Chapter 3
PROPERTIES OF PURE SUBSTANCES

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PROPERTIES OF PURE SUBSTANCES

3–1 Pure Substance

3–2 Phases of a Pure Substance

3–3 Phase-Change Processes of Pure Substances

Compressed Liquid and Saturated Liquid

Saturated Vapor and Superheated Vapor

Saturation Temperature and Saturation Pressure

Some Consequences of Tsat and Psat Dependence

3–4 Property Diagrams for Phase-Change Processes

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The P-v-T Surface

3–5 Property Tables

Enthalpy—A Combination Property

1a Saturated Liquid and Saturated Vapor States

1b Saturated Liquid–Vapor Mixture

2 Superheated Vapor

3 Compressed Liquid

Reference State and Reference Values

3–6 The Ideal-Gas Equation of State

Is Water Vapor an Ideal Gas?

3–7 Compressibility Factor—A Measure of Deviation from Ideal-Gas Behavior

3–8 Other Equations of State

Van der Waals - Beattie-Bridgeman -Benedict-Webb-Rubin and

Virial Equation of State

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.

N_2

AIR

VAPOR

LIQUID

$(a)\ H_2O$

VAPOR
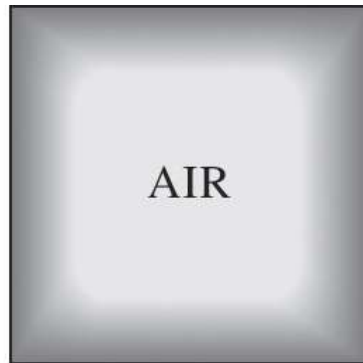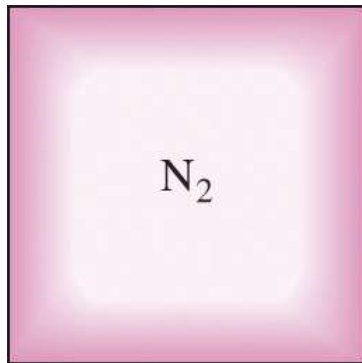
LIQUID

$(b)\ AIR$

Nitrogen and gaseous air are pure substances.
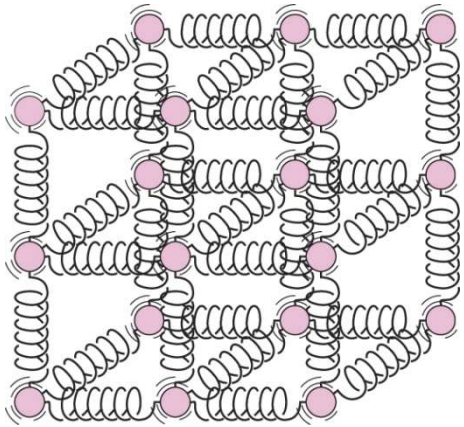
A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.
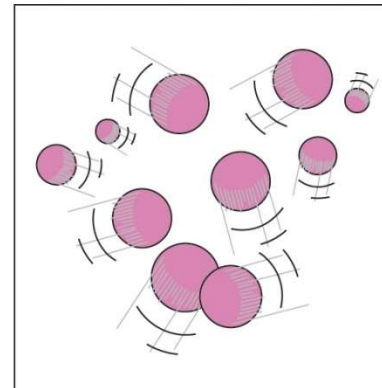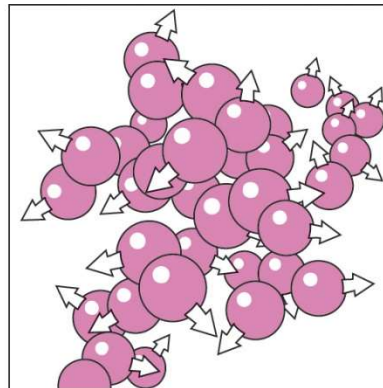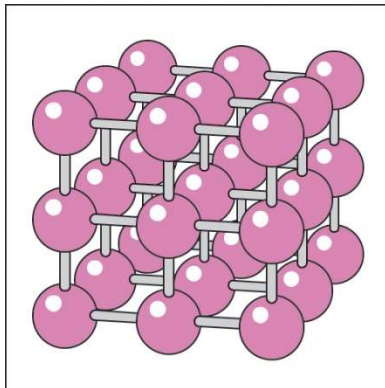
PHASES OF A PURE SUBSTANCE

The molecules in a solid are kept at their positions by the large spring like 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.

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

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

STATE 1

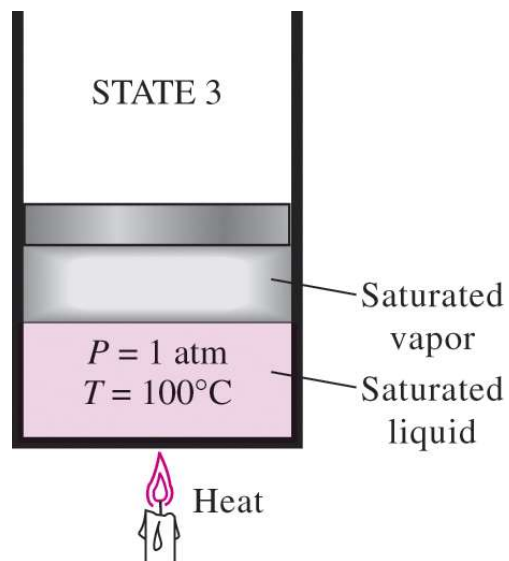$P = 1$ atm
$T = 20°C$

Heat

STATE 2

$P = 1$ atm
$T = 100°C$

Heat
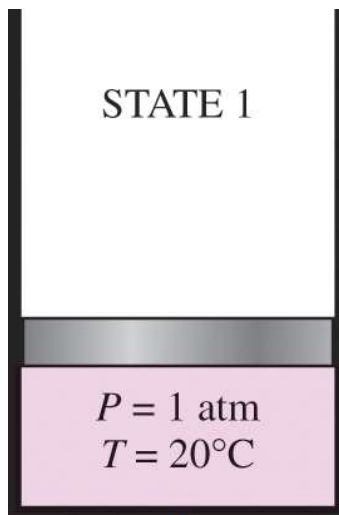
At 1 atm and 20°C, water exists in the liquid phase (*compressed liquid*).
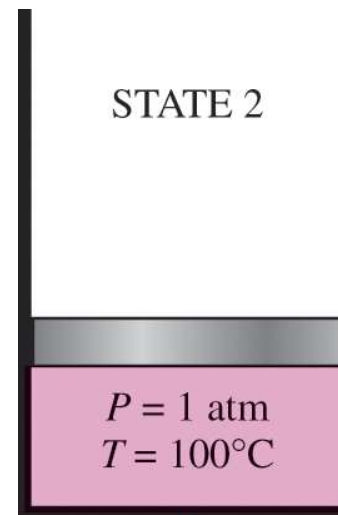
At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (*saturated liquid*).

- **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).

STATE 3

P = 1 atm
T = 100°C

Saturated vapor

Saturated liquid

Heat

STATE 4

P = 1 atm
T = 100°C

Heat

STATE 5

P = 1 atm
T = 300°C

Heat

As more heat is transferred, part of the saturated liquid vaporizes (*saturated liquid–vapor mixture*)
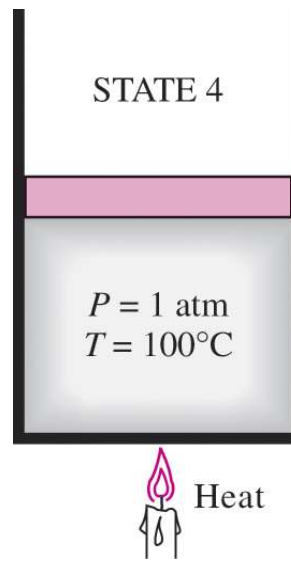
At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (*saturated vapor*).
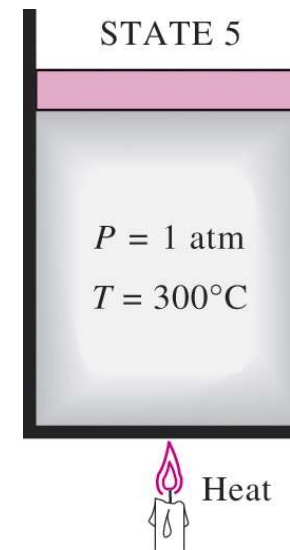
As more heat is transferred, the temperature of the vapor starts to rise (*superheated vapor*).

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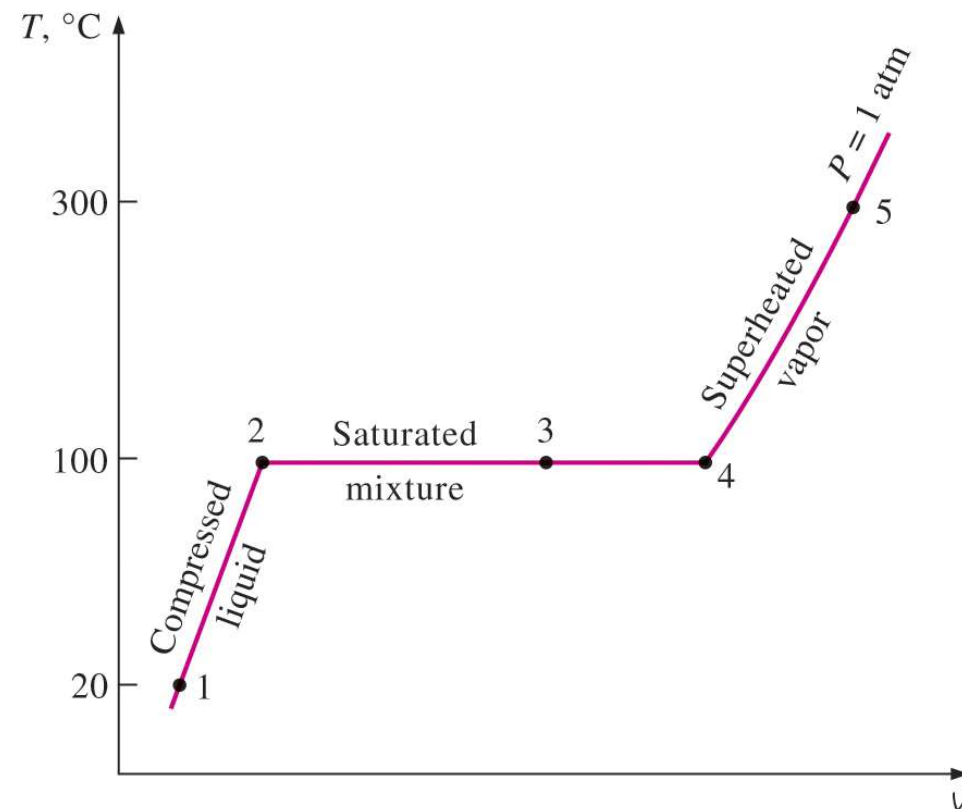
T-v diagram for the heating process of water at constant pressure.

o The temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.

o Water boils at 100°C at 1 atm pressure.

o **Saturation temperature T_{sat}**: The temperature at which a pure substance changes phase at a given pressure.
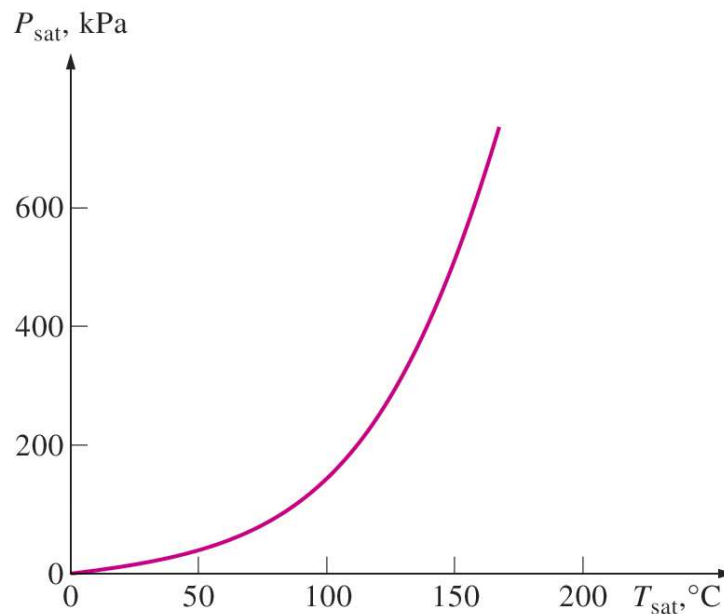
o **Saturation pressure P_{sat}**: The pressure at which a pure substance changes phase at a given temperature.

