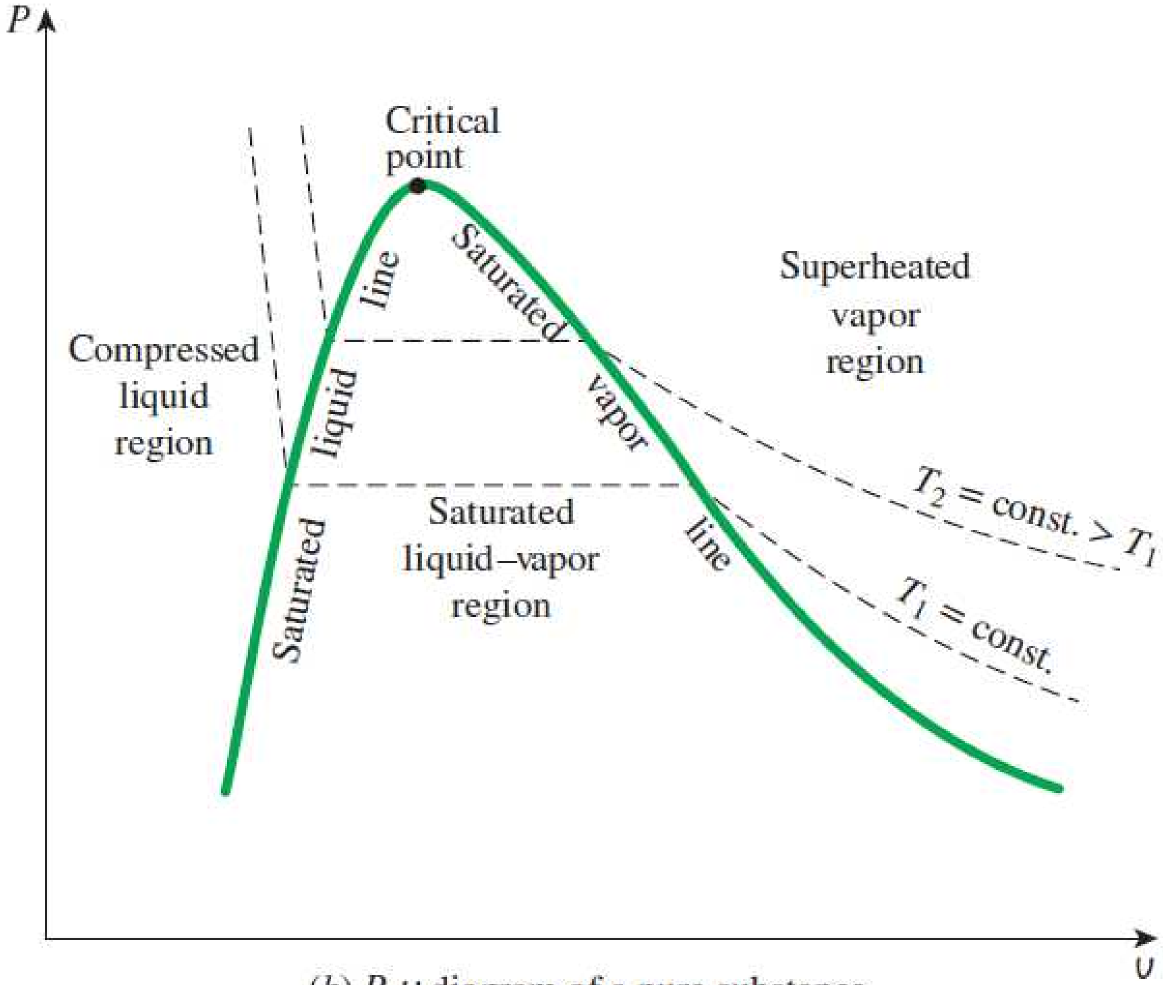
Saturated liquid–vapor mixture region (wet region)

Superheated vapor region



(*a*) T-υ diagram of a pure substance

3-4. PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES



(*b*) *P*-υ diagram of a pure substance

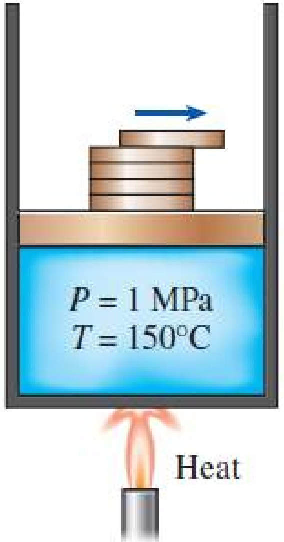


FIGURE 3–18
The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

3-5. 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.

