CH_3

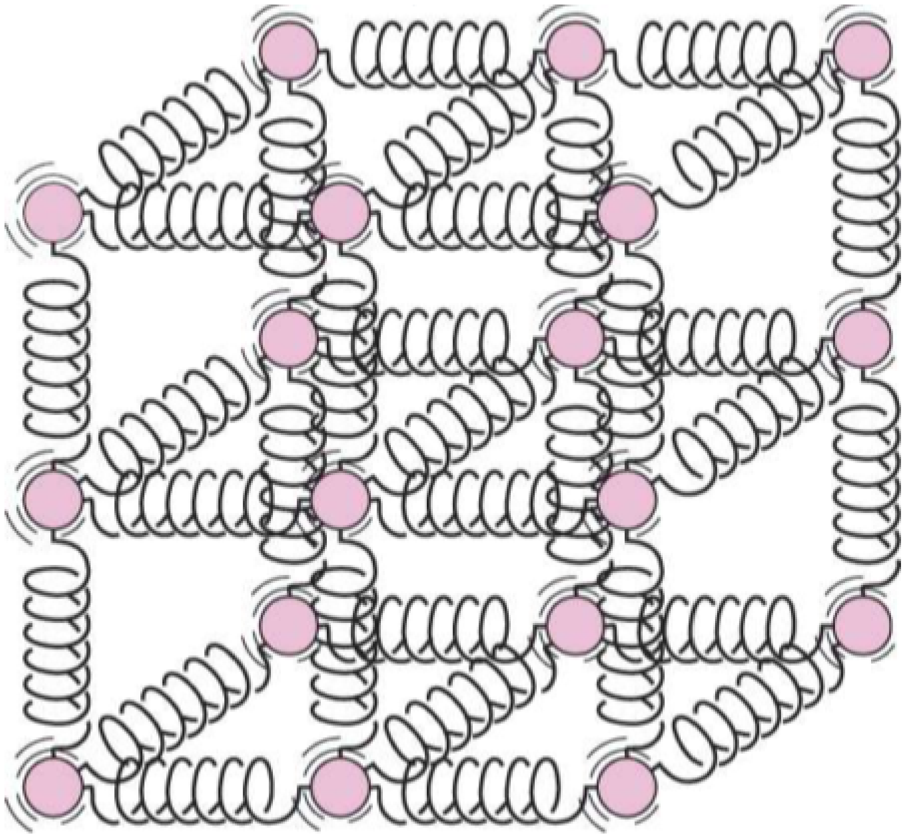
3.1 Pure Substance

Definition

a substance that has a fixed chemical composition throughout

3.2 Phases of a Pure Substance

Intermolecular Model



Solid

molecules: in fixed positions

intermolecular force: strong

Liquid

molecules: no longer at fixed positions and can rotate and translate freely

intermolecular force: weaker

distance between molecules: slight increase comparing to solid

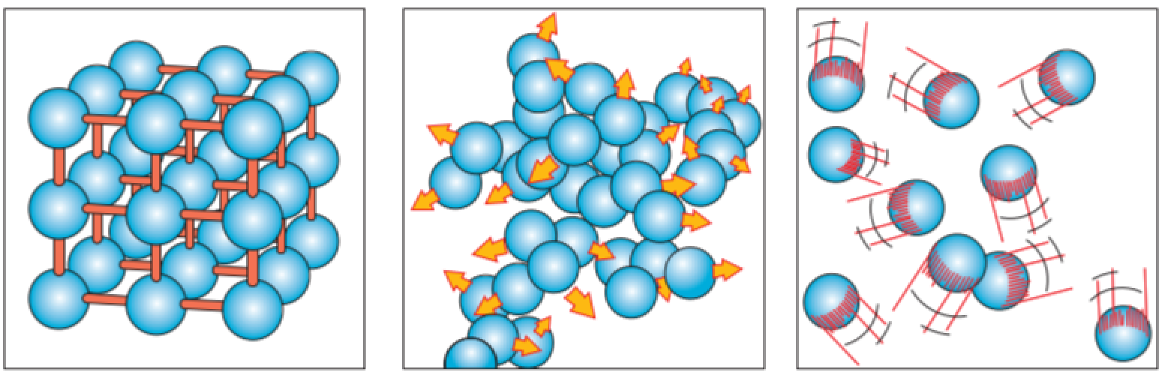
exception on water

Gas

molecules: orders are nonexistent and move at random

intermolecular force: vary small

Energy Level: higher than other phases



(*a*) (*b*) (*c*)

3.3 Phase-Change Processes of Pure Substances

Compressed Liquid and Saturated Liquid

- **compressed liquid**: liquid exists in liquid phase
- **saturated liquid**: liquid about to vaporize

