

**Thermodynamics: An Engineering Approach**

**8th Edition**

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**Topic 3**

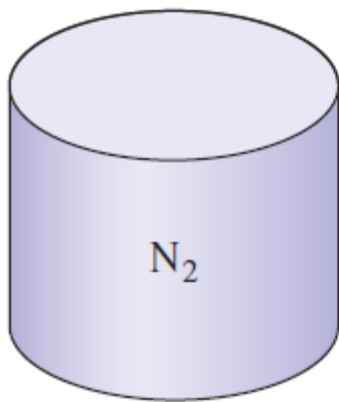
**PROPERTIES OF PURE  
SUBSTANCES**

# Objectives

- Introduce the concept of a pure substance.
- Discuss the physics of phase-change processes.
- Define compressed and saturation liquid.
- Define saturated and superheated vapor.
- Discuss effects of temperature and pressure on phase changes.
- 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.

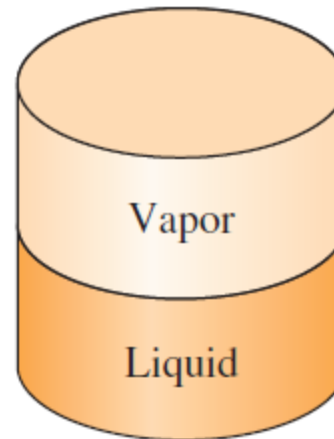
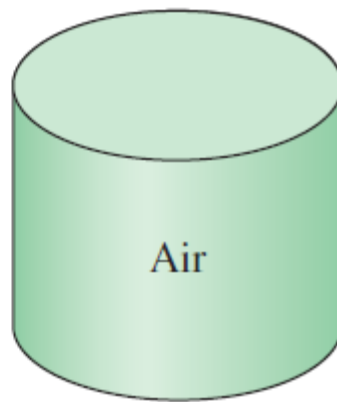
# PURE SUBSTANCE

- **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.

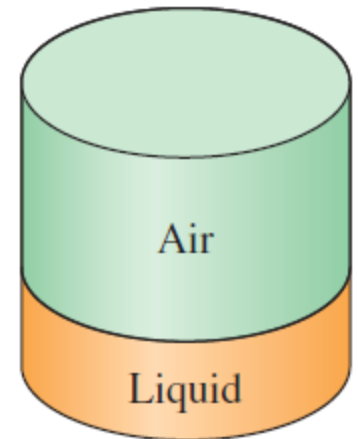


**FIGURE 3–1**

Nitrogen and gaseous air are pure substances.



(a)  $H_2O$



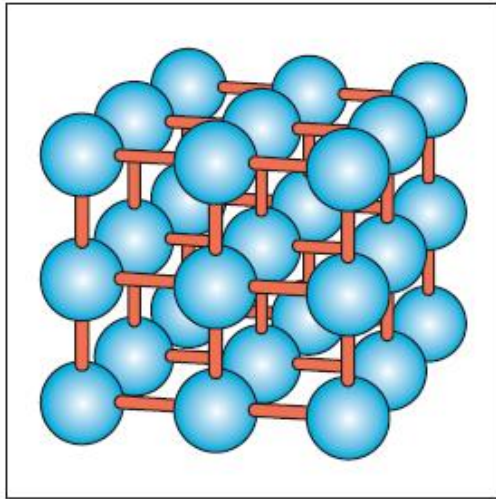
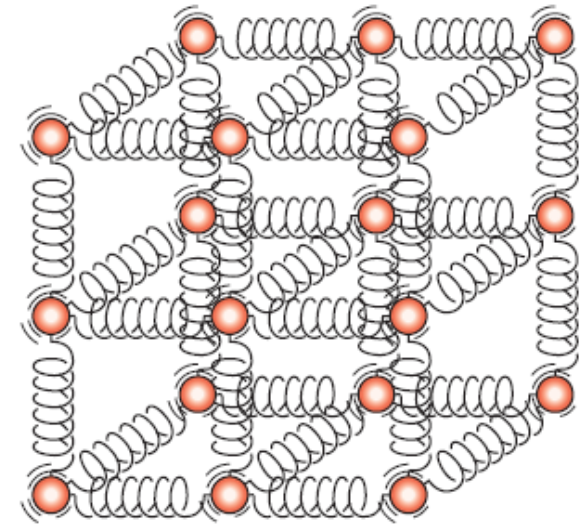
(b) Air

**FIGURE 3–2**

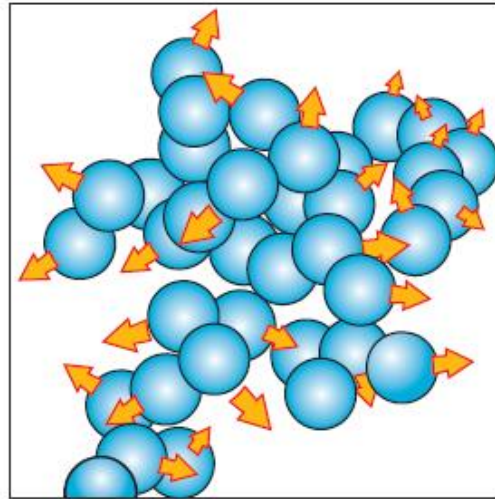
A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

# PHASES OF A PURE SUBSTANCE

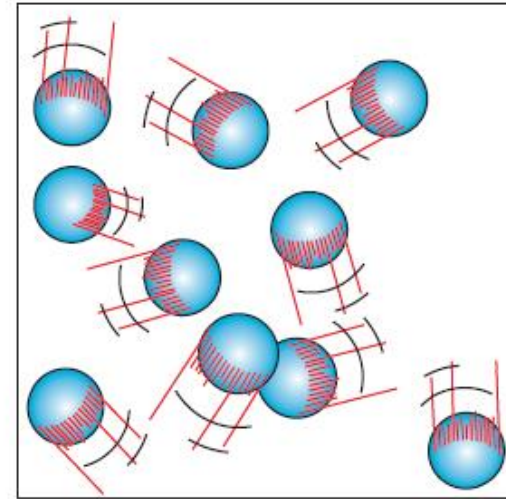
The molecules in a solid are kept at their positions by the large springlike inter-molecular forces.