3-5. PROPERTY TABLES

Enthalpy—A Combination Property

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

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

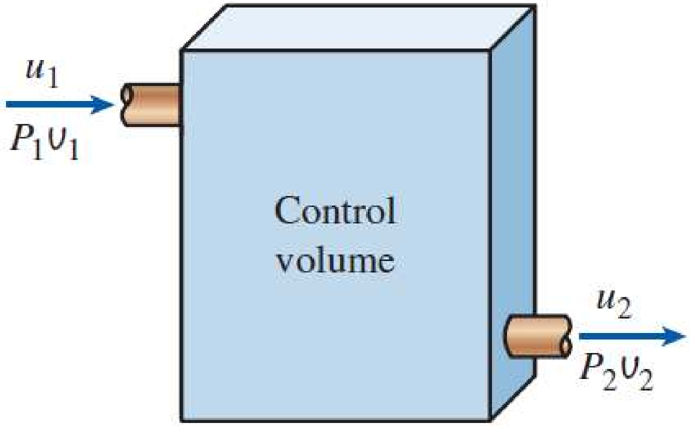
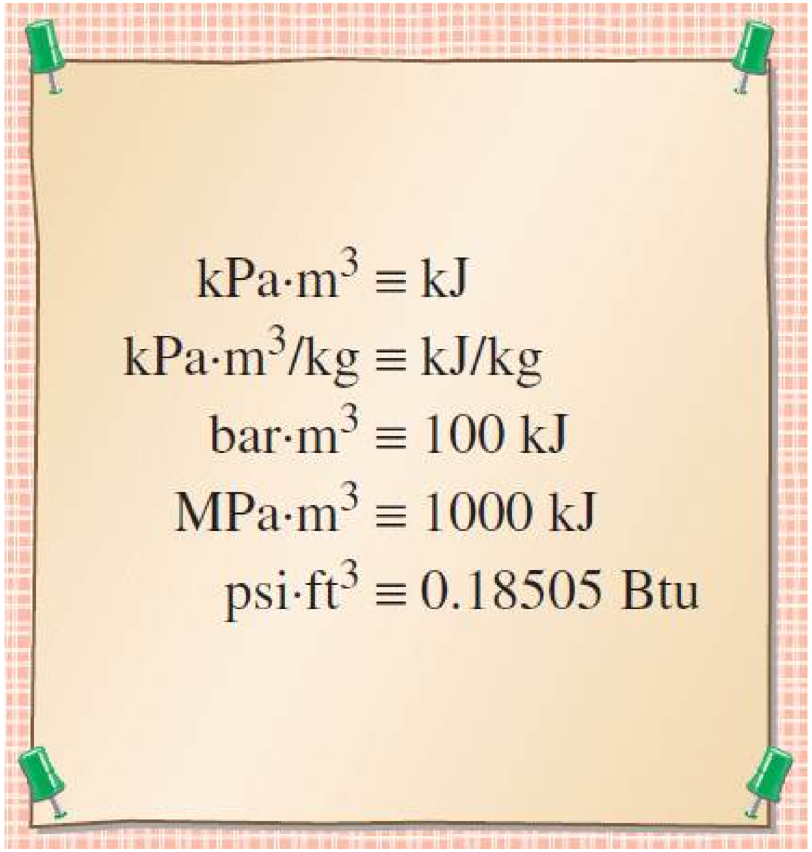


FIGURE 3–25
The combination $u + Pv$ is often encountered in the analysis of control volumes.



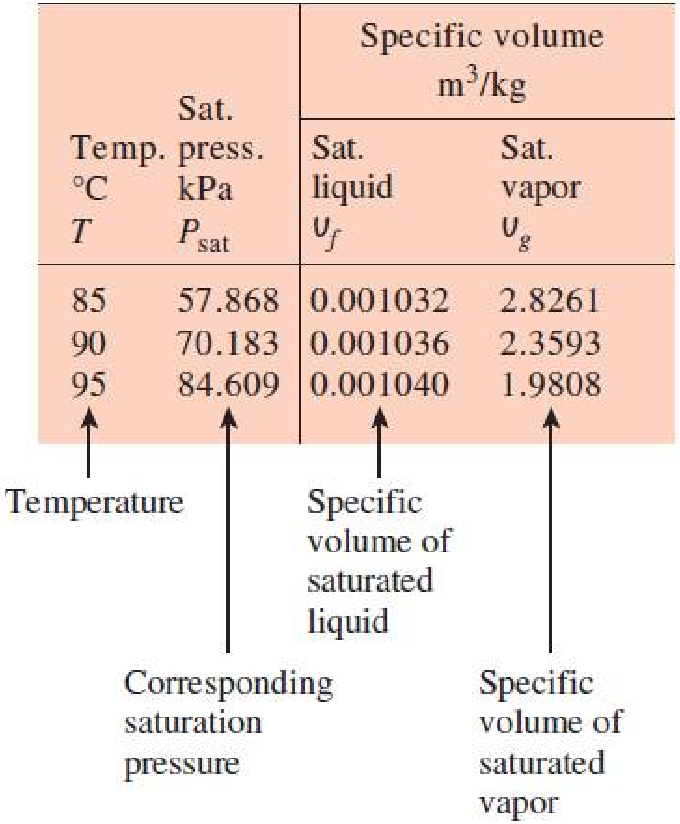
$$\text{kPa}\cdot\text{m}^3 \equiv \text{kJ}$$
$$\text{kPa}\cdot\text{m}^3/\text{kg} \equiv \text{kJ/kg}$$
$$\text{bar}\cdot\text{m}^3 \equiv 100\ \text{kJ}$$
$$\text{MPa}\cdot\text{m}^3 \equiv 1000\ \text{kJ}$$
$$\text{psi}\cdot\text{ft}^3 \equiv 0.18505\ \text{Btu}$$

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

3-5. PROPERTY TABLES

Saturated Liquid and Saturated Vapor States

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

Temperature

Corresponding saturation pressure

Specific volume of saturated liquid

Specific volume of saturated vapor

Table A–4: Saturation properties of water under temperature.

Table A–5: Saturation properties of water under pressure.

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 $v_{fg} = v_g - v_f$)

3-5. PROPERTY TABLES

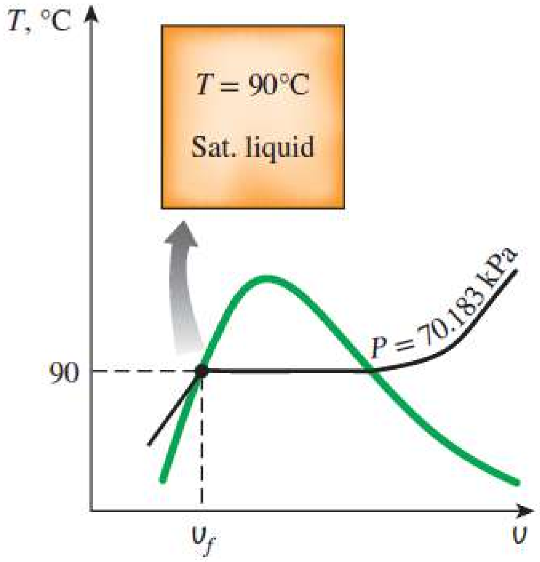
Enthalpy of vaporization, (Latent heat of vaporization) h_{fg}