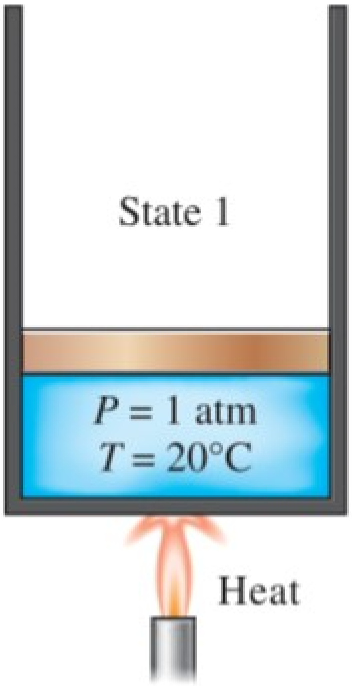


FIGURE 3–5
At 1 atm and 20°C, water exists in the liquid phase (*compressed liquid*).

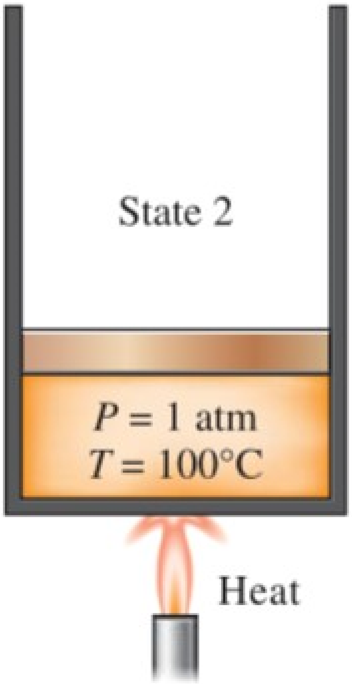


FIGURE 3–6
At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (*saturated liquid*).

Saturated Vapor and Superheated Vapor

- **saturated vapor**: vapor is about to condense
- **superheated vapor**: vapor is not about to condense

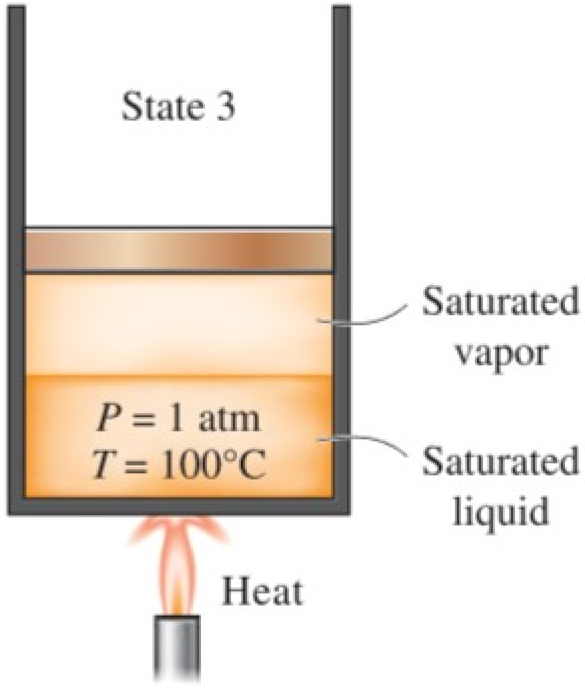


FIGURE 3–7

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

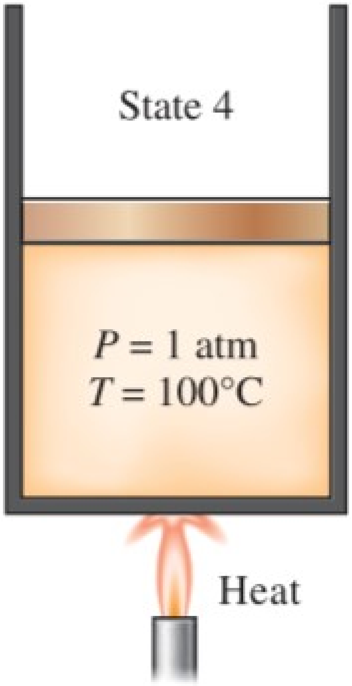


FIGURE 3–8
At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (*saturated vapor*).

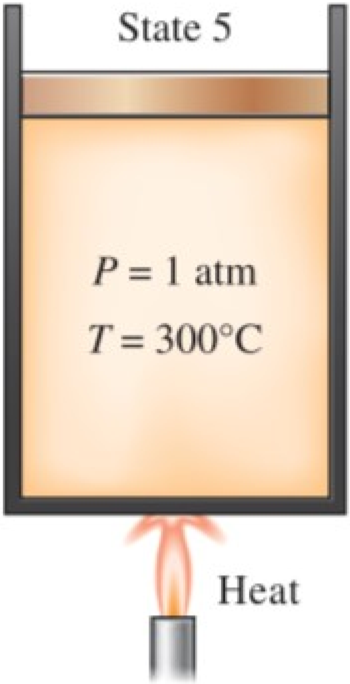


FIGURE 3–9
As more heat is transferred, the temperature of the vapor starts to rise (*superheated vapor*).