(a)



(b)



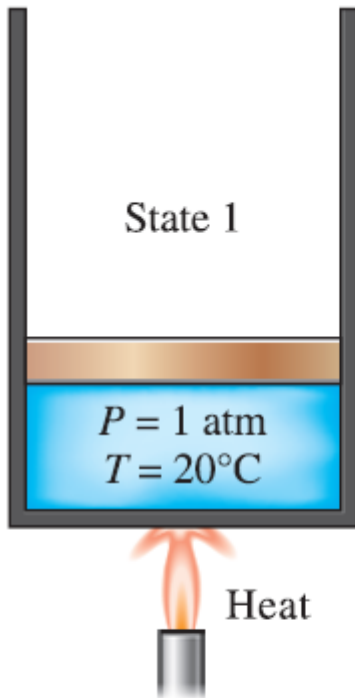
(c)

**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.

# PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

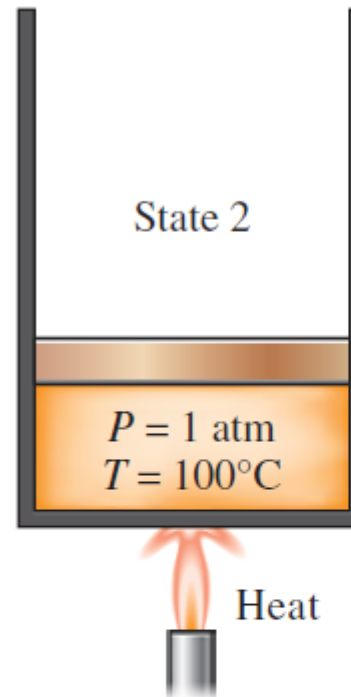
**Compressed liquid (subcooled liquid):** A substance that it is *not about to vaporize*



**FIGURE 3–5**

At 1 atm and  $20^\circ\text{C}$ , water exists in the liquid phase (*compressed liquid*).

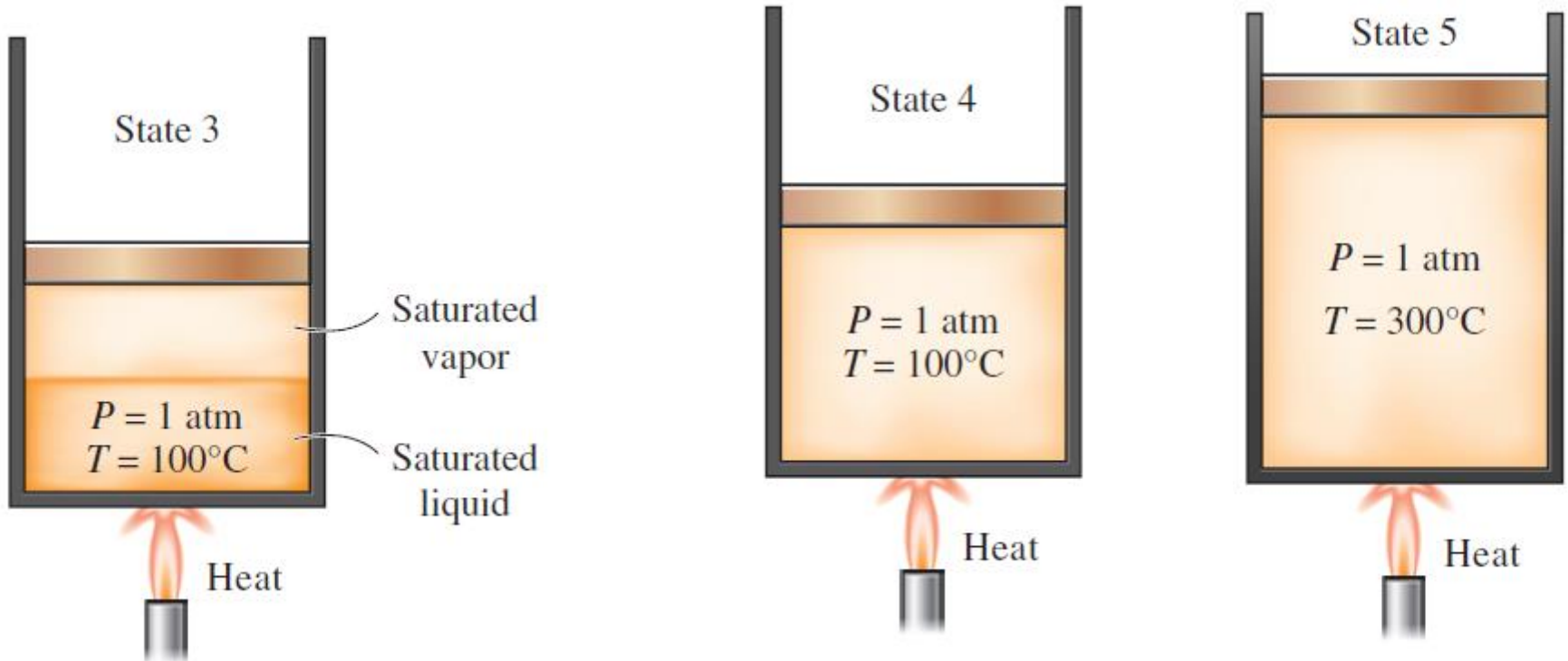
**Saturated liquid:** A liquid that is *about to vaporize*



**FIGURE 3–6**

At 1 atm pressure and  $100^\circ\text{C}$ , 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).