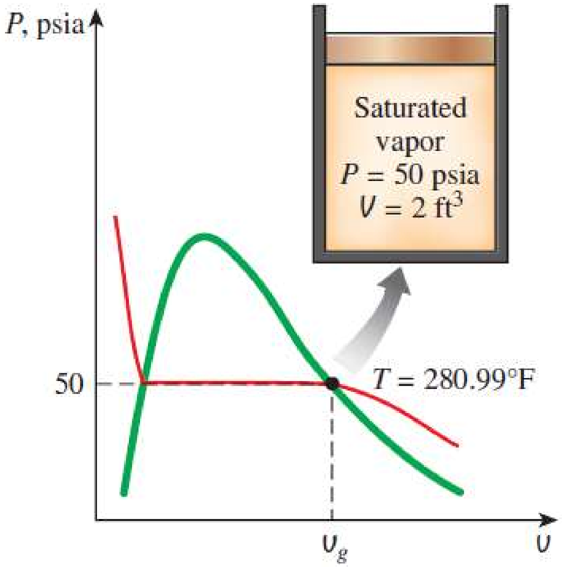
The amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure.

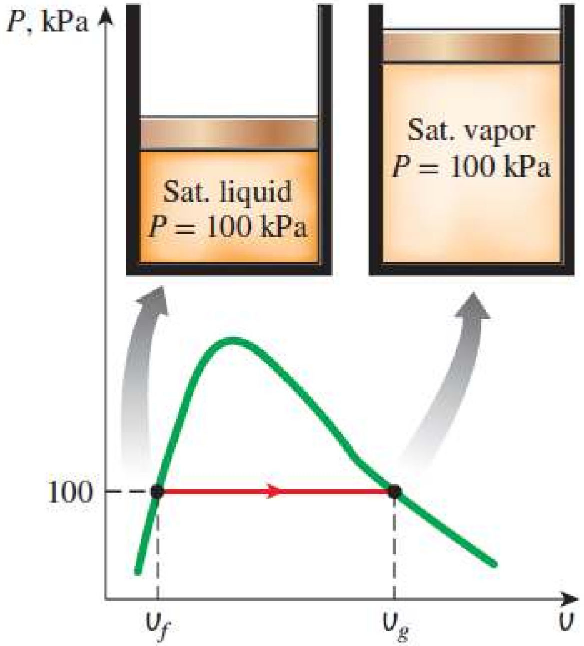
It represents the amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure.

It decreases as the temperature or pressure increases and becomes zero at the critical point.

3-5. PROPERTY TABLES







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

3-5. PROPERTY TABLES

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.

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

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

Temperature and pressure are dependent properties for a mixture.

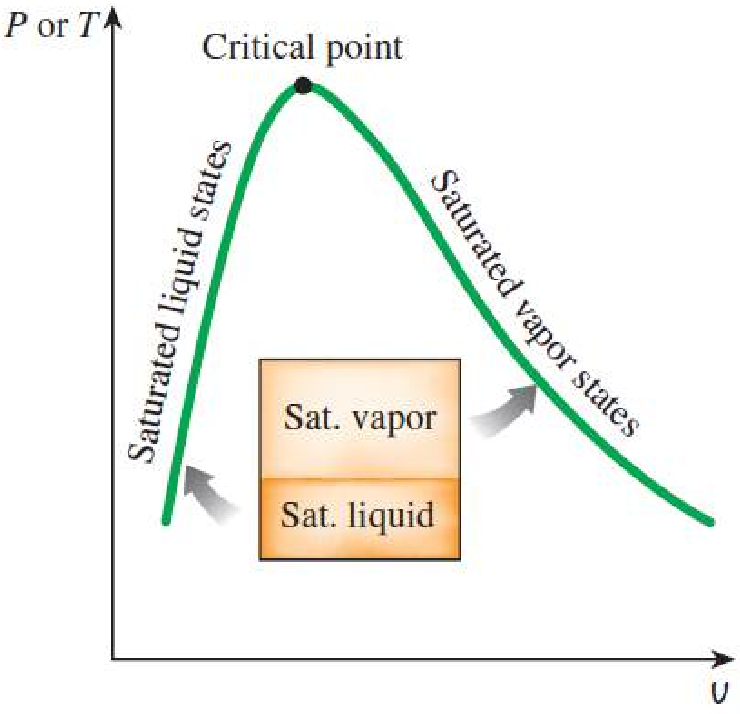


FIGURE 3–31

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

3-5. PROPERTY TABLES

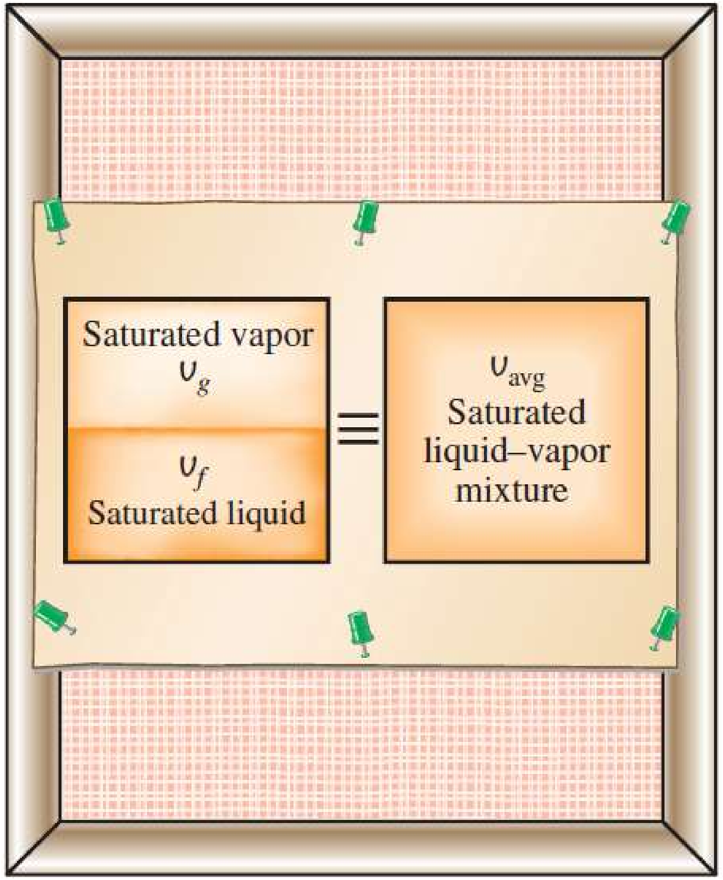


FIGURE 3–32
A two-phase system can be treated as a homogeneous mixture for convenience.