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

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.

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

N₂ vapor
–196°C

Test chamber –196°C

25°C

Liquid N₂ –196°C

Insulation

Temperature °C

Start of cooling (25°C, 100 kPa)

25

End of cooling (0°C, 0.61 kPa)

0

0   0.61 1   3.17   10   100
Pressure (kPa)

Vacuum pump

Insulation

Air + Vapor

Low vapor pressure

Evaporation

High   vapor   pressure

Ice

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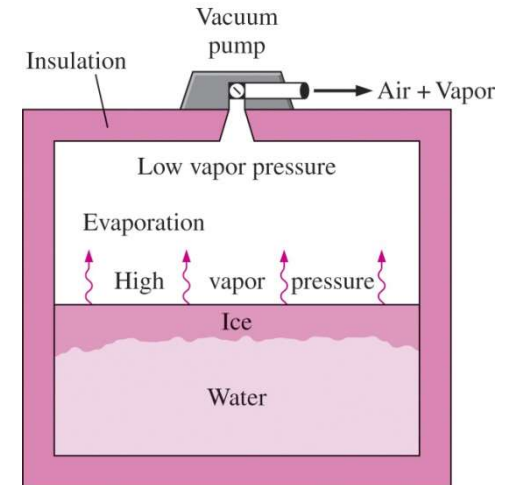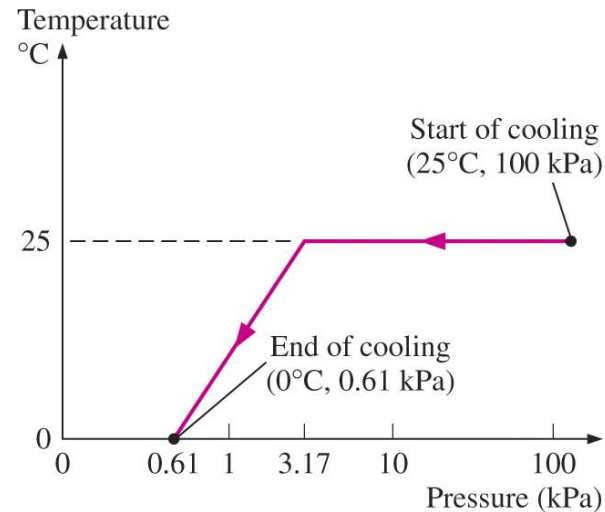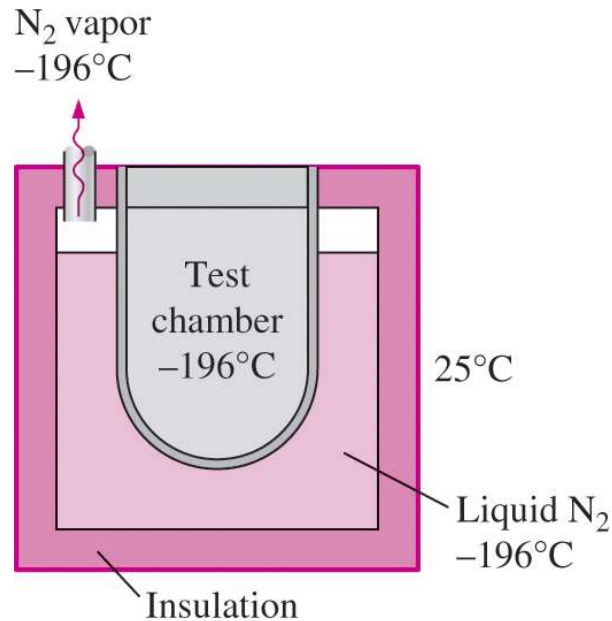
The temperature of liquid nitrogen exposed to the atmosphere remains constant at 196°C, and thus it maintains the test chamber at 196°C.

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.

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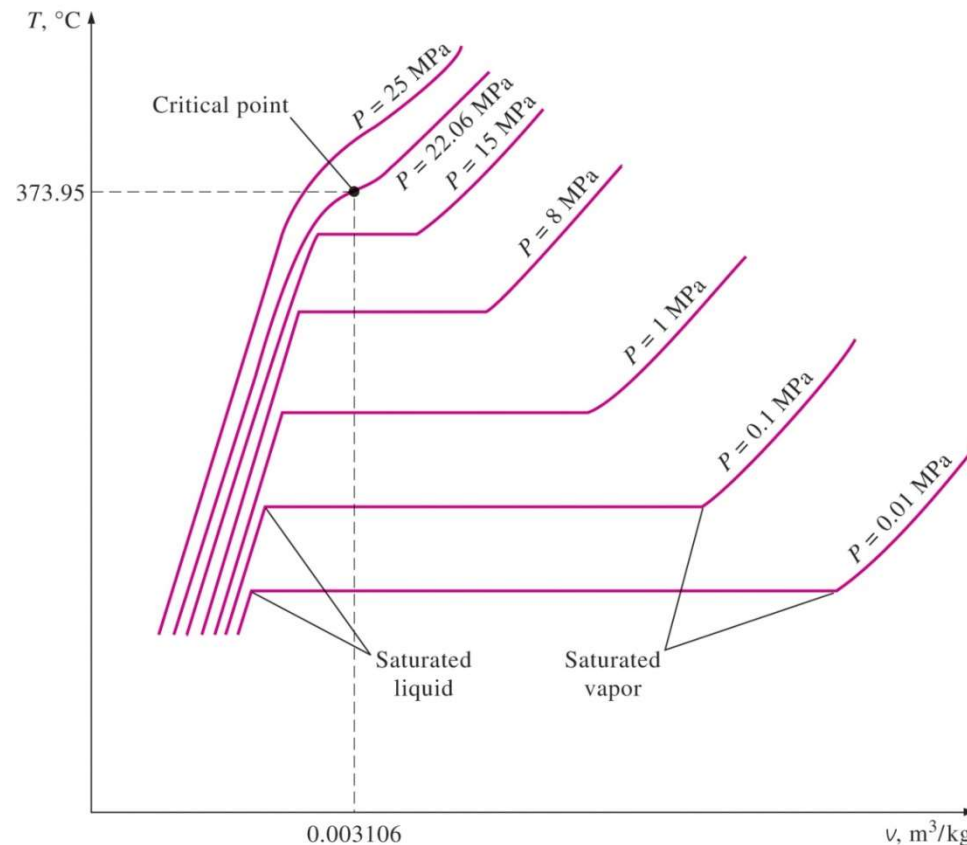
T-v diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

- **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.
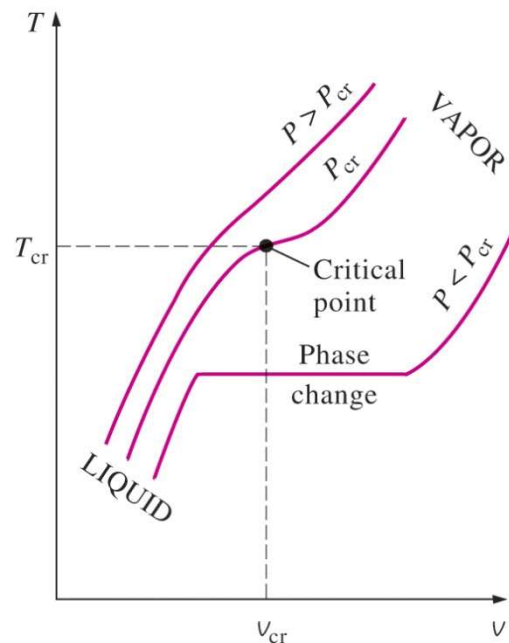
At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.
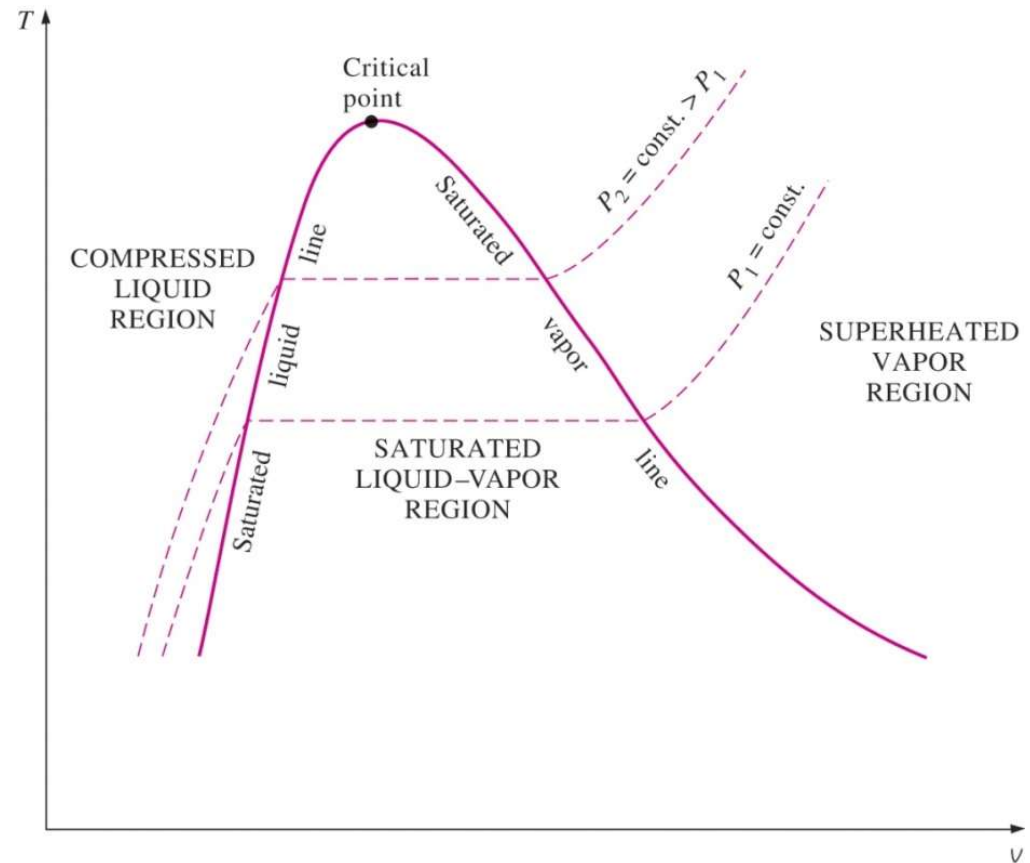
Critical point: The point at which the saturated liquid and saturated vapor states are identical.