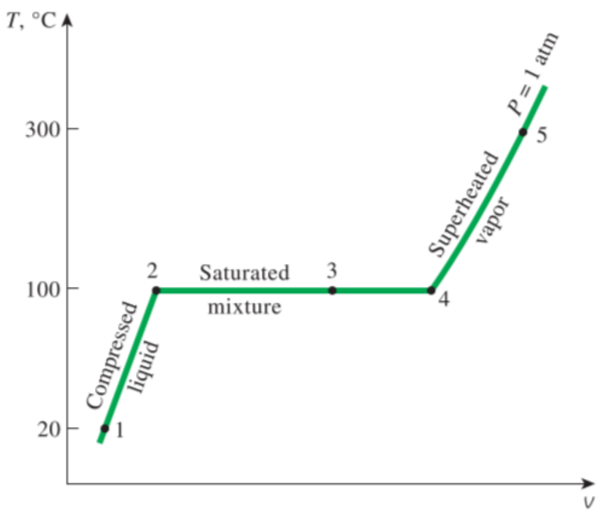
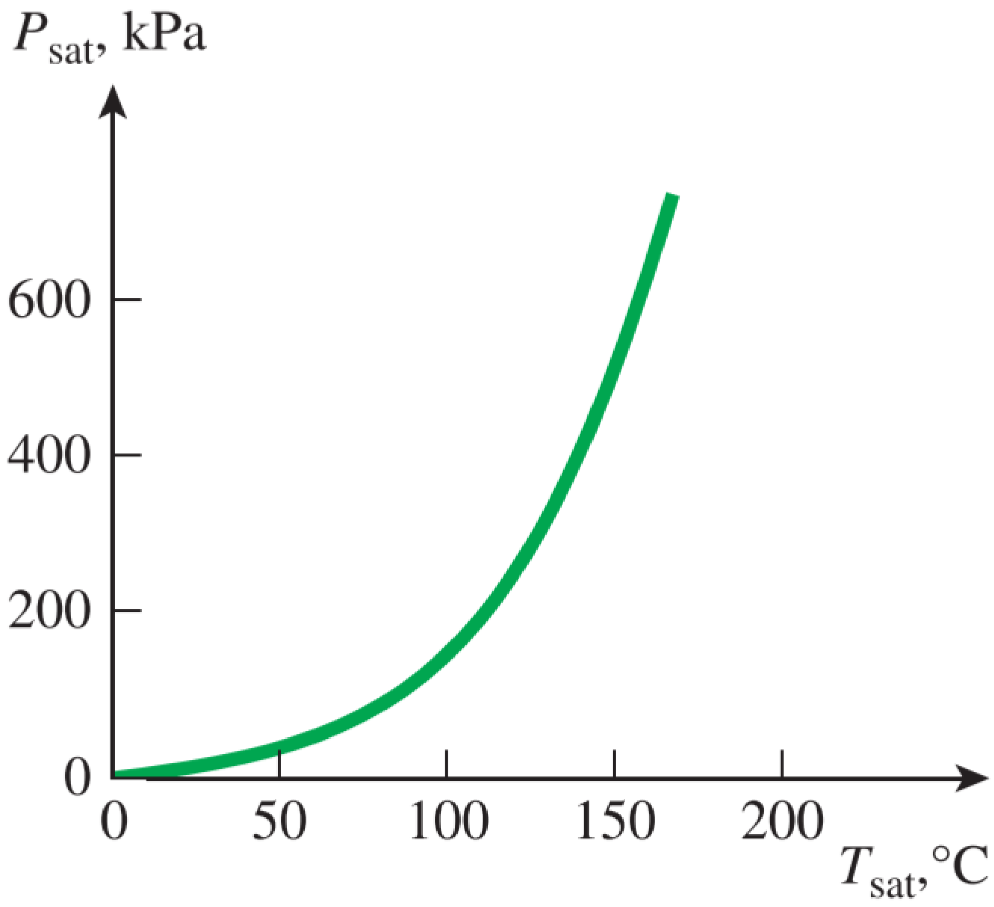


FIGURE 3–10
T-*v* diagram for the heating process of water at constant pressure.