3-5. PROPERTY TABLES

$$\mathrm{V} = \mathrm{V}_f + \mathrm{V}_g$$

$$\mathrm{V} = mv \longrightarrow m_t v_{\text{avg}} = m_f v_f + m_g v_g$$

$$m_f = m_t - m_g \longrightarrow m_t v_{\text{avg}} = (m_t - m_g) v_f + m_g v_g$$

$$v_{\text{avg}} = (1 - x) v_f + x v_g$$

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

$$v_{fg} = v_g - v_f \qquad x = m_g / m_t$$

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

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

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

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

y → v, u, or h

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

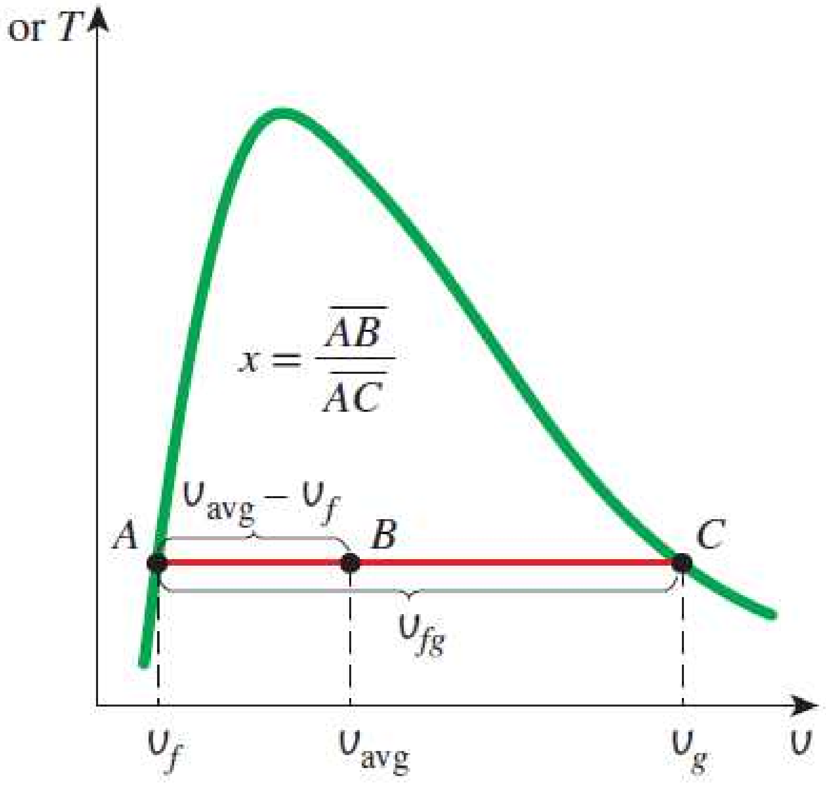


FIGURE 3–33