P-v diagram of a pure substance.

P = 1 MPa
T = 150°C

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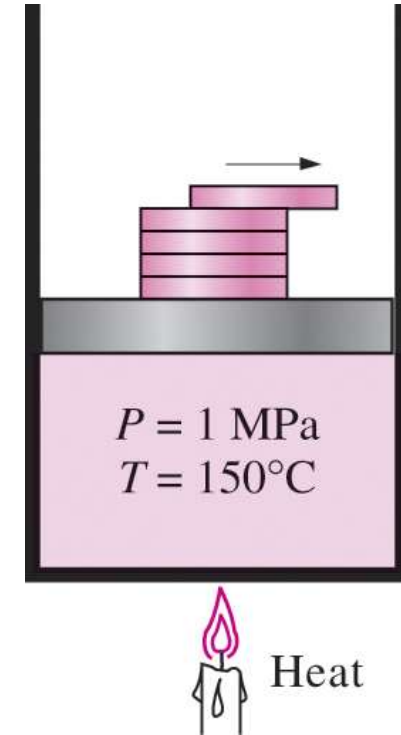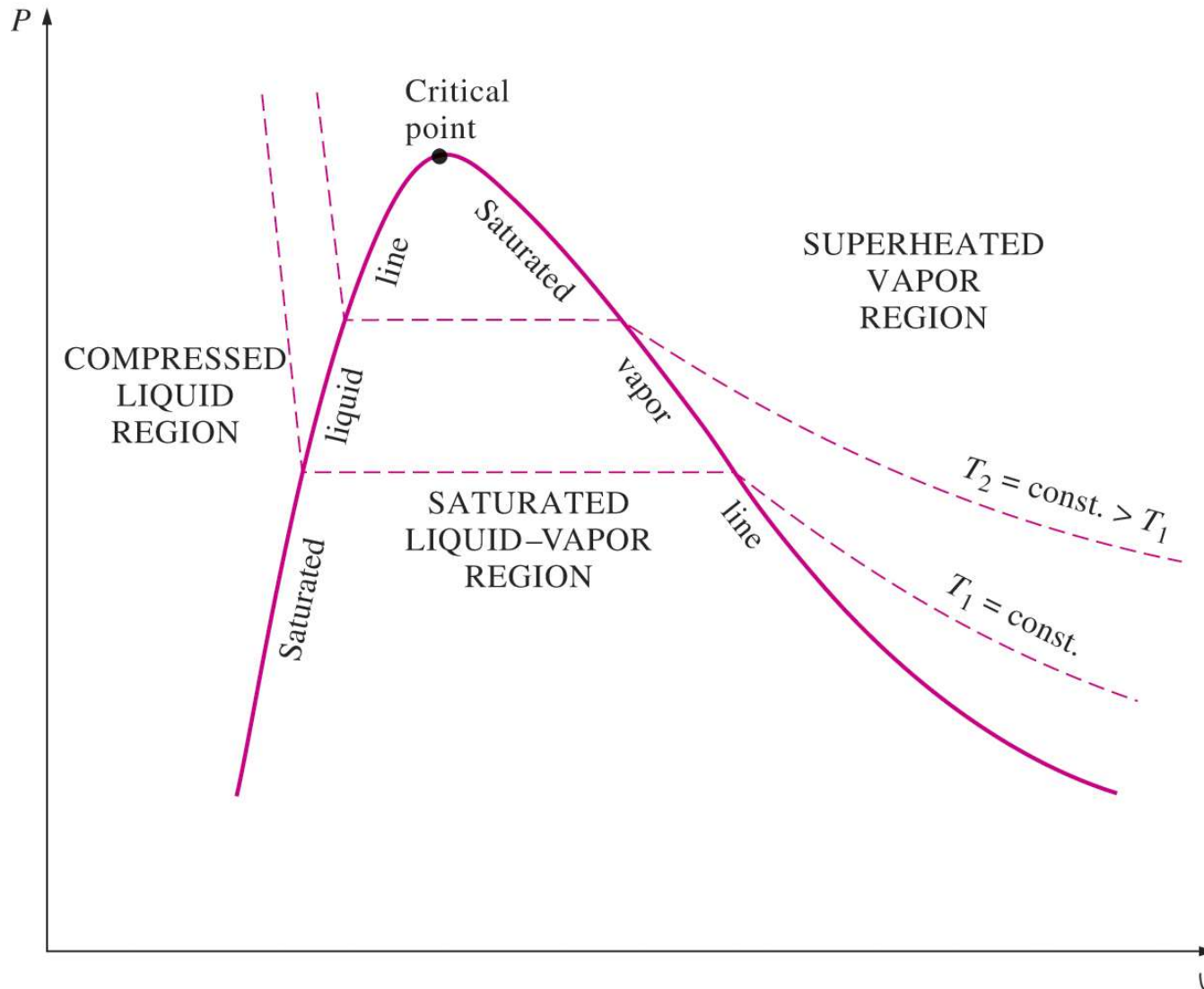
The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

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For water,
T_{tp} = 0.01°C
P_{tp} = 0.6117 kPa

At triple-point pressure and temperature, a substance exists in three phases in equilibrium.
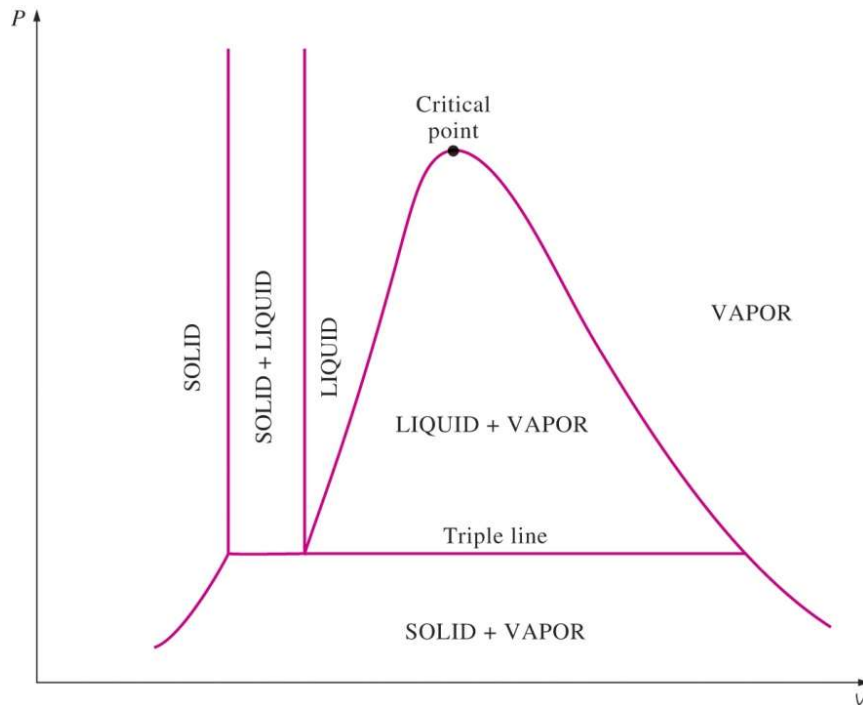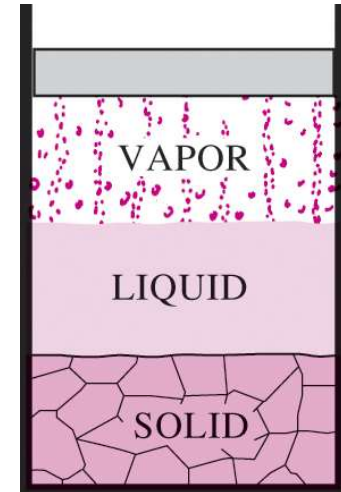
P-v diagram of a substance that contracts on freezing.
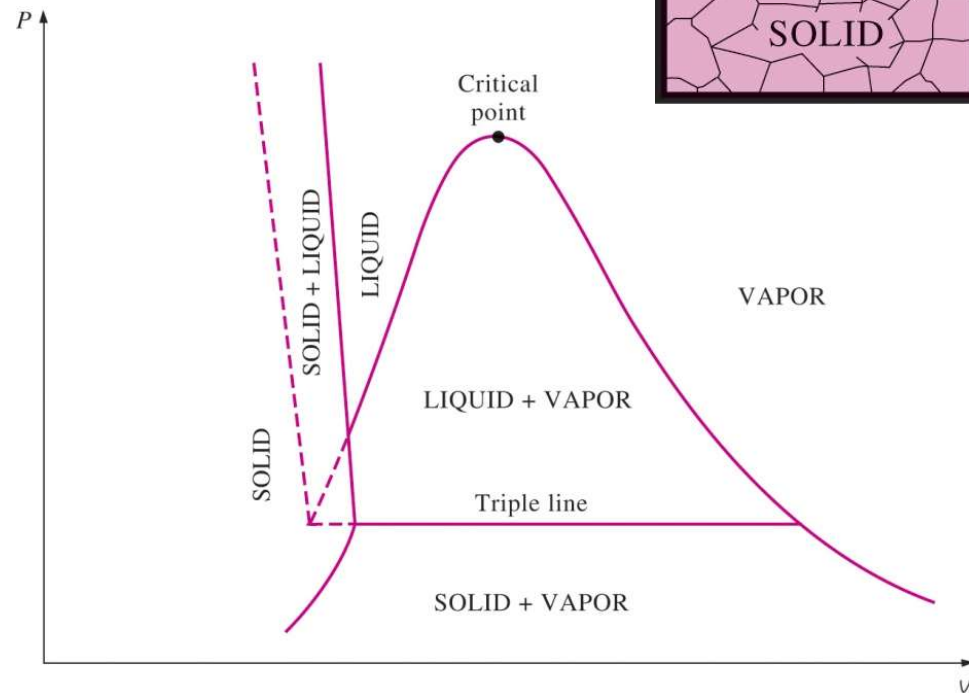
P-v diagram of a substance that expands on freezing (such as water).