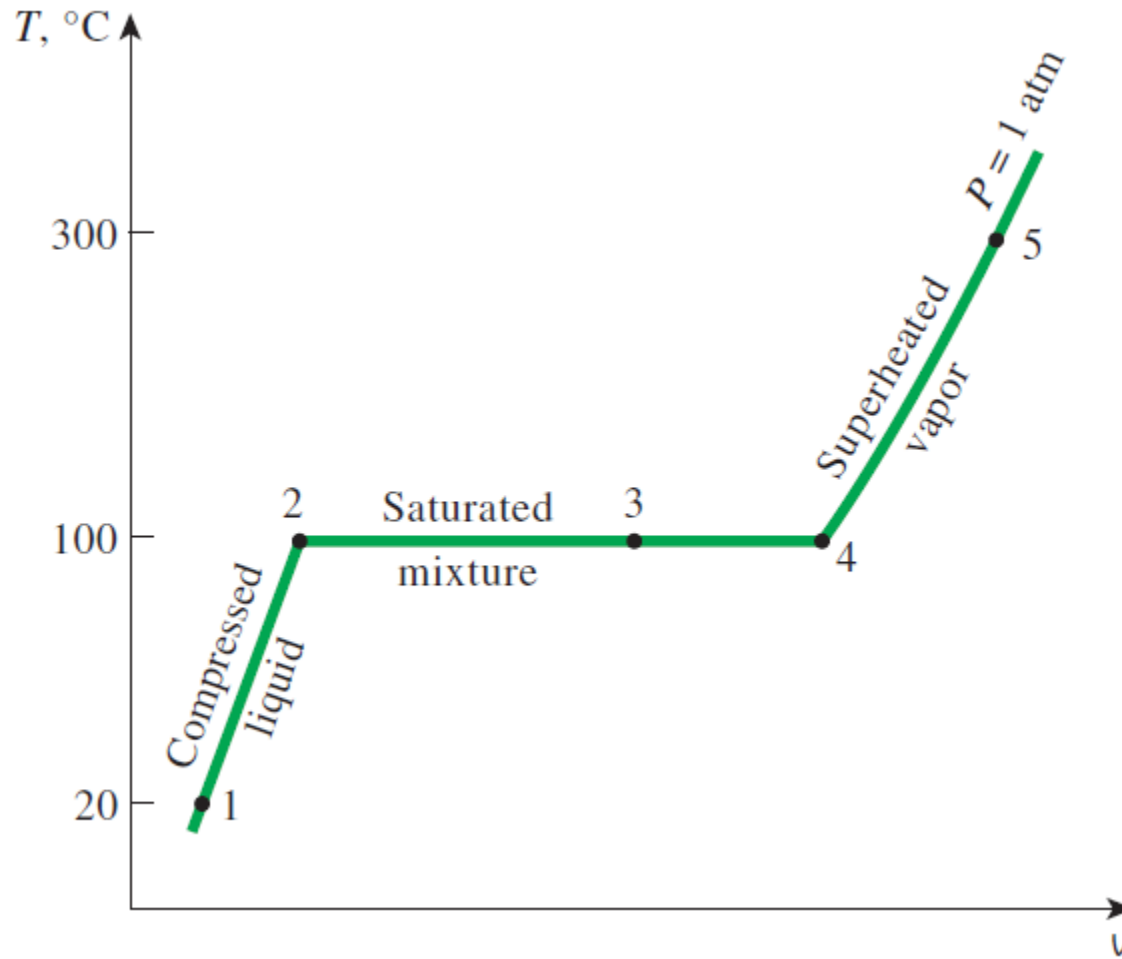


As more heat is transferred, part of the saturated liquid vaporizes (**saturated liquid–vapor mixture**).

At 1 atm pressure, the temperature remains constant at  $100^\circ\text{C}$  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 is reversed by cooling the water while maintaining the pressure at the same value, the water will go back to state 1, retracing the same path, and in so doing, the amount of heat released will exactly match the amount of heat added during the heating process.



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

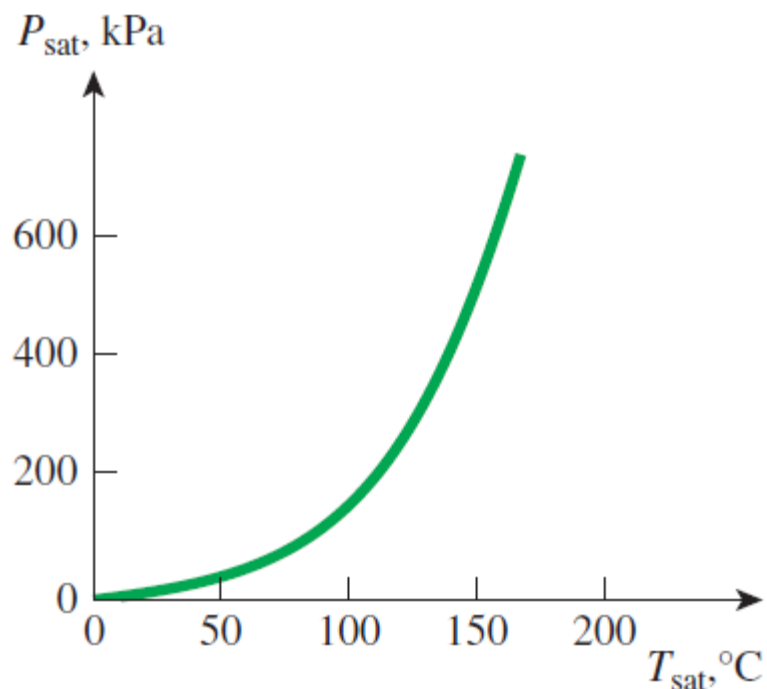
# Saturation Temperature and Saturation Pressure

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

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

**Saturation temperature  $T_{\text{sat}}$ :** The temperature at which a pure substance changes phase at a given pressure.

**Saturation pressure  $P_{\text{sat}}$ :** 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 (or vapor) pressure of water at various temperatures

| Temperature<br>$T, ^\circ\text{C}$ | Saturation<br>Pressure<br>$P_{\text{sat}}, \text{kPa}$ |
|------------------------------------|--|
| –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   |



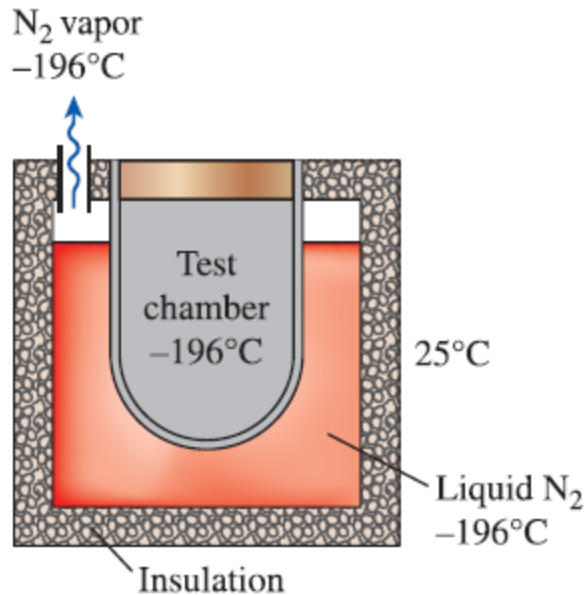
- **Latent heat:** The amount of energy absorbed or released during a phase-change process.
- **Latent heat of fusion:** The amount of energy absorbed during melting. It is equivalent to the amount of energy released during freezing.
- **Latent heat of vaporization:** The amount of energy absorbed during vaporization and it is equivalent to the energy released during condensation.
- The magnitudes of the latent heats depend on the temperature or pressure at which the phase change occurs.
- At 1 atm pressure, the latent heat of fusion of water is 333.7 kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.
- The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation.

**TABLE 3–2**

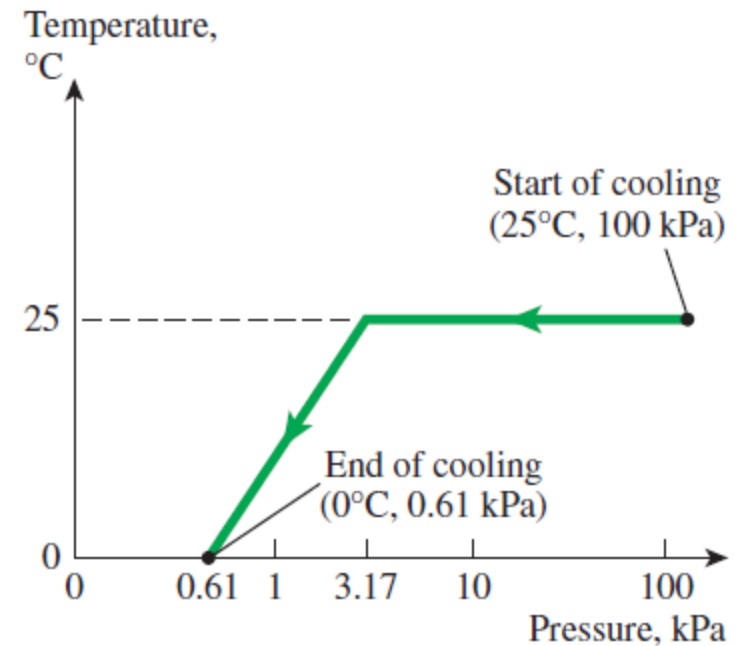
Variation of the standard atmospheric pressure and the boiling (saturation) temperature of water with altitude