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

3-5. PROPERTY TABLES

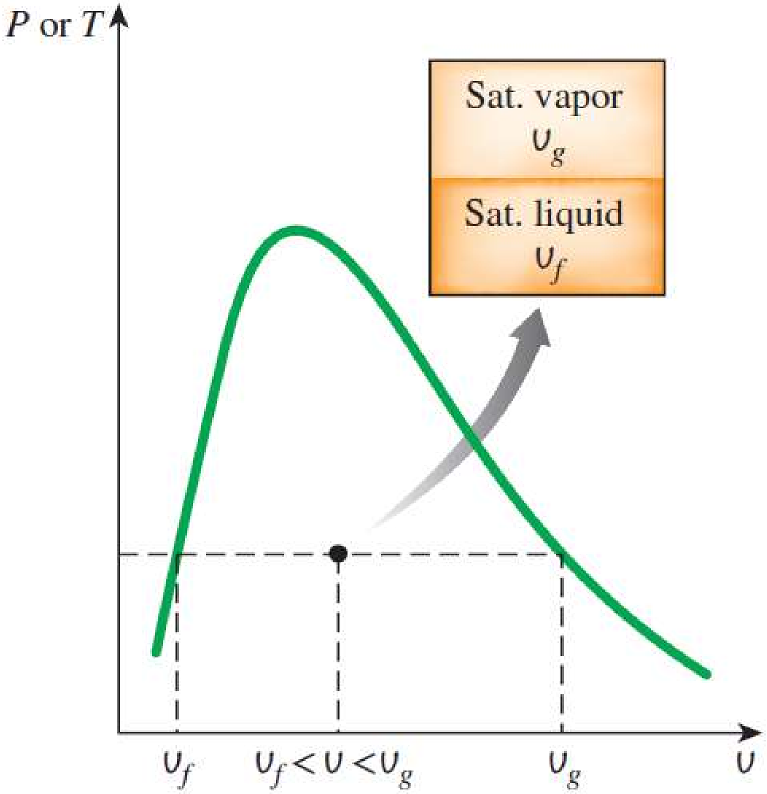
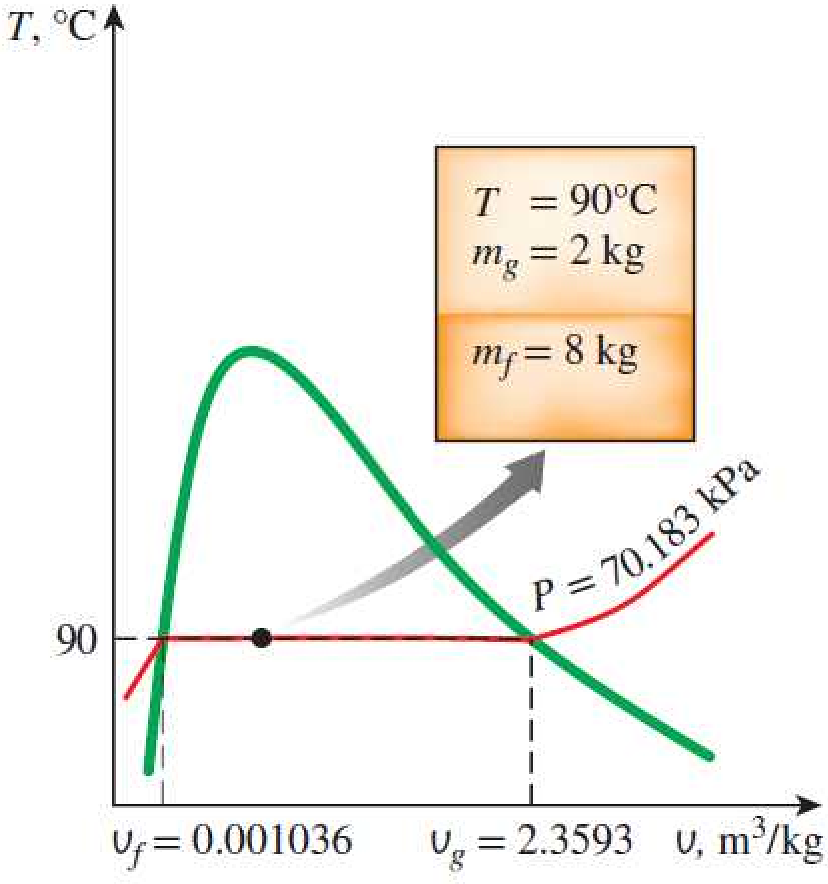
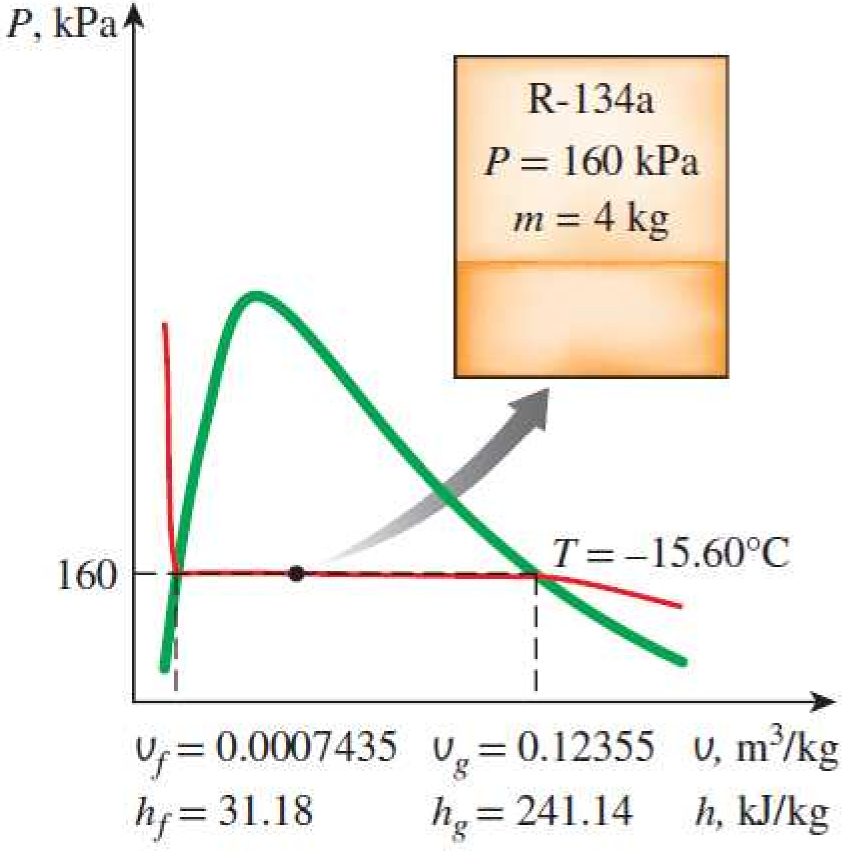


FIGURE 3–34
The v value of a saturated liquid–vapor mixture lies between the v_f and v_g values at the specified T or P.

3-5. PROPERTY TABLES

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





3-5. PROPERTY TABLES

Superheated Vapor

Compared to saturated vapor, superheated vapor is characterized by

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

Higher temperatures ($T > T_{sat}$ 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)

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.