Saturation Temperature and Saturation Pressure

- Saturation Temperature: T_{sat}
- Saturation Pressure: P_{sat}



Latent Heat

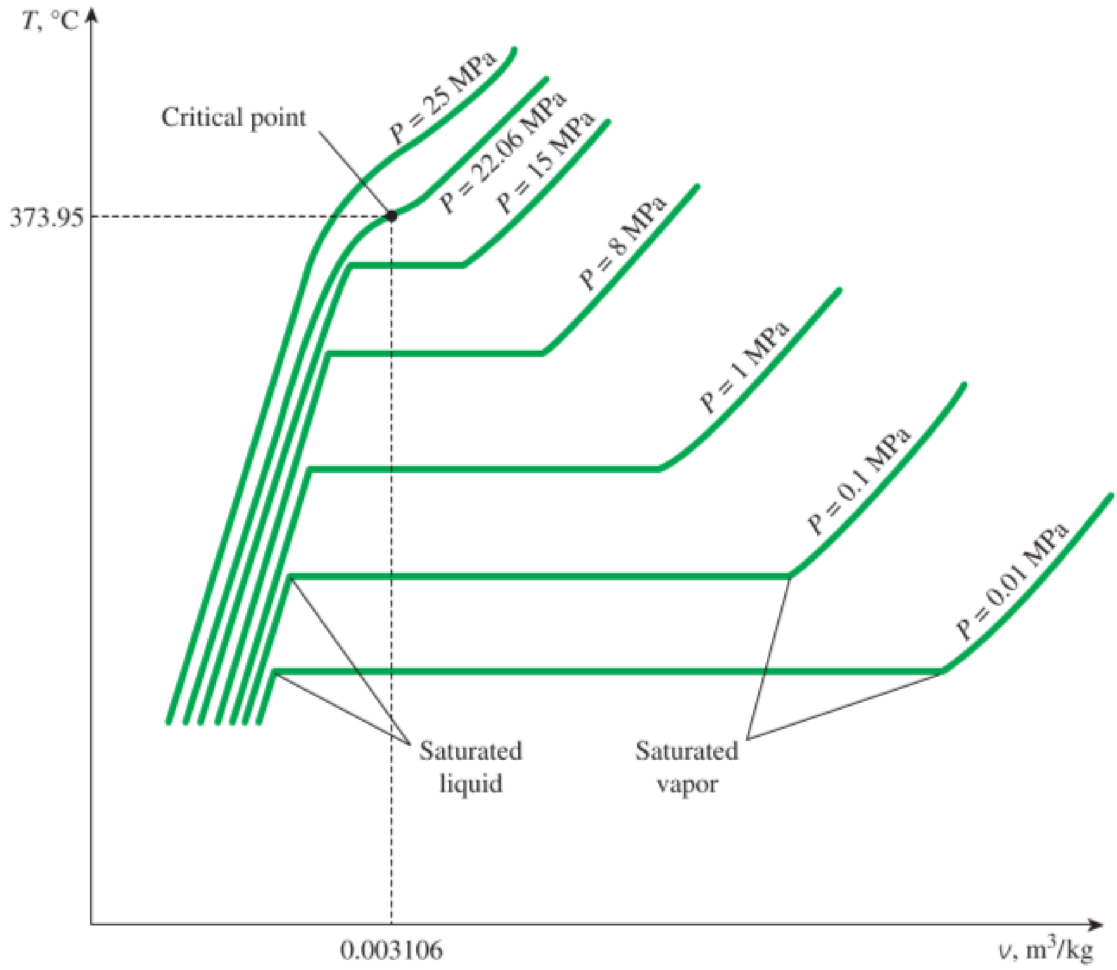
- **latent heat of fusion**: the amount of energy absorbed(released) during melting(freezing)
- **latent heat of vaporization**: the amount of energy absorbed(released) during vaporization(condensation)