Phase Diagram

Sublimation: Passing from the solid phase directly into the vapor phase.
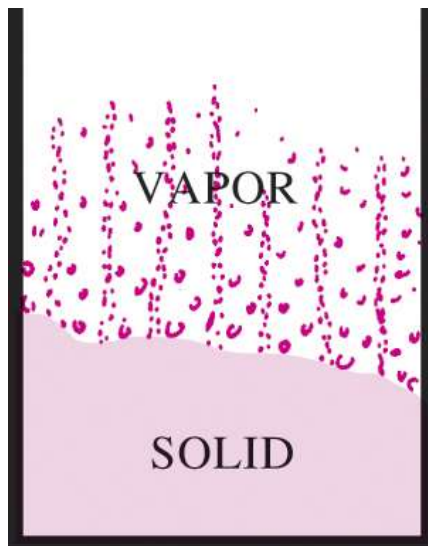
At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).
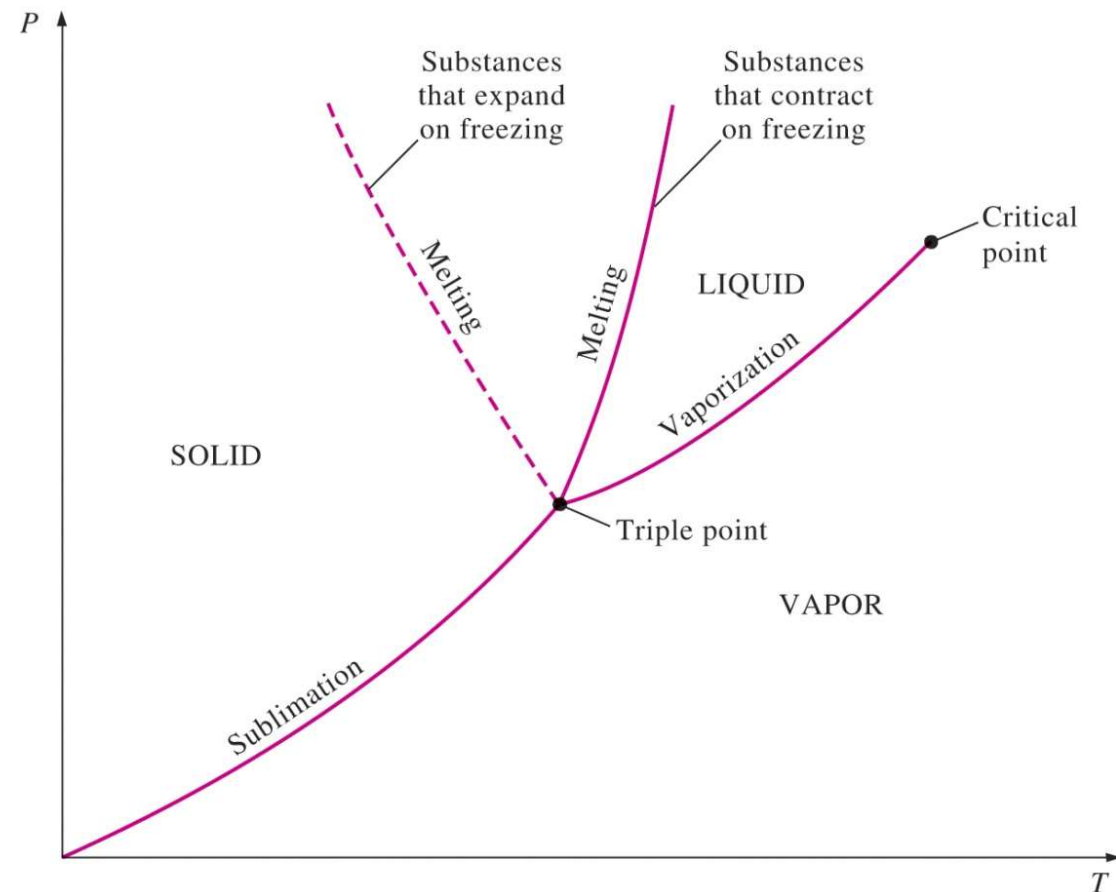
P-T diagram of pure substances.

PROPERTY TABLES

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

Enthalpy—A Combination Property

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

$$kPa \cdot m^3 \equiv kJ$$
$$kPa \cdot m^3/kg \equiv kJ/kg$$
$$bar \cdot m^3 \equiv 100 \ kJ$$
$$MPa \cdot m^3 \equiv 1000 \ kJ$$
$$psi \cdot ft^3 \equiv 0.18505 \ Btu$$
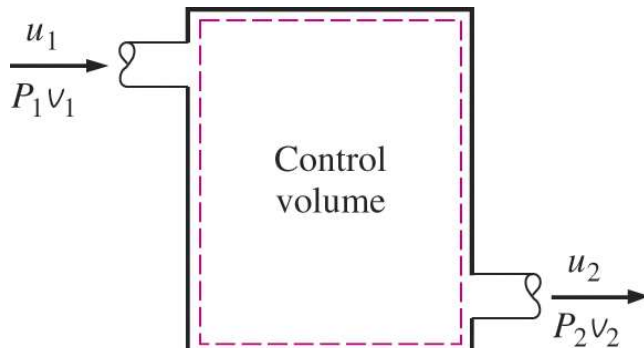
The combination $u + Pv$ is frequently encountered in the analysis of control volumes.

The product *pressure × volume* has energy units.

○ **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, $v_{fg} = v_g - v_f$)

A partial list of Table A–4.

Temp. °C T	Sat. press. kPa P_{sat}	Specific volume m³/kg	
		Sat. liquid v_f	Sat. vapor v_g
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

Specific temperature

Corresponding saturation pressure

Specific volume of saturated liquid

Specific volume of saturated vapor

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.

EXAMPLE 3-1

A rigid tank contains 50 kg of saturated liquid water at 90⁰C. Determine the pressure in the tank and the volume of the tank.
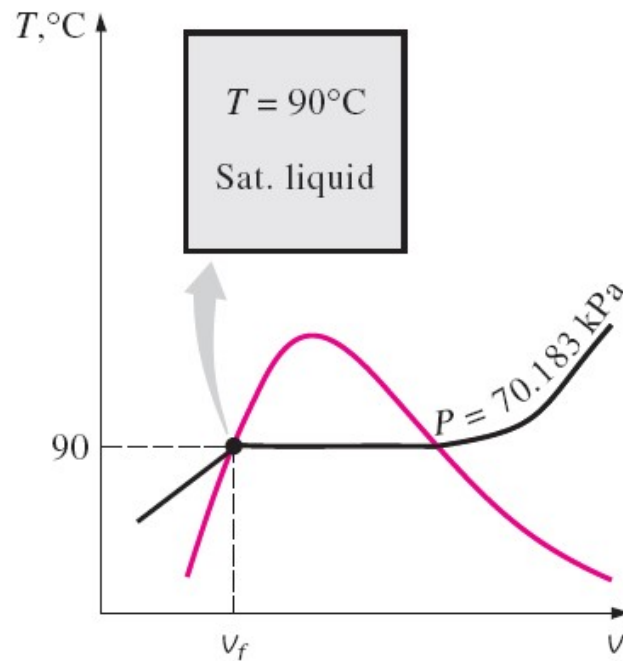
Solution A rigid tank contains saturated liquid water. The pressure and volume of the tank are to be determined.

Since saturation conditions exist in the tank, the pressure must be the saturation pressure at 90⁰C:

$$P = P_{sat\ @\ 90°C} = \mathbf{70.183\ kPa}$$

The specific volume of the saturated liquid at 90⁰C is

$$v = v_{f\ @\ 90°C} = 0.001036\ m^3/kg$$

The total volume of the tank is

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

EXAMPLE 3-2
A piston–cylinder device contains 0.06 m³ of saturated water vapor at 350-kPa pressure. Determine the temperature and the mass of the vapor inside the cylinder.

The temperature inside must be the saturation temperature at this pressure:

$$T = T_{doy \, @ \, 350 \, kPa} = 138.86°C \qquad (\text{Tablo A–5})$$

The specific volume of the saturated vapor at 350 kPa

$$v = v_{g \, @ \, 350 \, kPa} = 0.52422 \, m^3/kg$$

the mass of water vapor inside the cylinder becomes

$$m = \frac{V}{v} = \frac{0.06 \, m^3}{0.52422 \, m^3/kg} = 0.114 \, kg$$

P, kPa

Saturated vapor
$P = 350$ kPa
$V = 0.06$ m³

350

$T = 138.86°C$

v_g

v
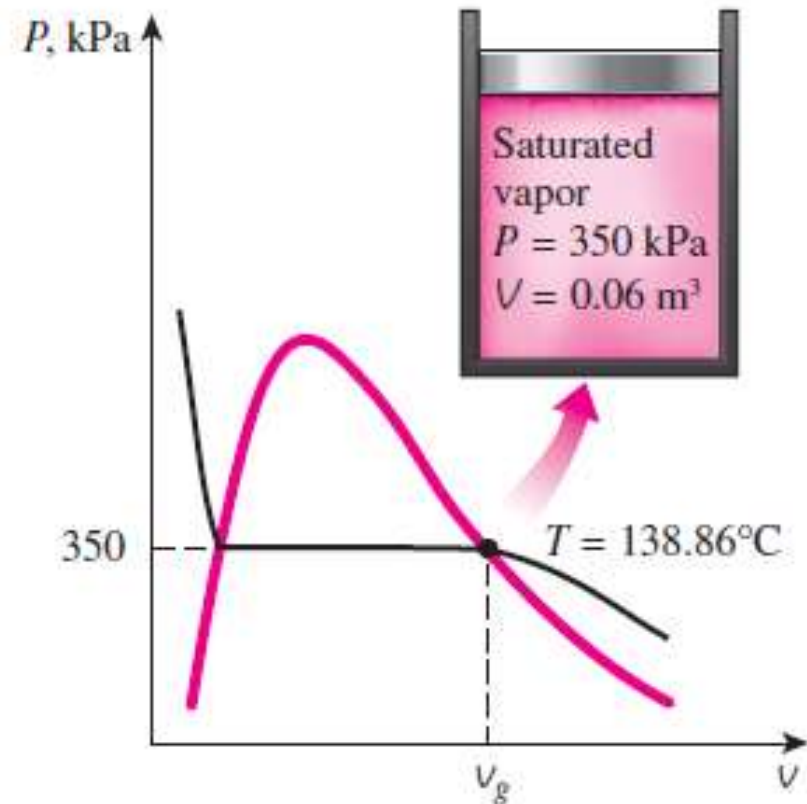
EXAMPLE 3-3

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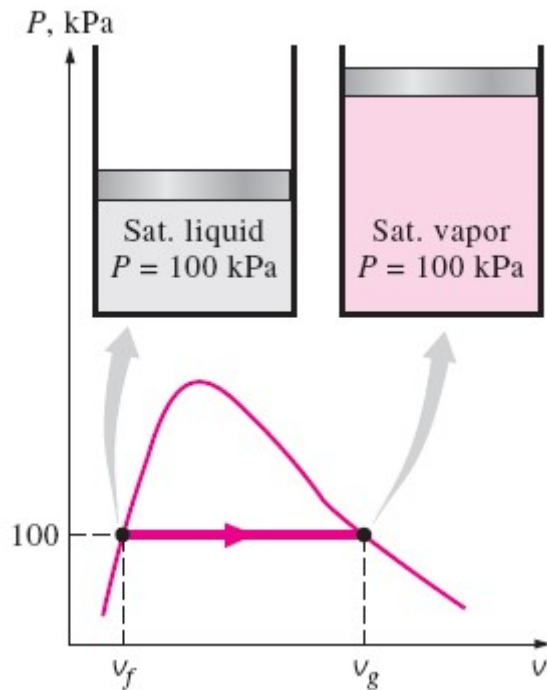
Solution Saturated liquid water is vaporized at constant pressure. The volume change and the energy added are to be determined.

(a) the volume change

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

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

(b) the amount of energy added to the water.

h_{fg} =2257.5 kJ/kg for water at 100 kPa.