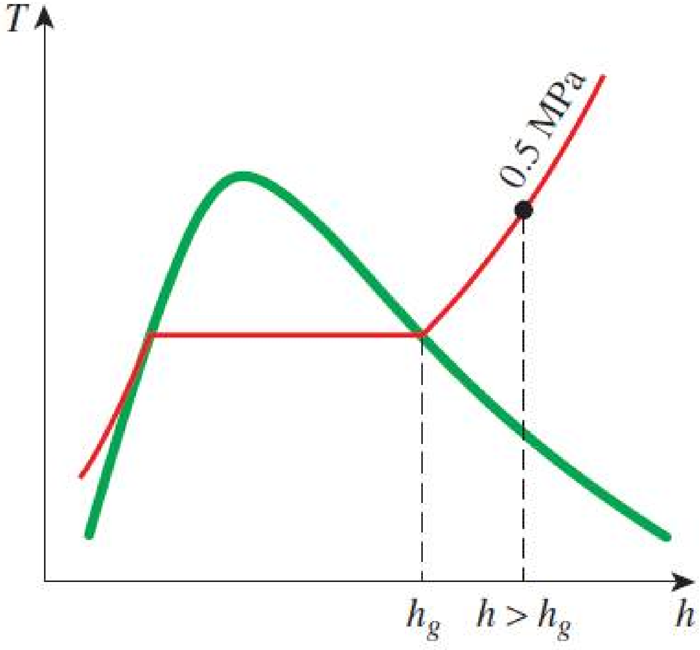
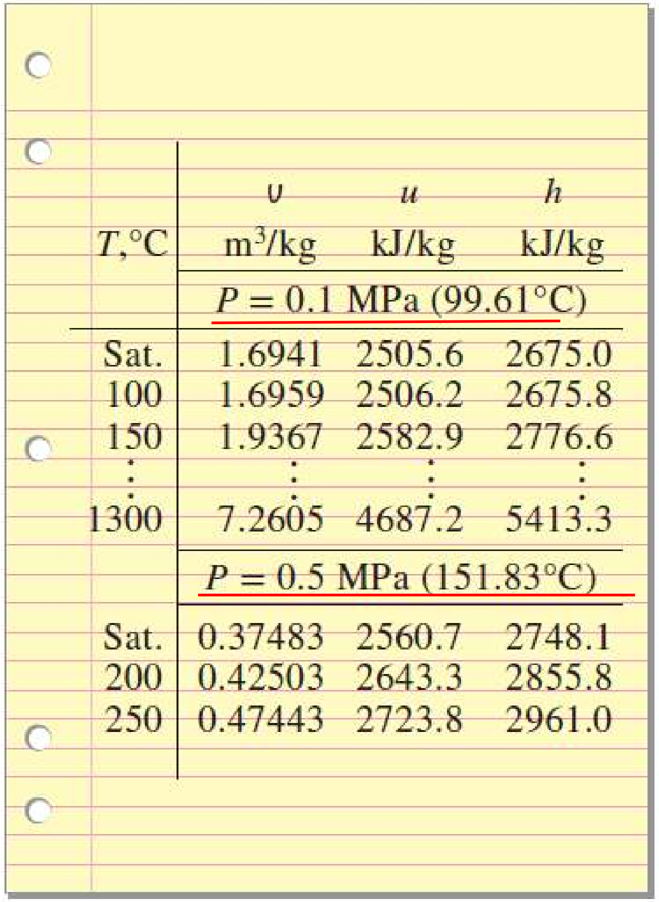


FIGURE 3–38

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

3-5. PROPERTY TABLES



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

FIGURE 3–37

A partial listing of Table A–6.

3-5. PROPERTY TABLES

Compressed Liquid

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

$y \cong y_{f@T}$ $y \rightarrow v, u, \text{or } h$

A more accurate relation for *h*

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

Compressed liquid is characterized by

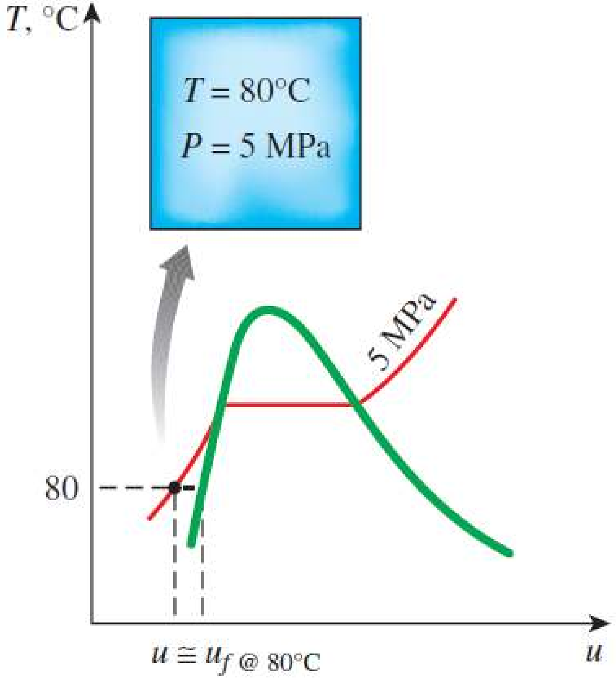
Higher pressures ($P > P_{\text{sat}}$ at a given T)

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

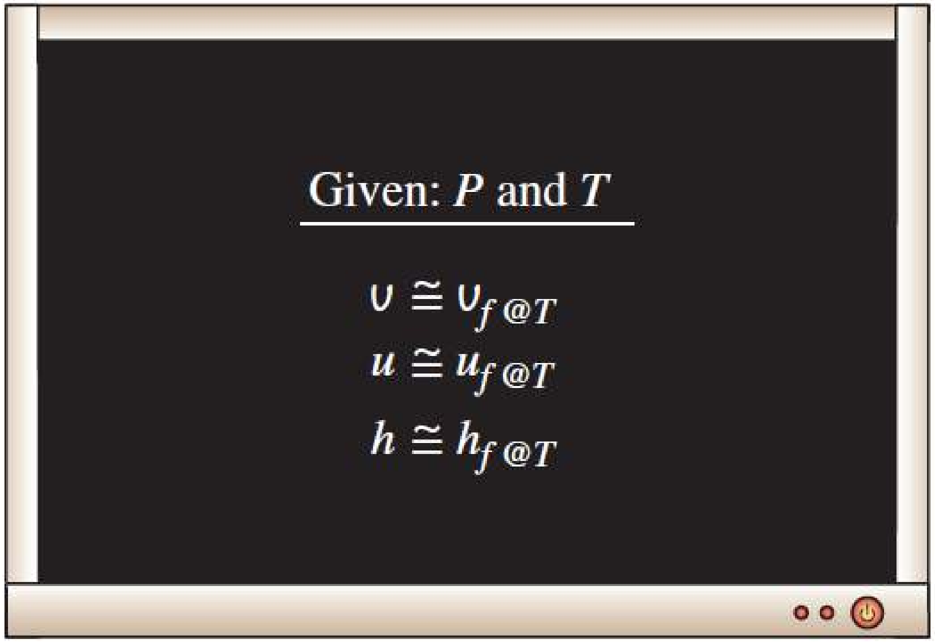
Lower specific volumes ($v < v_f$ at a given P or T)