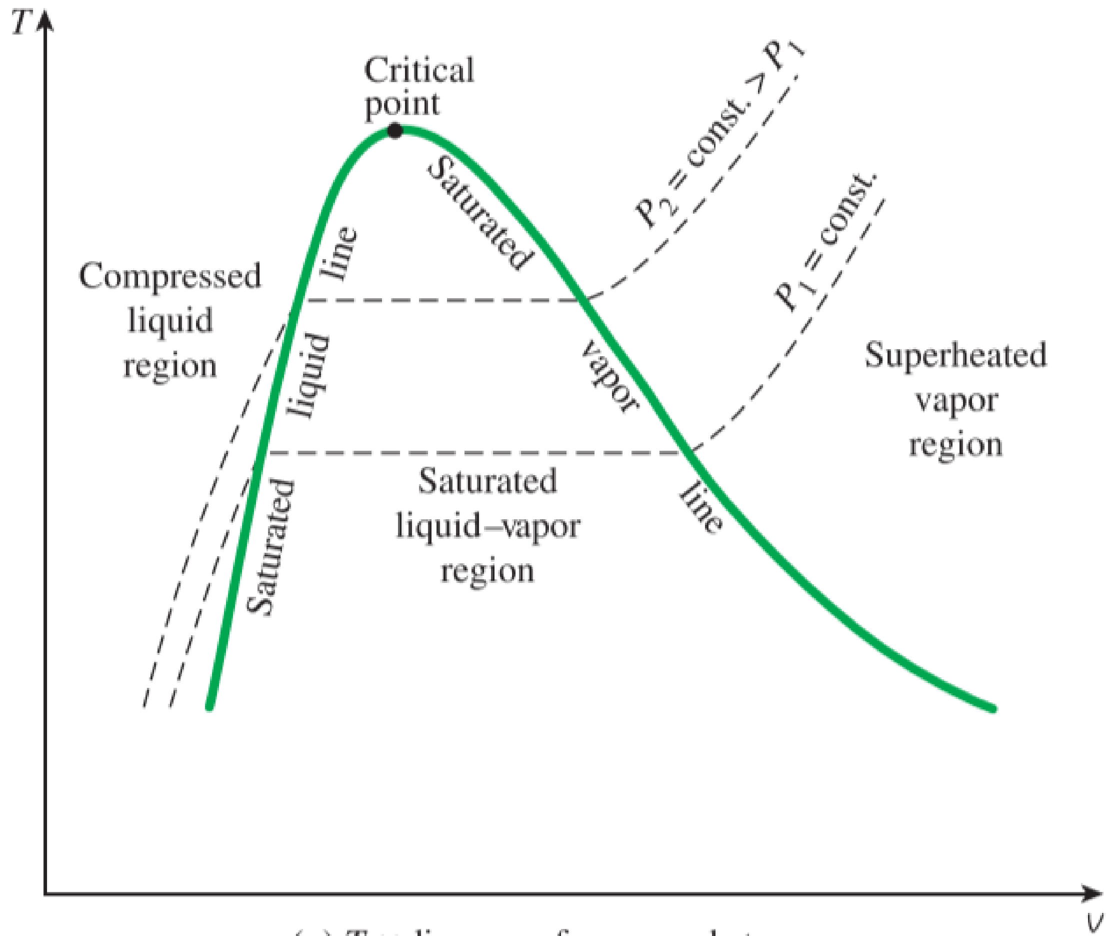
3.4 Property Diagrams for Phase-Change Processes

The $T-v$ Diagram

as pressure increased

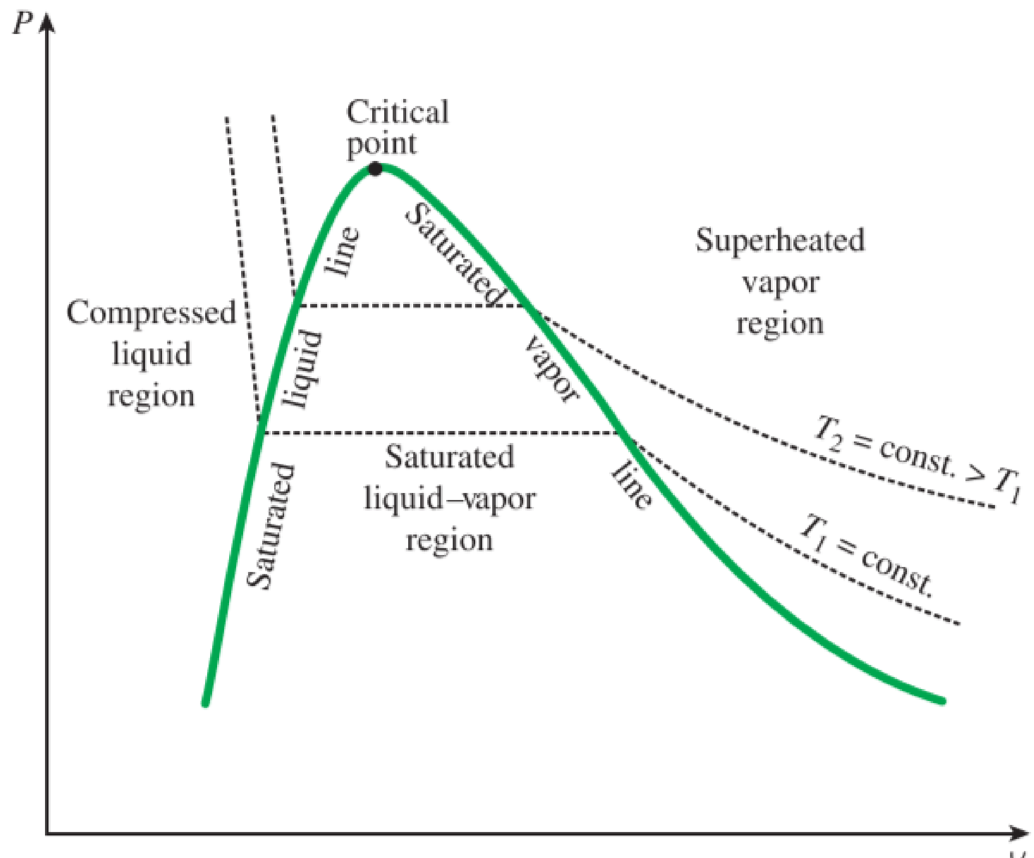
property	status
T_{sat}	$\uparrow$
v_{sat}	$\uparrow$
$v_{sat,vapor}$	$\downarrow$
Horizontal Line	$\downarrow$