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

P, kPa

Sat. liquid
P = 100 kPa

Sat. vapor
P = 100 kPa

100

v_f v_g v

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.
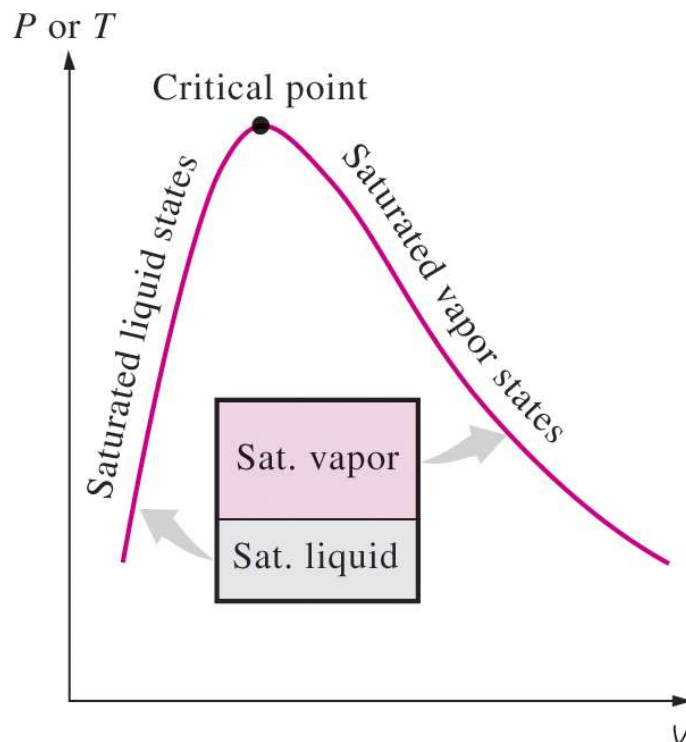
$$x = \frac{m_{vapor}}{m_{total}} \qquad m_{total} = m_{liquid} + m_{vapor} = m_f + m_g$$

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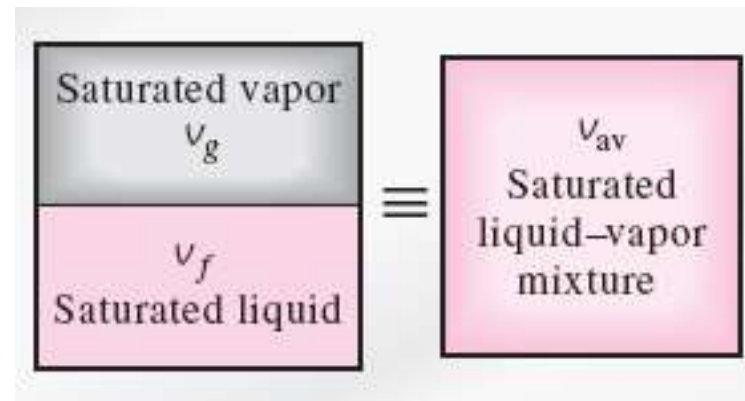
The relative amounts of liquid and vapor phases in a saturated mixture are specified by the *quality x*.

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

$$V = V_f + V_g$$

$$V = mv \longrightarrow m_t v_{av} = m_f v_f + m_g v_g$$

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

$$v_{av} = (1 - x)v_f + xv_g$$

$$v_{av} = v_f + xv_{fg} \qquad (m^3/kg)$$

$$x = \frac{\overline{AB}}{\overline{AC}}$$

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

$$u_{av} = u_f + xu_{fg} \qquad (kJ/kg)$$

$$h_{av} = h_f + xh_{fg} \qquad (kJ/kg)$$

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

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

$$y_f \leq y_{avg} \leq y_g$$
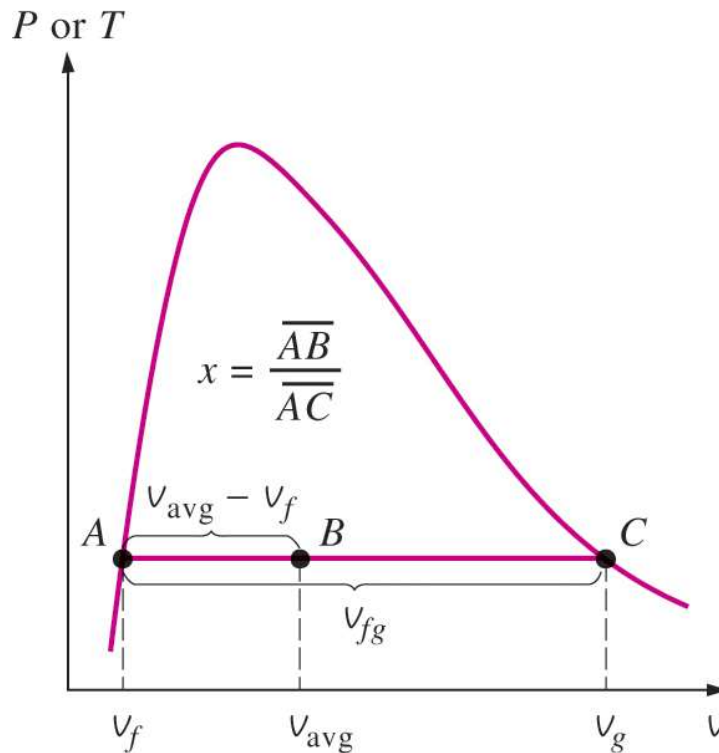
The *v* value of a saturated liquid–vapor mixture lies between the v_f and v_g values at the specified *T* or *P*.

P or T

Sat. liquid
v_g

Sat. liquid
v_f

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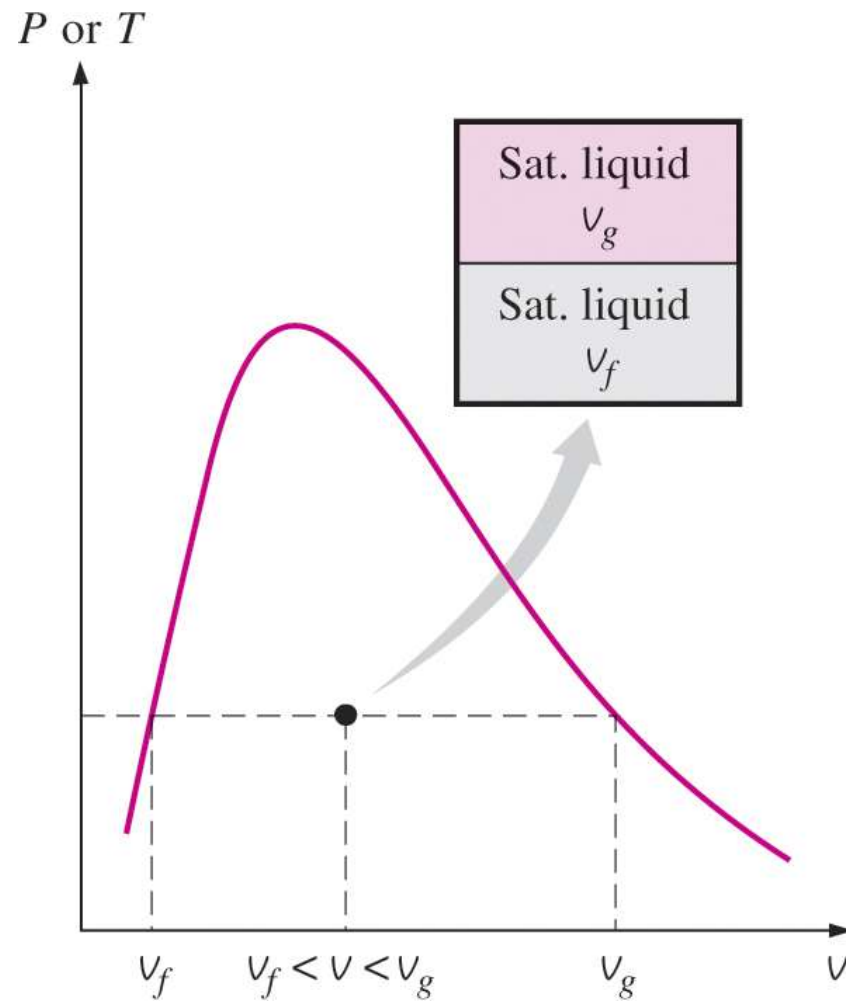
Quality is related to the horizontal
distances on *P-v* and *T-v* diagrams.

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EXAMPLE 3-4

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.

P or T

Sat. liquid
v_g

Sat. liquid
v_f

v_f $v_f < v < v_g$ v_g v
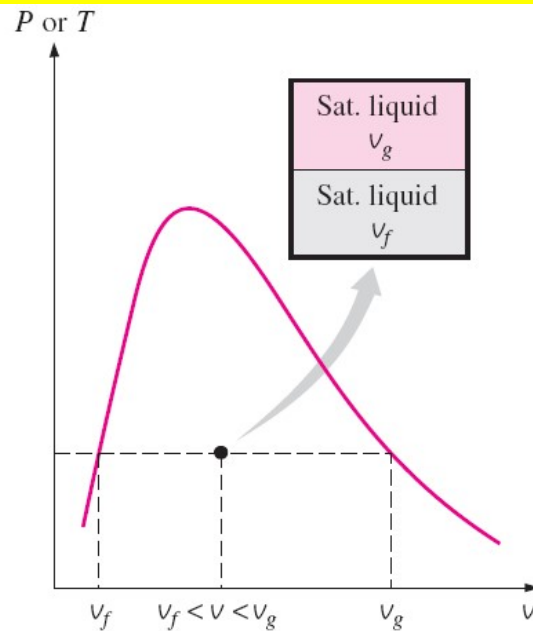
Solution A rigid tank contains saturated mixture. The pressure and the volume of the tank are to be determined.

(a) the pressure in the tank

$$P = P_{sat \ @ \ 90°C} = \mathbf{70.183 \ kPa}$$

(b) the volume of the tank.

At 90°C, we have v_f =0.001036 m³/kg, v_g=2.3593 m³/kg

$$V = V_f + V_g = m_f v_f + m_g v_g$$

$$= (8 \ kg)(0.001036 \ m^3/kg) + (2 \ kg)(2.3593 \ m^3/kg)$$

$$= \mathbf{4.73 \ m^3}$$

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

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

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

EXAMPLE 3–5

An 80-L vessel contains 4 kg of refrigerant-134a at a pressure of 160 kPa. Determine (a) the temperature of the refrigerant, (b) the quality, (c) the enthalpy of the refrigerant, and (d) the volume occupied by the vapor phase.
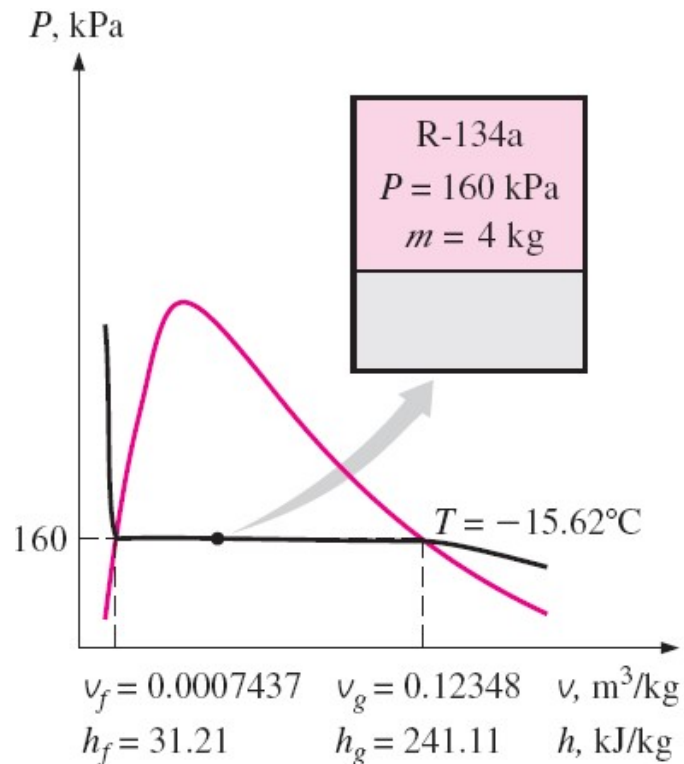
Solution A vessel is filled with refrigerant-134a. Properties of the refrigerant are to be determined.