Lower internal energies ($u < u_f$ at a given P or T)

Lower enthalpies ($h < h_f$ at a given P or T)



3-5. PROPERTY TABLES



Given: P and T

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

FIGURE 3–40

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

3-5. PROPERTY TABLES

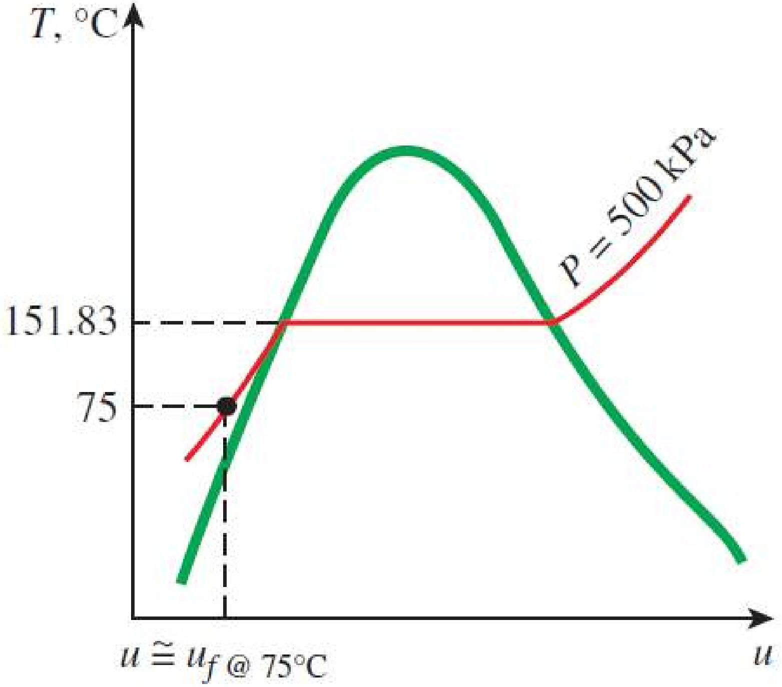


FIGURE 3–41
At a given P and T, a pure substance will exist as a compressed liquid if $T < T_{sat\ @\ P}$.

3-5. PROPERTY TABLES

Reference State and Reference Values

The values of *u*, *h*, and *s* cannot be measured directly, and they are calculated from measurable properties using the relations between properties.

However, those relations give the *changes* in properties, not the values of properties at specified states.

Therefore, we need to choose a convenient *reference state* and assign a value of *zero* for a convenient property or properties at that state.

The reference state for water is 0.01°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.

3-5. PROPERTY TABLES

TABLE A–4

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

TABLE A–11

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	0.0007053	0.36064	−0.036	207.42	207.38	0.00	225.86	225.86	0.00000	0.96869	0.96869
−38	56.86	0.0007082	0.32718	2.472	206.06	208.53	2.512	224.62	227.13	0.01071	0.95516	0.96588

3-6. 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

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

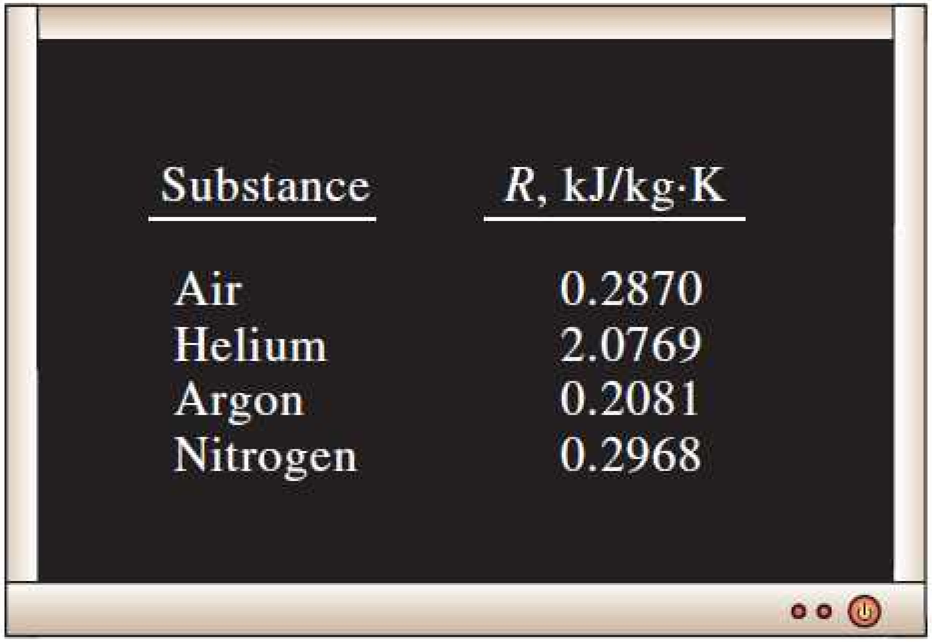
$$R_u = \begin{cases} 8.31447 \text{ kJ/kmol·K} \\ 8.31447 \text{ kPa·m}^3\text{/kmol·K} \\ 0.0831447 \text{ bar·m}^3\text{/kmol·K} \\ 1.98588 \text{ Btu/lbmol·R} \\ 10.7316 \text{ psia·ft}^3\text{/lbmol·R} \\ 1545.37 \text{ ft·lbf/lbmol·R} \end{cases}$$

R gas constant

M molar mass (kg/kmol)

R_u universal gas constant

3-6. THE IDEAL-GAS EQUATION OF STATE



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

FIGURE 3–42
Different substances have different gas constants.