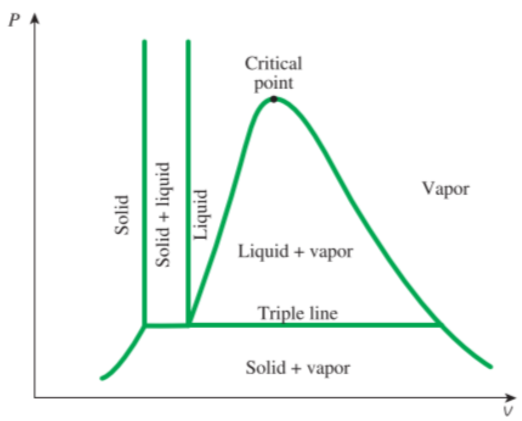
(*a*) *T*-*v* diagram of a pure substance

The $P - v$ Diagram

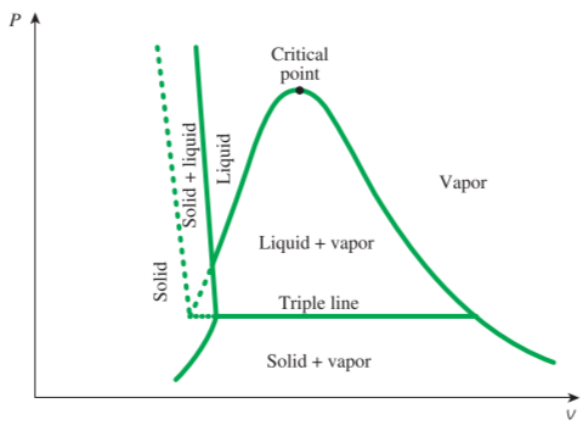


(b) P-v diagram of a pure substance

Extending with Solid Phase



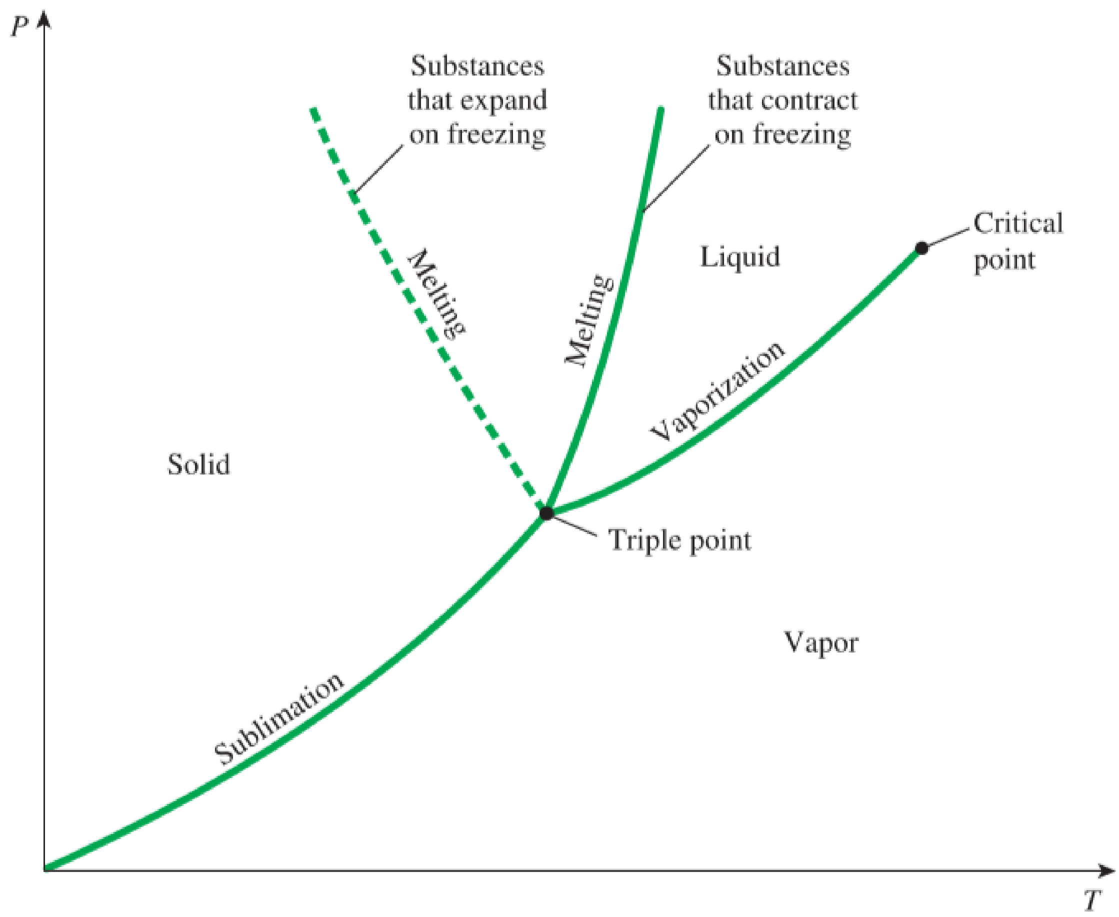
(a) P-v diagram of a substance that contracts on freezing