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

# Some Consequences of $T_{\text{sat}}$ and $P_{\text{sat}}$ Dependence



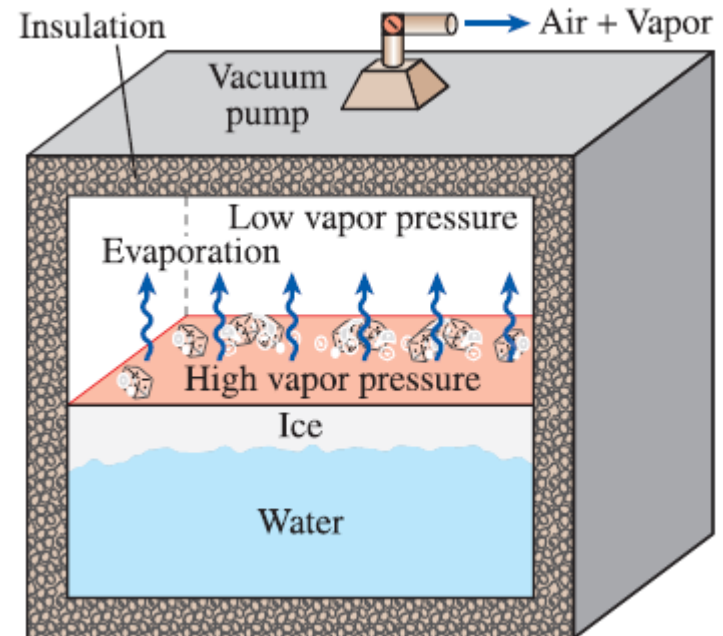
The variation of the temperature of fruits and vegetables with pressure during vacuum cooling from  $25^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ .



**FIGURE 3-12**

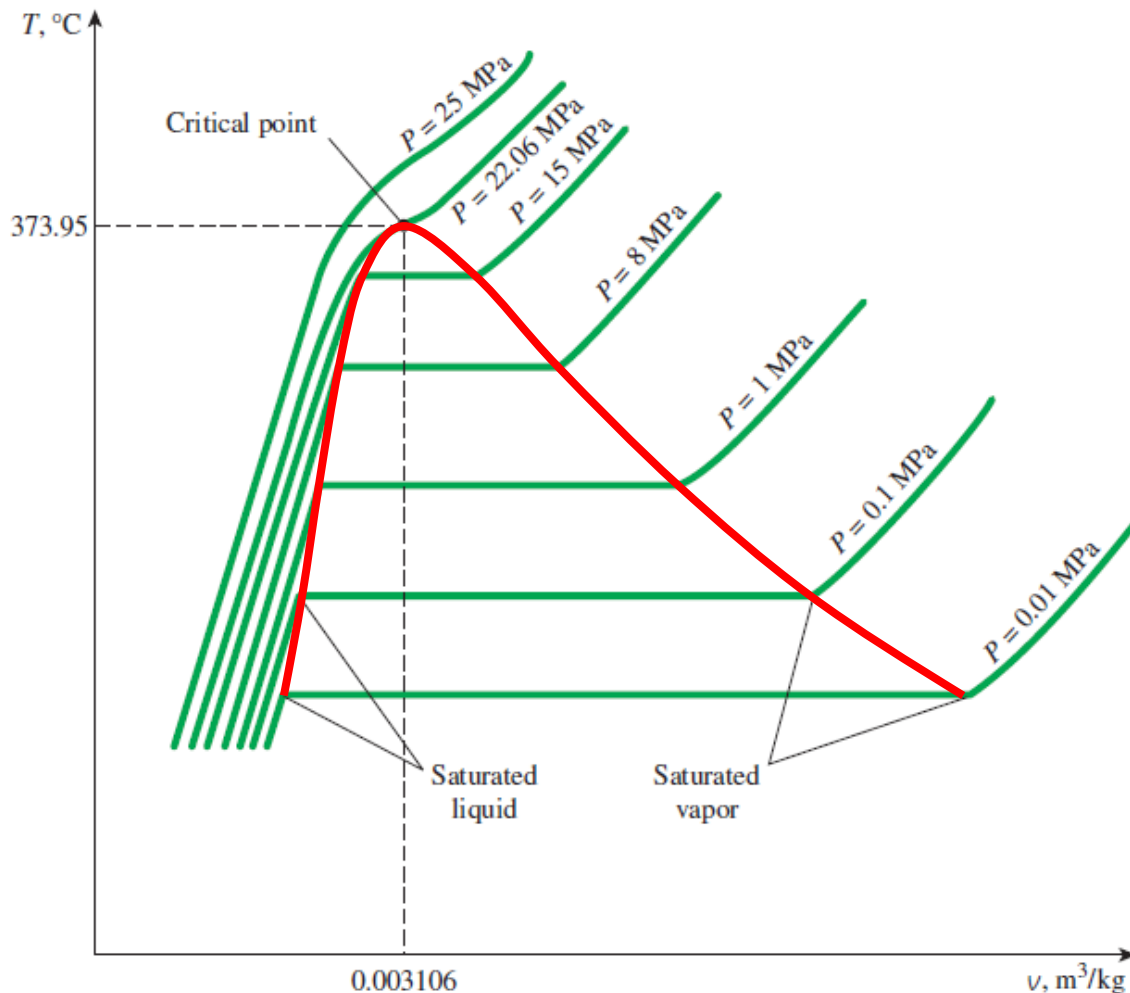
The temperature of liquid nitrogen exposed to the atmosphere remains constant at  $-196^{\circ}\text{C}$ , and thus it maintains the test chamber at  $-196^{\circ}\text{C}$ .