P, kPa

R-134a
P = 160 kPa
m = 4 kg

T = −15.62°C

160

$v_f = 0.0007437$ $v_g = 0.12348$ v, m³/kg
$h_f = 31.21$ $h_g = 241.11$ h, kJ/kg

(a) the temperature of the refrigerant,

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

$$v_f = 0.0007437 \ m^3/kg$$

$$v_g = 0.12348 \ m^3/kg$$

$$v_f < v < v_g$$

(Table A–12) $T = T_{sat \ @ \ 160 \ kPa} = \mathbf{-15.60°C}$

(b) the 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,

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

(d) the volume occupied by the vapor phase.

The mass of the vapor is
$$m_g = xm_t = (0.157)(4 \text{ kg}) = 0.628 \text{ kg}$$

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

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

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.

Compared to saturated vapor, superheated vapor is characterized by

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

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

$T,^\circ C$	v, m³/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 (151.86°C)			
Sat.	0.37483	2560.7	2748.1
200	0.42503	2643.3	2855.8
250	0.47443	2723.8	2961.0
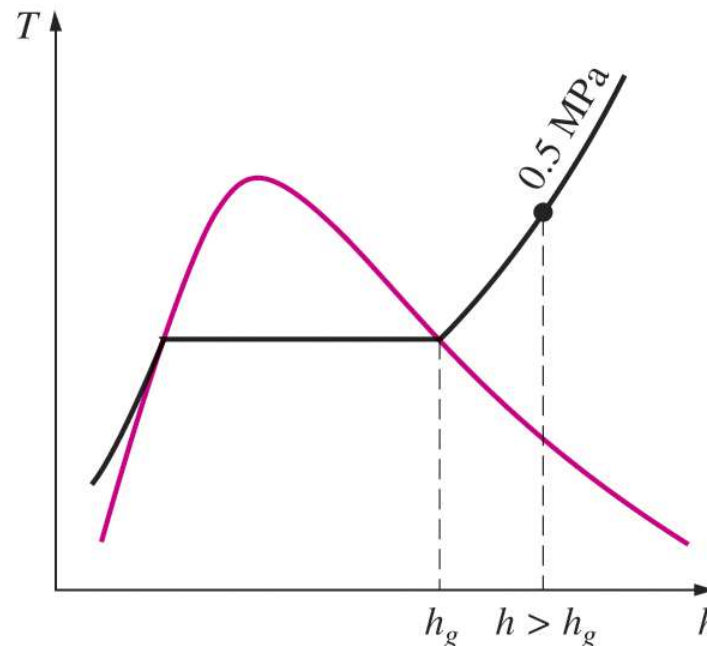
At a specified P, superheated vapor exists at a higher h than the saturated vapor.

At 300 kPa, the saturation temperature is 120.21⁰C. Since $T > T_{sat}$, 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.

$$u = 2808.8 \text{ kJ/kg}$$

EXAMPLE 3-7

Determine the temperature of water at a state of $P = 0.5$ MPa and $h = 2890$ kJ/kg.
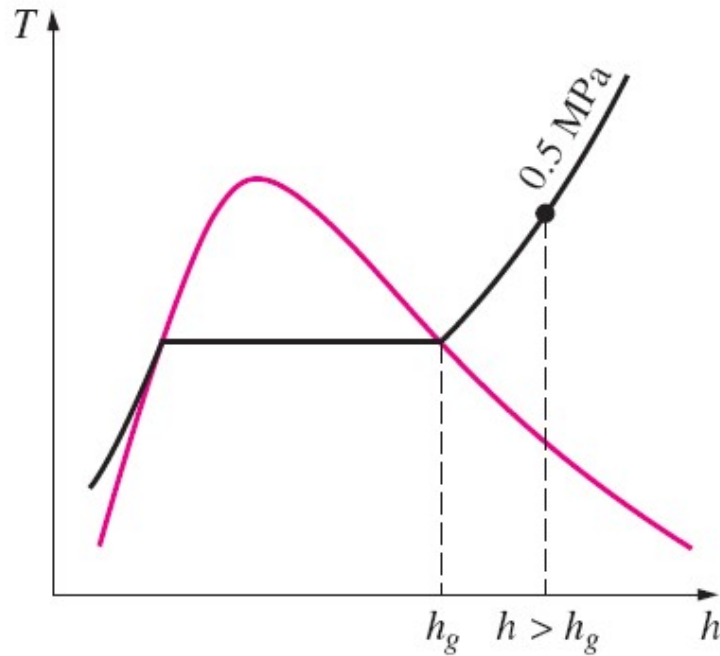
Solution The temperature of water at a specified state is to be determined.

At 0.5 MPa, the enthalpy of saturated water vapor is $h_g = 2748.1$ kJ/kg. Since $h > h_g$, as shown in Figure, 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

By linear interpolation it is determined to be

$$T = 216.3°C$$

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

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

A more accurate relation for

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

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

$T,\ ^\circ C$

151.83

75

$P = 500\ kPa$

$u \cong u_{f\,@\,75^\circ C}$

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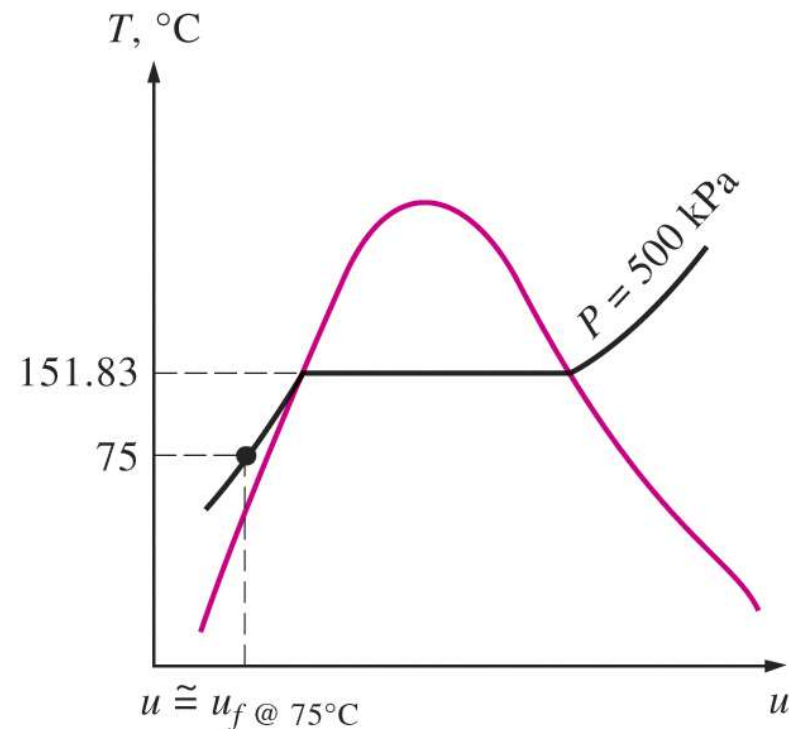
At a given P and T, a pure substance will exist as a compressed liquid if

EXAMPLE 3-8

Determine the internal energy of compressed liquid water at 80⁰C 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?

T, °C

$T = 80°C$
$P = 5$ MPa

5 MPa

80

$u \cong u_{f\,@\,80°C}$

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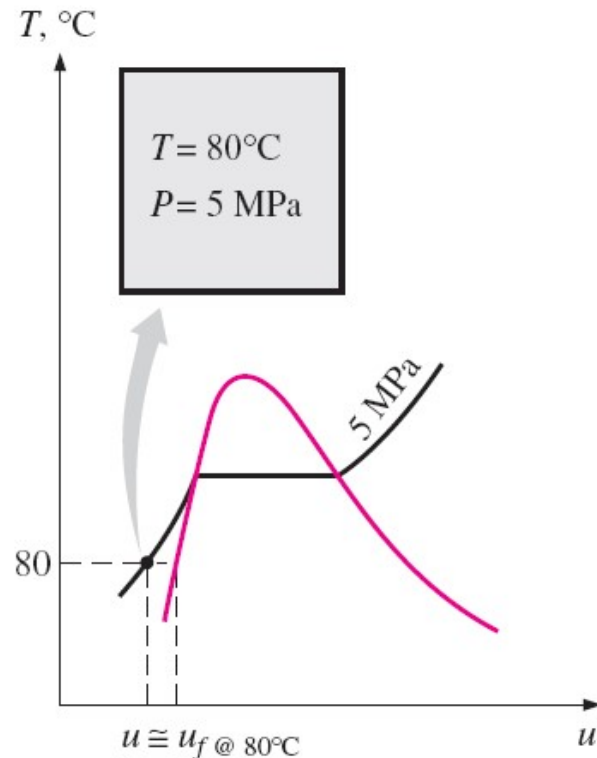
Solution The exact and approximate values of the internal energy of liquid water are to be determined.

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

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

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

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

The error involved is

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

- 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.

EXAMPLE 3-9

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	

(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:

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

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

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

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(b) First go to the saturation table and determine the u_f and u_g values at the given temperature. At 125⁰C, we read u_f =524.83 kJ/kg and u_g =2534.3 kJ/kg. Compare the given u value to these u_f and u_g values, keeping in mind that

if	$u < u_f$	we have *compressed liquid*
if	$u_f \leq u \leq u_g$	we have *saturated mixture*
if	$u > u_g$	we have *superheated vapor*

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

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

(c) At 1 Mpa 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. Superheated vapor, and the temperature at this state is determined from the superheated vapor table by interpolation to be

$$T = \textbf{395.2°C} \qquad (\text{Table A–6})$$

(d) The temperature and pressure are given, to determine the region, 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} =151.83C.

if	$T < T_{sat\ @\ given\ P}$	we have *compressed liquid*
if	$T = T_{sat\ @\ given\ P}$	we have *saturated mixture*
if	$T > T_{sat\ @\ given\ P}$	we have *superheated vapor*

$$u \cong u_{f\ @\ 75°C} = \textbf{313.99 kJ/kg} \qquad (\text{Table A–4})$$
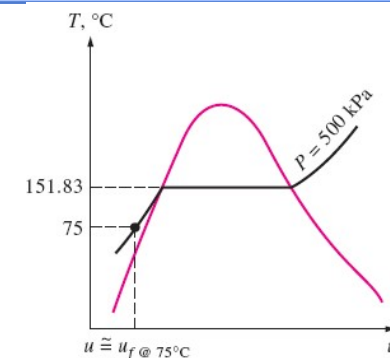
(e) The quality is given to be x 0, and thus we have saturated liquid at the specified pressure of 850 kPa. Then the temperature must be the saturation temperature at the given pressure, and the internal energy must have the saturated liquid value:

$$T = T_{sat \text{ @ } 850 \text{ kPa}} = \textbf{172.94°C} \qquad \text{(Table A–5)}$$

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

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.
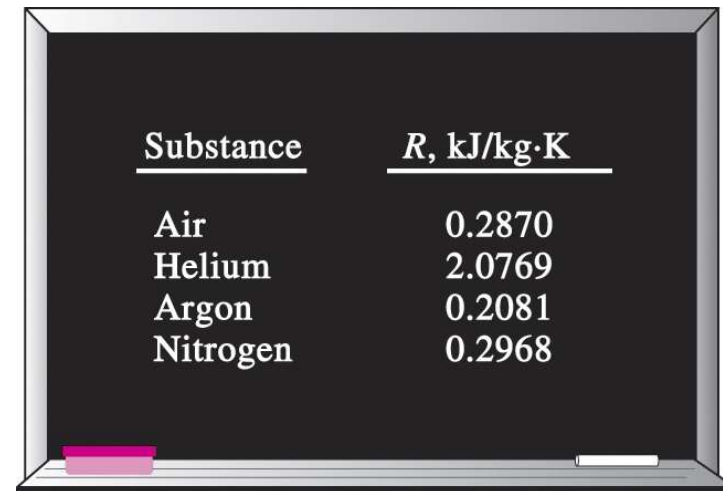
Ideal gas equation of state

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

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

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

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

Different substances have different gas constants.