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

- **Triple Line**: the line formed by triple-phase states
- **Triple Point**: the point appeared by triple line on $P-T$ diagram
- **Sublimation**: the solid turns into vapor at pressures below thw triple point value

The $P-T$ Diagram



The $P-v-T$ Surface

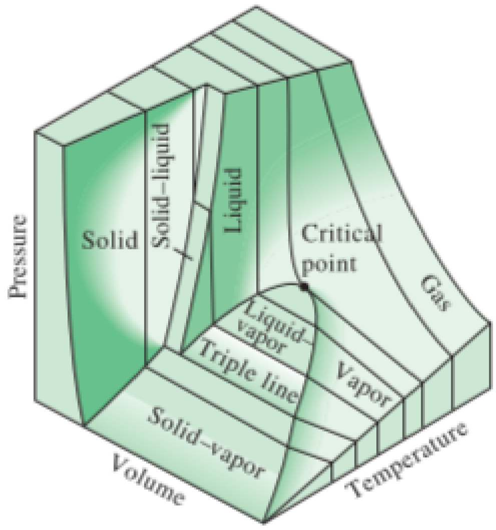


FIGURE 3–23
P-*v*-*T* surface of a substance that *contracts* on freezing.

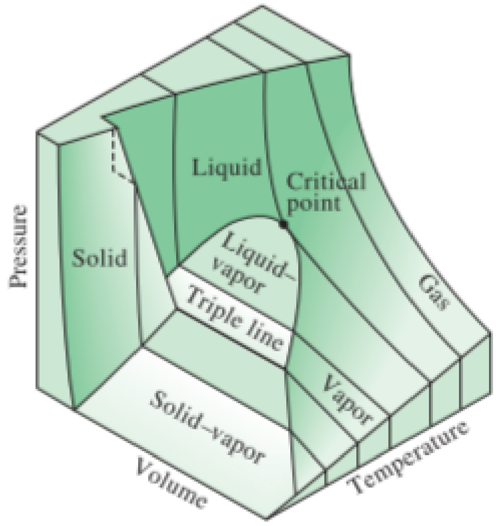


FIGURE 3–24
P-*v*-*T* surface of a substance that *expands* on freezing (like water).

3.5 Property Tables

Enthalpy

which is a combination property

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

Saturated Liquid and Saturated Vapor States

two forms

status	table
Under Temperature	Table A-4
Under Pressure	Table A-5

- Subscript **g**: saturated vapor
- Subscript **f**: saturated liquid
- Subscript **fg**: the difference between the saturated vapor and saturated liquid values of the same property

$$v_{fg} = v_g - v_f$$

Saturated Liquid - Vapor Mixture

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

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

$$\Rightarrow \qquad y_{avg} = h_f + xh_{fg}$$

where y is v, u and h

Superheated Vapor

status	given status
$P < P_{sat}$	T
$T > T_{sat}$	P
$v > v_g$	P or T
$u > u_g$	P or T
$h > h_g$	P or T

Compressed Liquid

status	given status
$P > P_{sat}$	T
$T < T_{sat}$	P
$v < v_g$	P or T
$u < u_g$	P or T
$h < h_g$	P or T

Reference State and Reference State

Since the 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 the state.