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



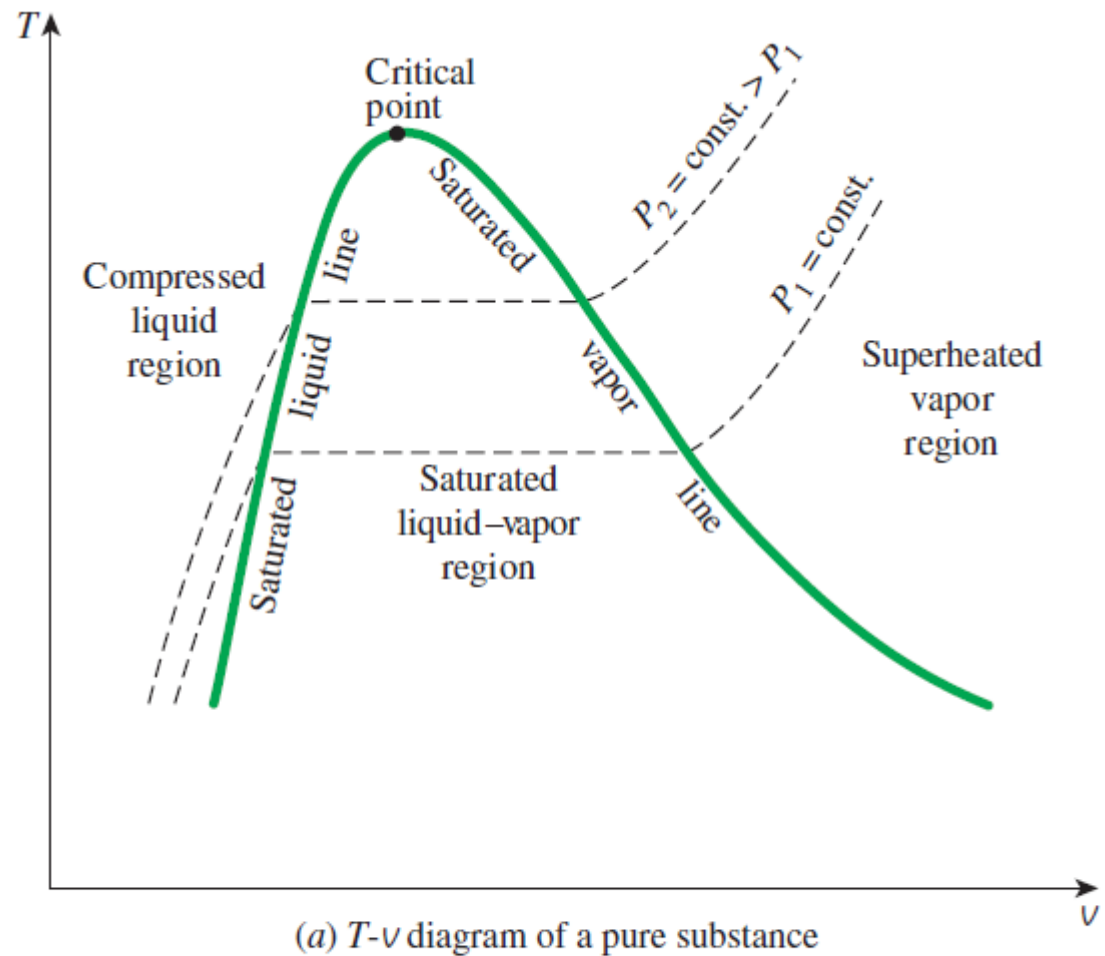
# PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

The variations of properties during phase-change processes are best studied and understood with the help of property diagrams such as the  $T$ - $v$ ,  $P$ - $v$ , and  $P$ - $T$  diagrams for pure substances.



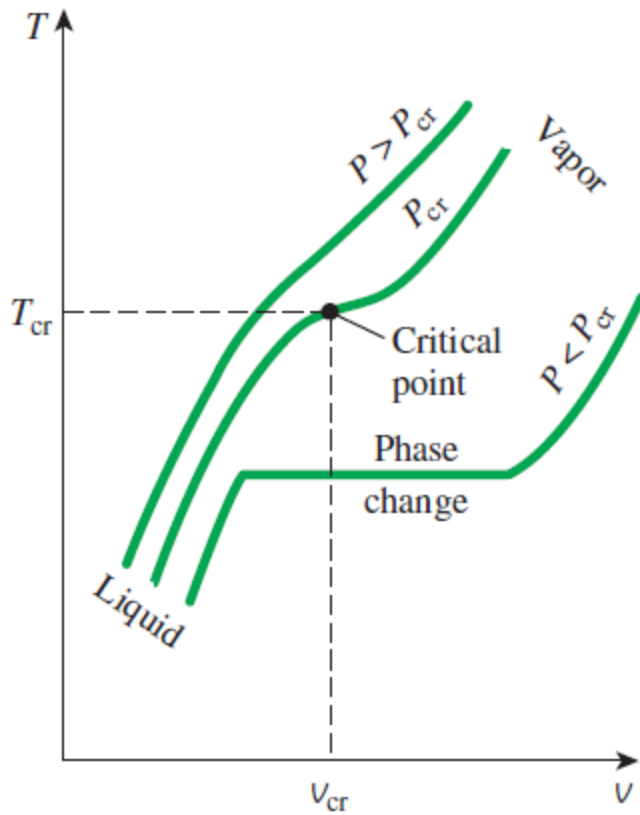
$T$ - $v$  diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

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



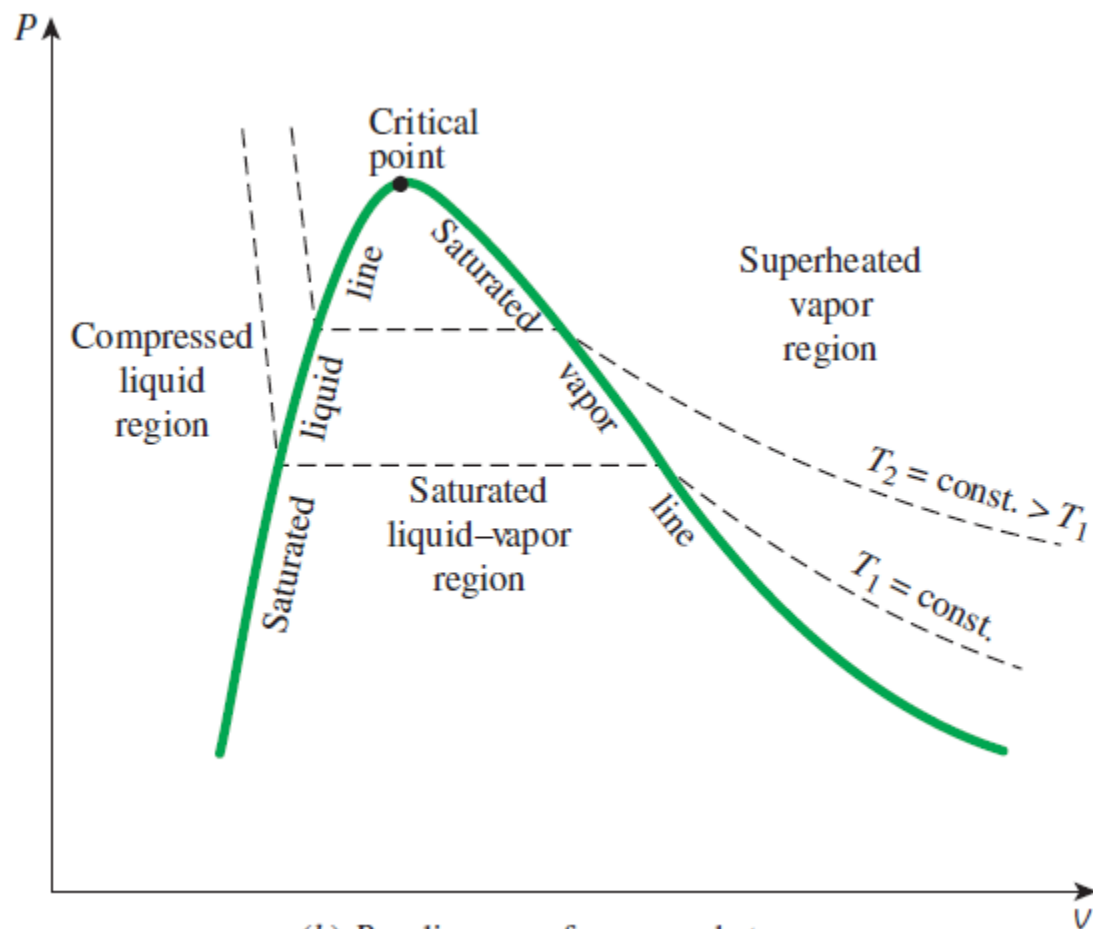
**FIGURE 3–17**

Property diagrams of a pure substance.