R: gas constant
M: molar mass (kg/kmol)
R_u: universal gas constant

Mass = Molar mass × Mole number

Ideal gas equation at two states for a fixed mass

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

$$m = MN$$

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

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

$$V = N\overline{v} \longrightarrow P\overline{v} = R_u T$$

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

Per unit mass	Per unit mole
v, m³/kg	$\overline{v}$, m³/kmol
u, kJ/kg	$\overline{u}$, kJ/kmol
h, kJ/kg	$\overline{h}$, kJ/kmol

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

IDEAL GAS!

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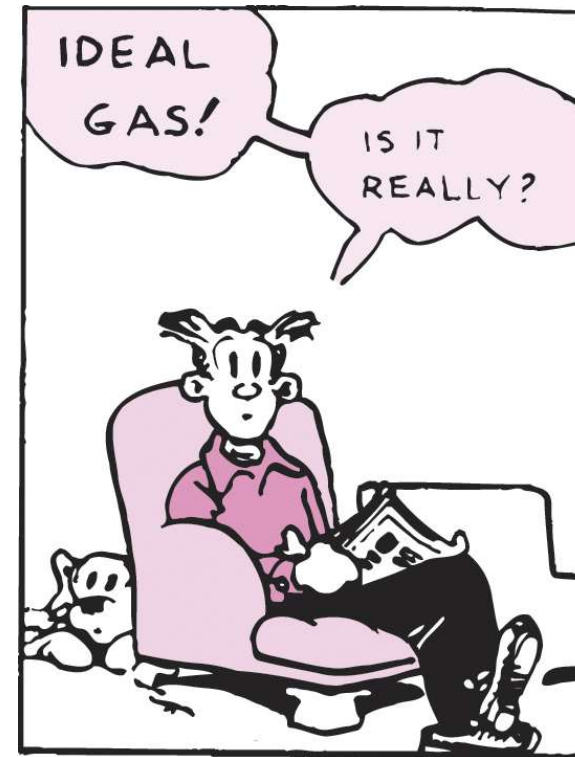
The ideal-gas relation often is not applicable to real gases; thus, care should be exercised when using it.

EXAMPLE 3-10

Determine the mass of the air in a room whose dimensions are 4mx 5m x6m at 100 kPa and 25⁰C.

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

AIR
$P = 100$ kPa
$T = 25°C$
$m = ?$

6 m

4 m

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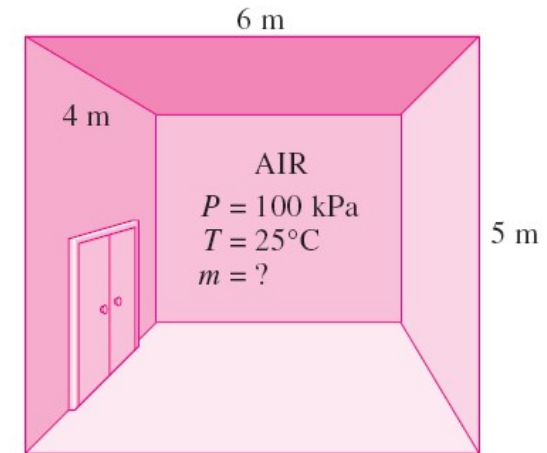
$$V = (4 \text{ m})(5 \text{ m})(6 \text{ m}) = 120 \text{ m}^3$$

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

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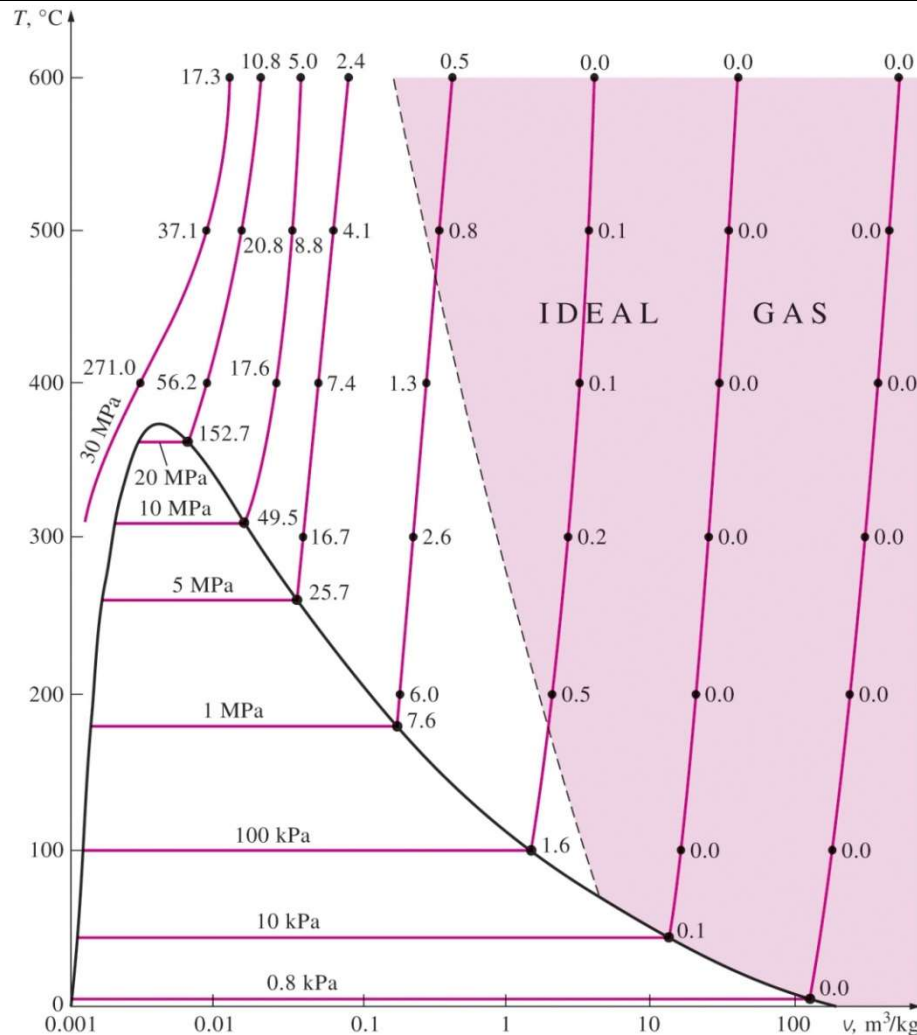
- At pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent).

- 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 ($[|v_{table} - v_{ideal}|/v_{table}] \times 100$) 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 Z
A factor that accounts for the deviation of real gases from ideal-gas behavior at a given temperature and pressure.

$$Pv = ZRT$$

$$Z = \frac{Pv}{RT} \qquad Z = \frac{v_{actual}}{v_{ideal}}$$

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

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

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

Answer: The pressure or temperature of a gas is high or low relative to its critical temperature or pressure.

IDEAL GAS

$Z = 1$

REAL GASES

$Z \begin{cases} > 1 \\ = 1 \\ < 1 \end{cases}$

REAL GAS

as $P \to 0$

IDEAL GAS

The compressibility factor is unity for ideal gases.
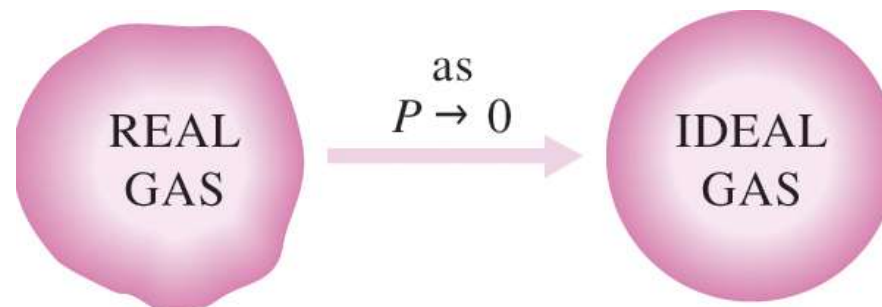
At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).

Reduced pressure and temperature

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

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

Pseudo-reduced specific volume

$$\left. \begin{array}{c} P_R = \dfrac{P}{P_{cr}} \\[2mm] v_R = \dfrac{v}{RT_{cr}/P_{cr}} \end{array} \right\} Z = \ldots \quad \text{(Fig. A–34)}$$

Z can also be determined from a knowledge of P_R and v_R.
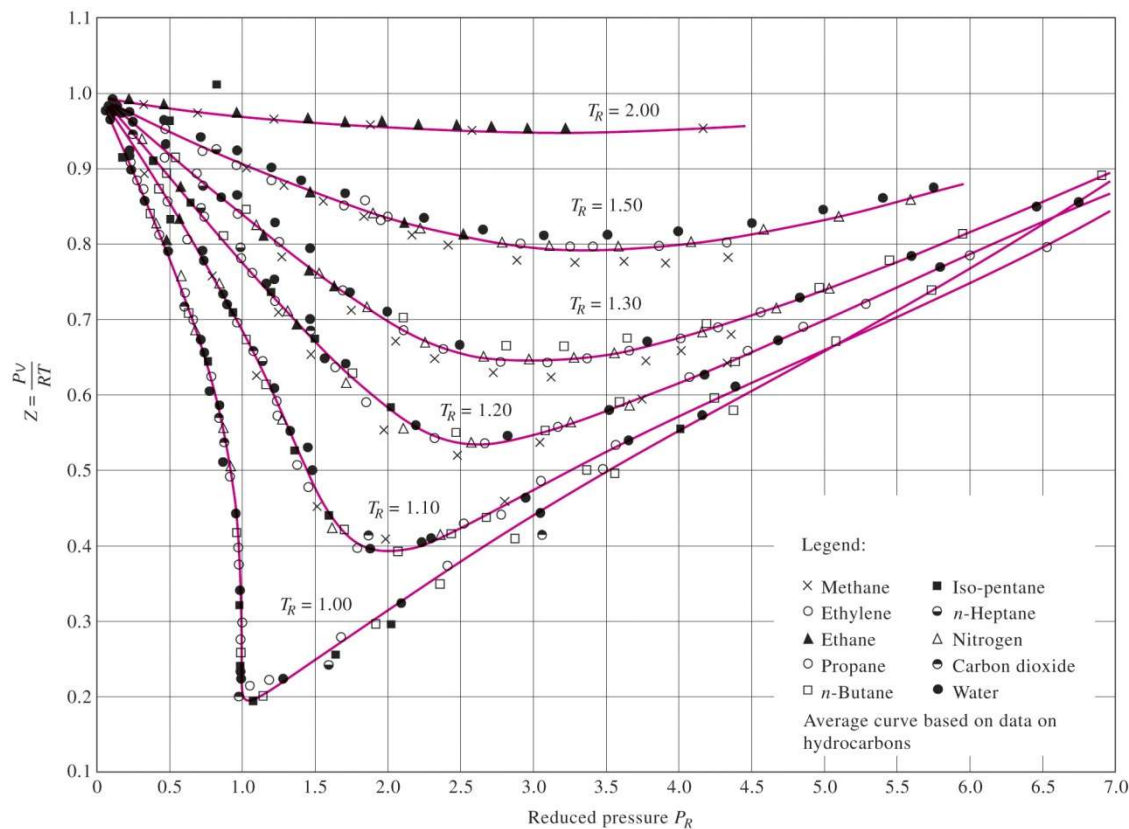
Comparison of Z factors for various gases.
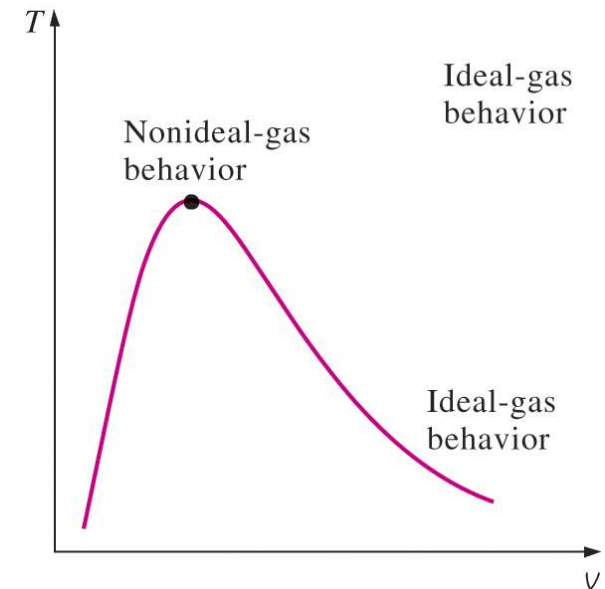
Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