For water: the state of saturated liquid at $0.01°C$

3.6 The Ideal-Gas Equation of State

Ideal Gas

- the modules of gas are flexible, and everyone is a mass point with no volume
- there is not any force between molecules in addition to molecular collisions

When $p \to 0$, $v \to \infty$, the real gas can be treated as the ideal gas

Ideal-gas Equation of State

$$P\nu = RT$$

$$PV = nR_uT$$

$$R = \frac{R_u}{M}$$

$$R_u = 8.31447 \text{ kJ}/(\text{kmol} \cdot K) \qquad m = MN(\text{kg})$$

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

3.7 Compressibility Factor

Compressibility Factor Z

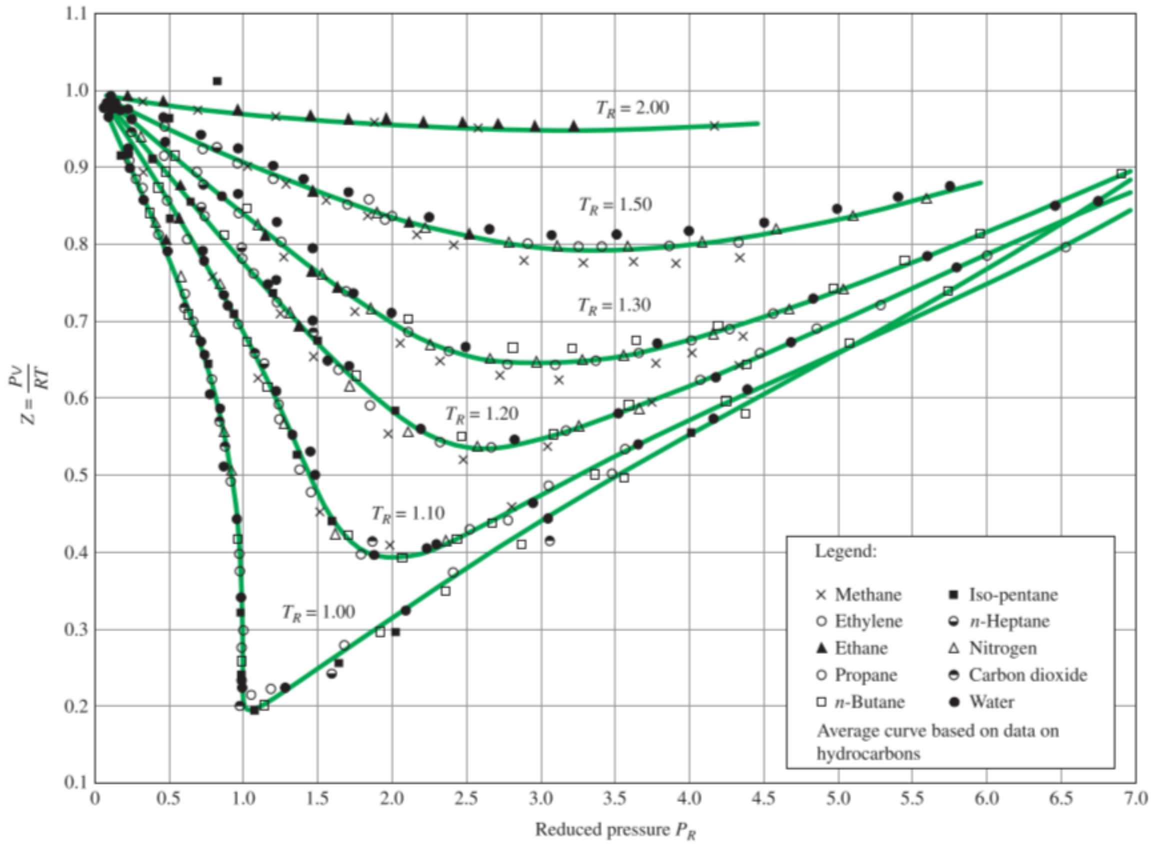
$$Z = \frac{P\nu}{RT} \qquad P\nu = ZRT$$

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

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

also called **the principle of corresponding states**

Generalized Compressibility Chart



1. At very low pressure ($P_R \ll 1$), gases behave as an ideal gas regardless of temperature
2. At high temperature ($P_R > 2$), ideal-gad behavior can be assumed with good accuracy regardless od pressure
3. The deviation of a gad fro, ideal-gad behavior is greatest in the vicinity od critical point.

The Pseudo-Reduced Specific Volume

$$\nu_R = \frac{\nu_{actual}}{RT_{cr}/P_{cr}}$$

which is defined differently from P_R and T_R.

3.8 Other Equations of State

Van Der Waals Equation of State

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

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

Beattie-Bridgeman Equation of State

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

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

Benedict-Webb-Rubin Equation of State

$$P = \frac{R_uT}{\bar{v}} + (B_0R_uT - A_0 - \frac{C_0}{T^2})\frac{1}{\bar{v}^2} + \frac{bR_uT - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3T^2}(1 + \frac{\gamma}{\bar{v}^2})e^{-\gamma/\bar{v}^2}$$

Virial Equation of State

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