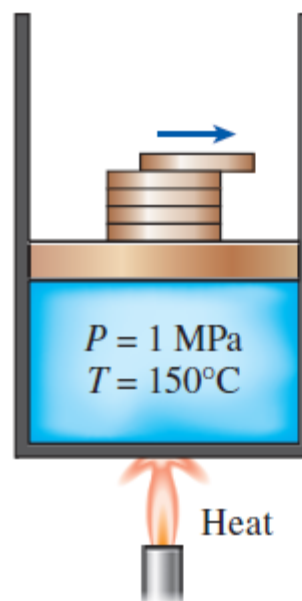


At supercritical pressures ( $P > P_{cr}$ ), there is no distinct phase-change (boiling) process.

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



(b)  $P$ - $v$  diagram of a pure substance



**FIGURE 3-18**

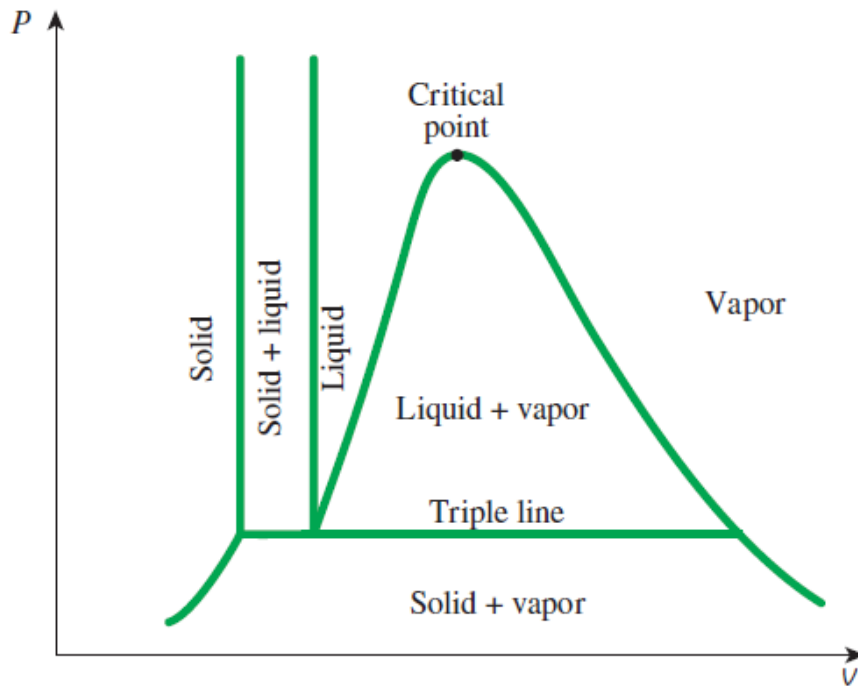
The pressure in a piston-cylinder device can be reduced by reducing the weight of the piston.

# Extending the Diagrams to Include the Solid Phase

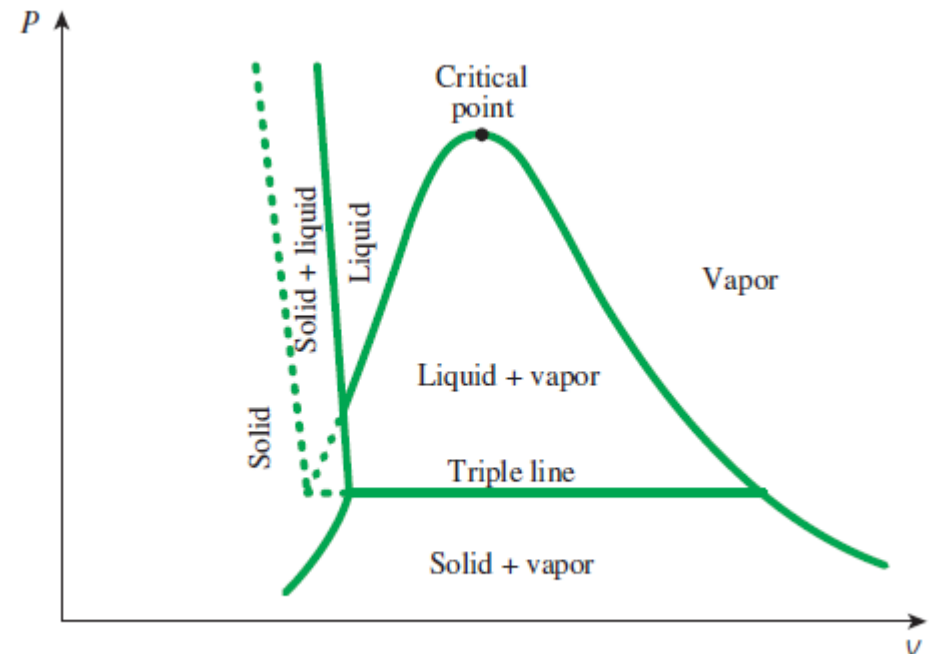
For water,  
 $T_{tp} = 0.01^\circ\text{C}$   
 $P_{tp} = 0.6117 \text{ kPa}$



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



(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)