EXAMPLE 3-11

Determine the specific volume of refrigerant-134a at 1 MPa and 50⁰C, 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 m³/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.

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

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

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

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

$$v = \frac{RT}{P} = \frac{(0.0815 \text{ kPa} \cdot \text{m}_3/\text{kg} \cdot \text{K})(323 \text{ K})}{1000 \text{ kPa}} = \mathbf{0.026325 \text{ m}^3/\text{kg}}$$

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:

$$\left. \begin{array}{l} P_R = \dfrac{P}{P_{cr}} = \dfrac{1 \text{ MPa}}{4.059 \text{ MPa}} = 0.246 \\[3mm] T_R = \dfrac{T}{T_{cr}} = \dfrac{323 \text{ K}}{374.2 \text{ K}} = 0.863 \end{array} \right\} \quad Z = 0.84$$

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

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

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

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

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

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.

van der Waals
Berthelet
Redlich-Kwang
Beattie-Bridgeman
Benedict-Webb-Rubin
Strobridge
Virial
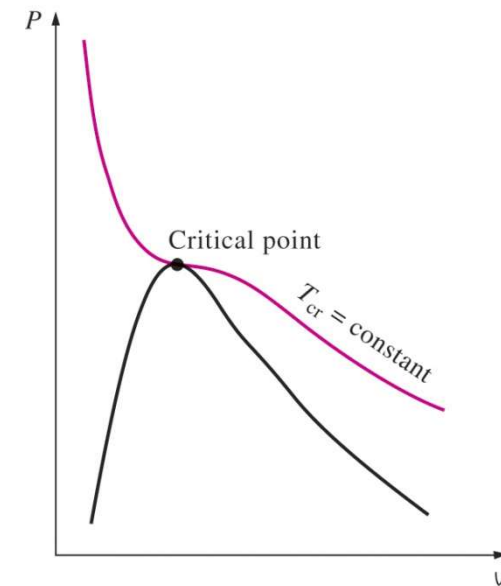
Critical isotherm of a pure substance has an inflection point at the critical state.

Beattie-Bridgeman Equation of State

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

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

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

Benedict-Webb-Rubin Equation of State

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

The constants are given in Table 3–4. This equation can handle substances at densities up to about 2.5 ρ_{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 = $[(|v_{table} - v_{equation}|)/v_{table}] \times 100$).
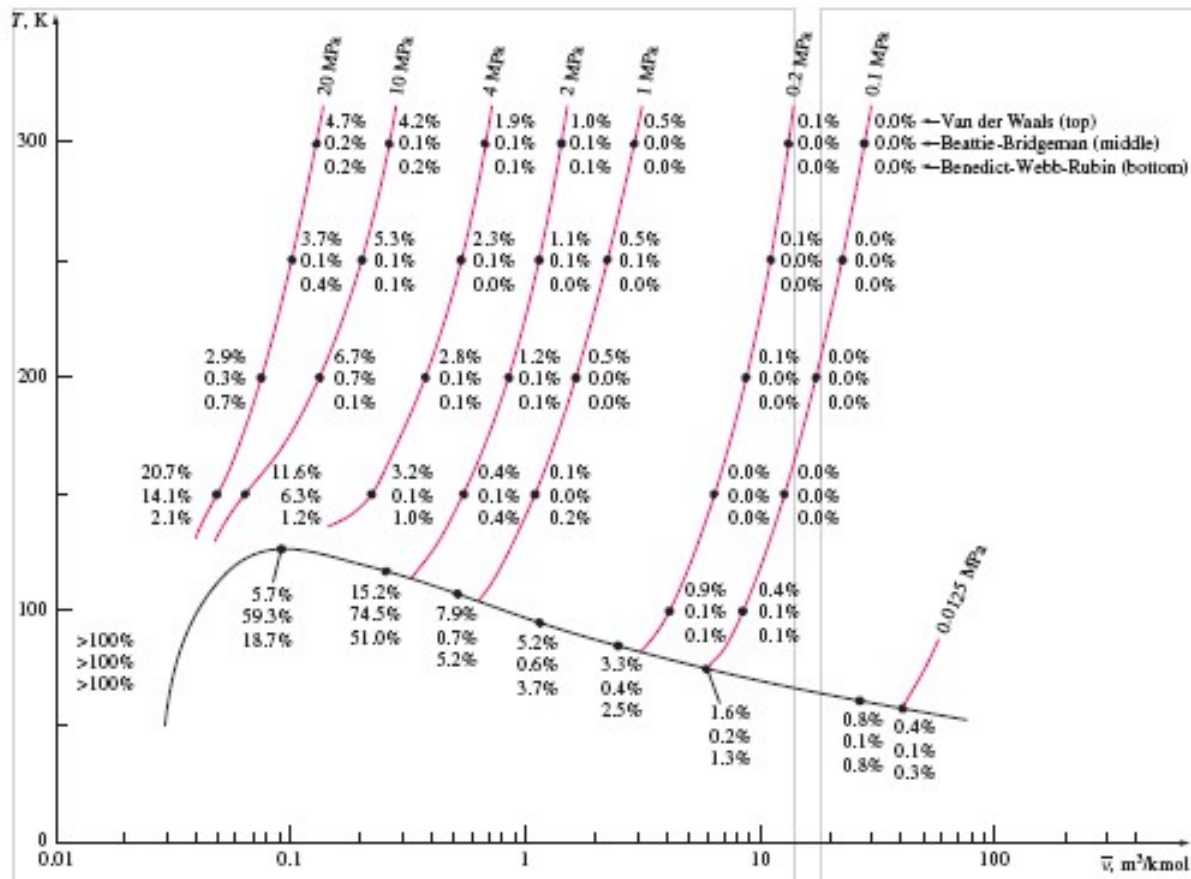
van der Waals: 2 constants. Accurate over a limited range.

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

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

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.

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

Madde	P(kPa)	T(^{0}C)	x(%)	h(kj/kg)	Faz Durumu
Su	200	50			
R-134a		0		100	
Su	1700	300			
Hava	200	1000			

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Madde	P(kPa)	T(^{0}C)	x(%)	h(kj/kg)	Faz Durumu
Su	200	50	-	340,54	Sıkıştırılmış sıvı
R-134a	293,01	0	24	100	Islak buhar
Su	1700	300	-	3032,65	Kızgın buhar
Hava	200	1000	-	1363,95	İdeal gaz

	Madde	P(kPa)	T(^{0}C)	h(kj/kg)	x(%)	Faz Durumu
a)	Su	300		3486,6		
b)	Su	500	100			
c)	SA-134a		-20	100		
d)	SA-134a	140			60	

50

	Madde	P(kPa)	T(^{0}C)	h(kj/kg)	x(%)	Faz Durumu
a)	Su	300	**500**	3486,6	**-**	**Kızgın Bölge**
b)	Su	500	100	**419,17**	**-**	**Sıkıştırılmış sıvı**
c)	SA-134a	**132,82**	-20	100	**34,9**	**Ara Bölge**
d)	SA-134a	140	**-18,77**	**154,328**	60	**Ara Bölge**

	Madde	P(kPa)	T(^{0}C)	u(kj/kg)	x(%)	Faz Durumu
a)	Su	500	200			
b)	Su		140	1600		
c)	SA-134a	500	-14			
d)	SA-134a	200			60	

	Madde	P(kPa)	T(^{0}C)	u(kj/kg)	x(%)	Faz Durumu
a)	Su	500	200	**2643,3**	**-**	**Kızgın buhar**
b)	Su	**361,53**	140	1600	**51,5**	**Ara bölgede**
c)	SA-134a	500	-14	**33,17**	**-**	**Sıkıştırılmış sıvı**
d)	SA-134a	200	**-10,09**	**150,006**	60	**Ara bölgede**

QUİZ-1

SORU 1- Aşağıda suya ait beş hal verilmiştir. Tablodaki boşlukları doldurunuz.

Hal	P(kPa)	T(^{0}C)	x(%)	v(m^3/kg)	Faz Durumu
1	200		80		
2	300	133.52			
3	2000	300			
4		150		0.361	
5	5000	100			

SORU 2- 1 Atm basınçtaki potasyum yaklaşık 760^{0}C sıcaklıkta buharlaşır. Bu basınca ait doymuş sıvı ve kuru doymuş buharın özgül hacimleri sırasıyla 0.0015 m^3/kg ve 1.991 m^3/kg'dır. Kuruluk derecesi 0.70 ise özgül hacmi bulunuz.

QUİZ-1

SORU 1- **Aşağıda suya ait beş hal verilmiştir. Tablodaki boşlukları doldurunuz.**

Hal	P(kPa)	T(^{0}C)	x(%)	v(m^3/kg)	Faz Durumu
1	300	200			
2	300		65		
3		200		0.1050	
4	10.000			0.0584	
5		120		0.620	

SORU 2- **0.050 m^3 hacmindeki bir kabın hacminin % 80'i 25^{0}C sıcaklıkta doymuş buhar, % 20'si aynı sıcaklıkta doymuş sıvı tarafından kaplanmıştır. Kaptaki sıvı ve buhar iyice karıştırılmaktadır. Karışımın kuruluk derecesini bulunuz.**

Hal	P(kPa)	T(^{0}C)	x(%)	v(m^3/kg)	Faz Durumu
1	300	200	M	0.7163	Kızgın Buhar
2	300	133.6	65	0.394	Islak Buhar
3	1553.7	200	0.823	0.1050	Islak Buhar
4	10.000	1000	M	0.0584	Kızgın Buhar
5	198.48	120	0.695	0.620	Islak Buhar

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