3-6. THE IDEAL-GAS EQUATION OF STATE

Mass = Molar mass × Mole number

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

Various expressions of ideal gas equation

$$V = mv \longrightarrow PV = mRT$$

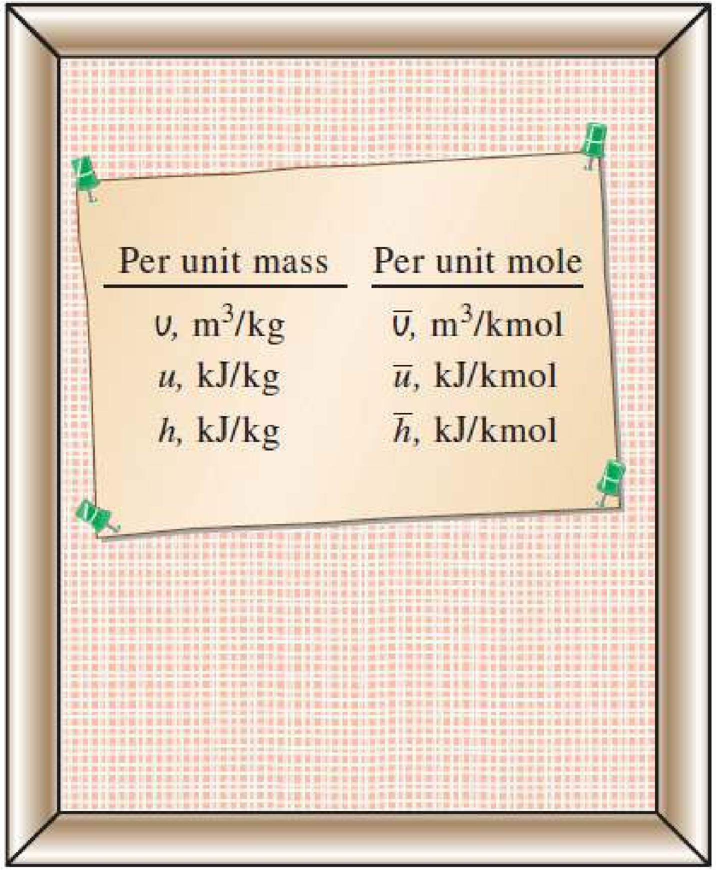
$$mR = (MN)R = NR_u \longrightarrow PV = NR_uT$$

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

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

Ideal gas equation at two states for a fixed mass

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

FIGURE 3–44

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

Is Water Vapor an Ideal Gas?

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

At higher pressures, 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.

3-6. THE IDEAL-GAS EQUATION OF STATE

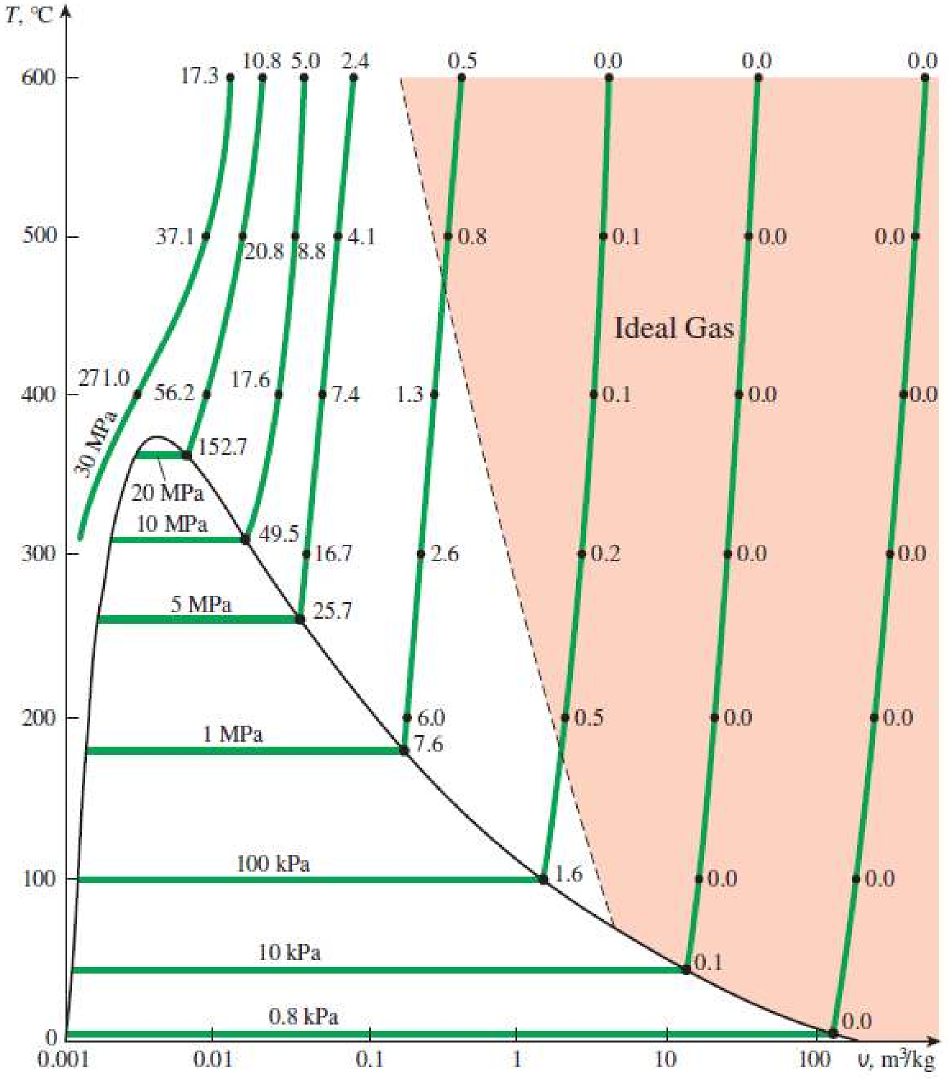


FIGURE 3–46

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

Summary

Pure substance

Phases of a pure substance

Phase-change processes of pure substances

Property diagrams for phase change processes

Property tables

The ideal gas equation of state

Compressibility factor

Other equations of state