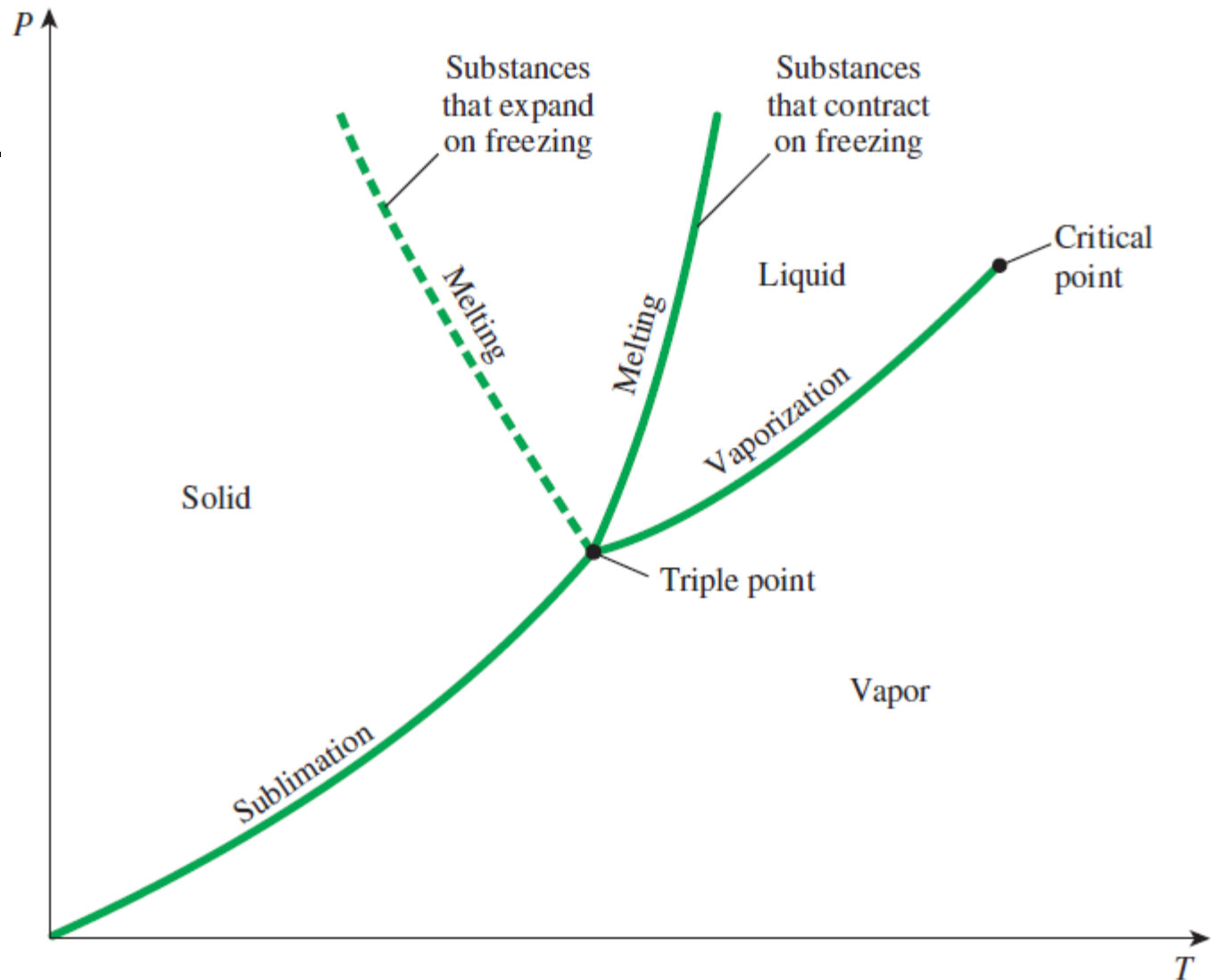
# Phase Diagram

## Sublimation:

Passing from the solid phase directly into the vapor phase.



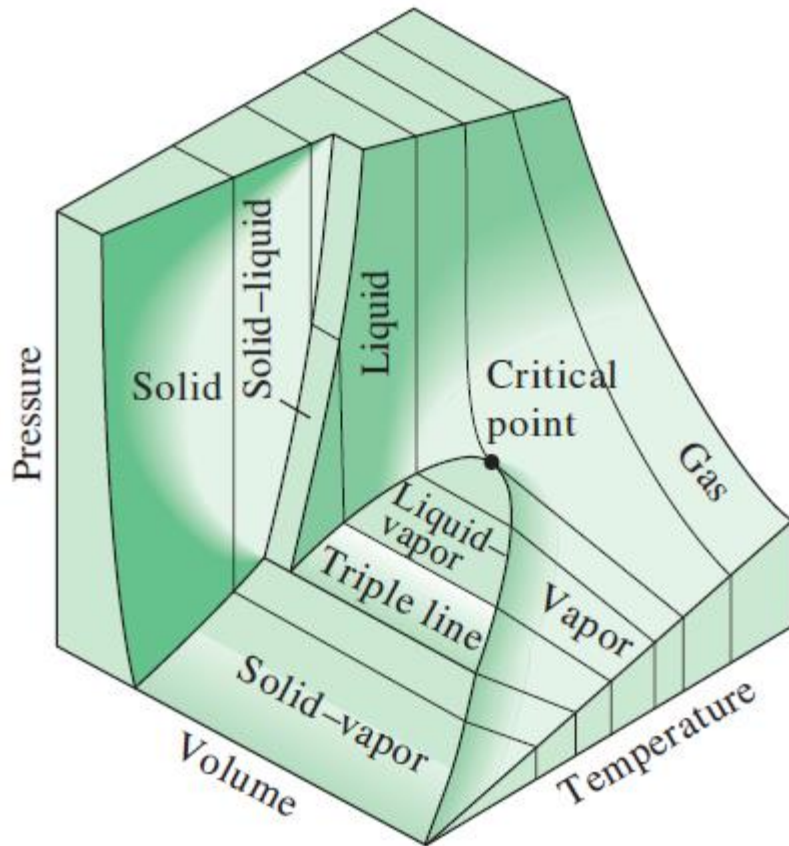
At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).



$P$ - $T$  diagram of pure substances.

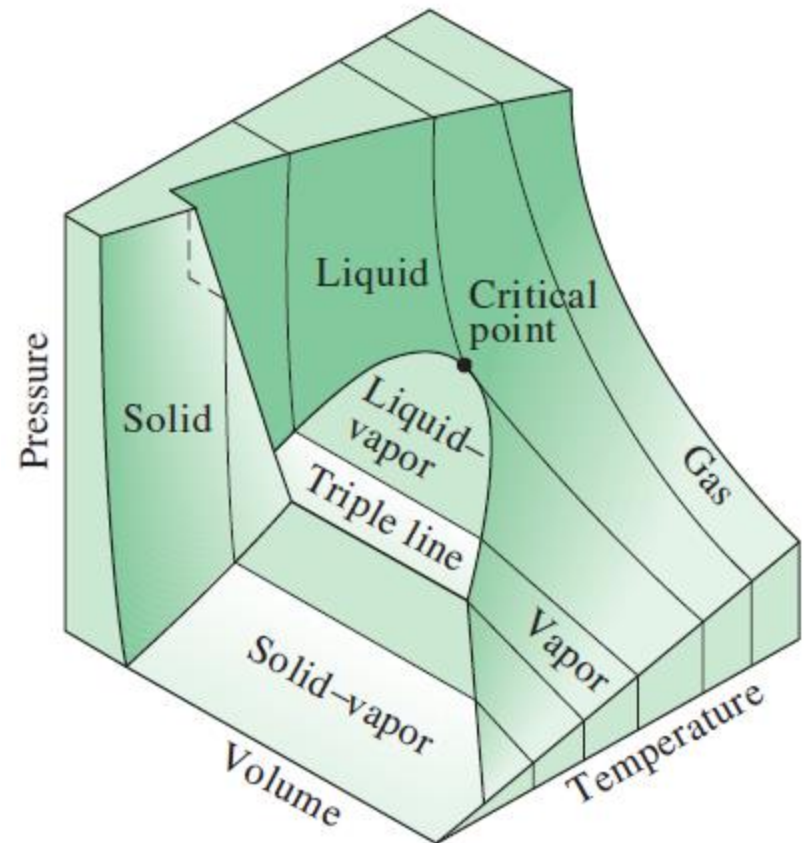


The  $P$ - $v$ - $T$  surfaces present a great deal of information at once, but in a thermodynamic analysis it is more convenient to work with two-dimensional diagrams, such as the  $P$ - $v$  and  $T$ - $v$  diagrams.



**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).



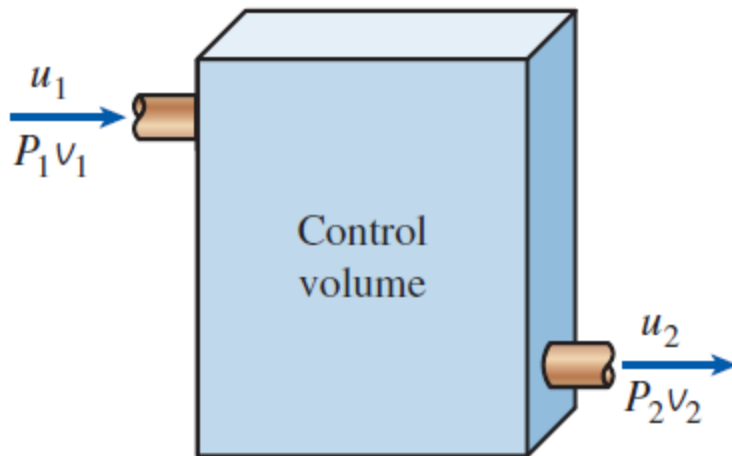
# PROPERTY TABLES

- 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

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

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



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

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

The product *pressure*  $\times$  *volume* has energy units.<sup>17</sup>

## Saturated Liquid and Saturated Vapor States

$v_f$  = specific volume of saturated liquid

$v_g$  = specific volume of saturated vapor

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

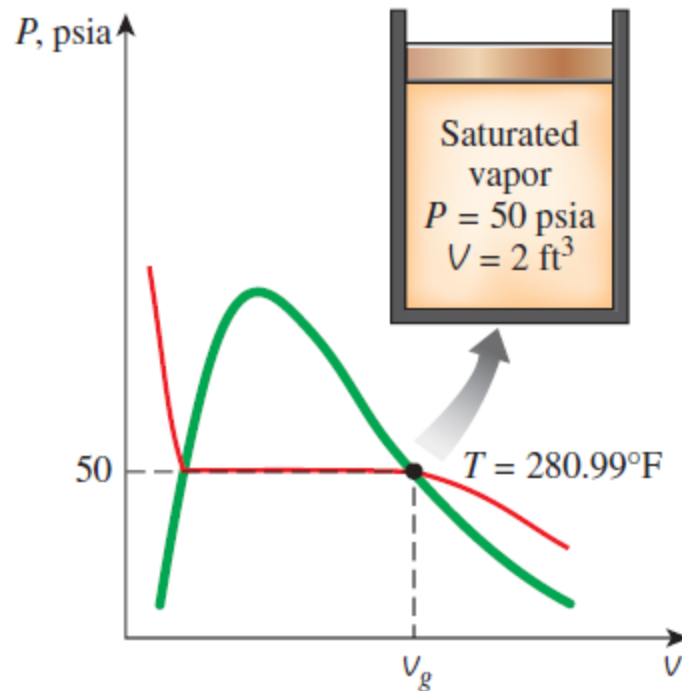
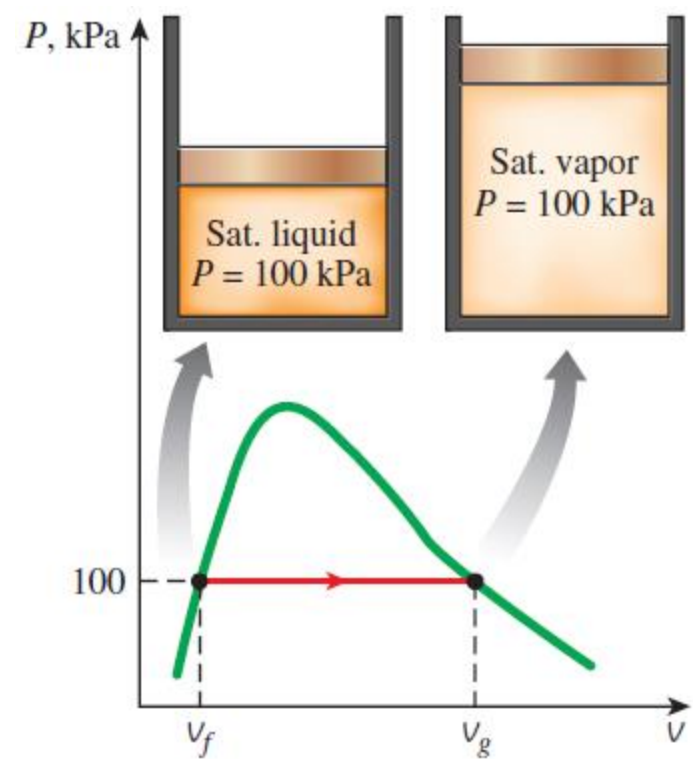
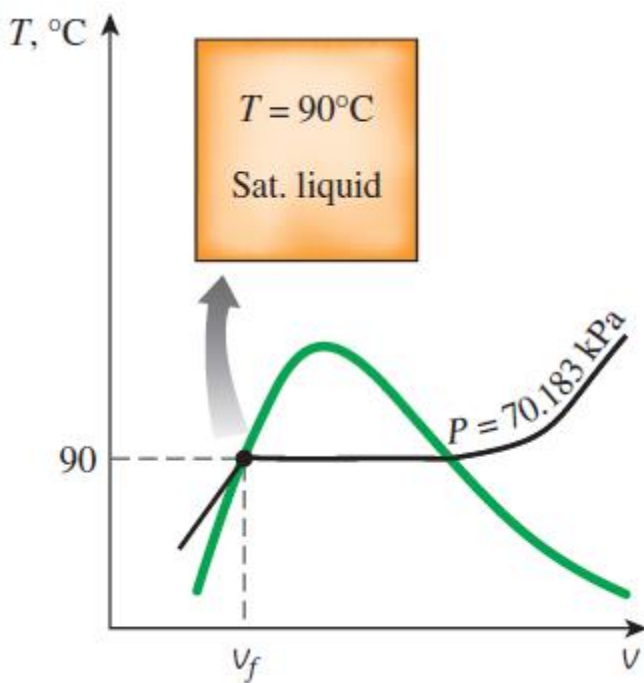
A partial list of Table A–4.

| Temp.<br>°C<br>$T$ | Sat. press.<br>kPa<br>$P_{\text{sat}}$ | Specific volume<br>m <sup>3</sup> /kg |                     |
|--------------------|--|---------------------------------------|---------------------|
|                    |  | Sat. liquid<br>$v_f$                  | Sat. vapor<br>$v_g$ |
| 85                 | 57.868                                 | 0.001032                              | 2.8261              |
| 90                 | 70.183                                 | 0.001036                              | 2.3593              |
| 95                 | 84.609                                 | 0.001040                              | 1.9808              |

- **Table A–4:** Saturation properties of water under temperature.
- **Table A–5:** Saturation properties of water under pressure.

**Enthalpy of vaporization,  $h_{fg}$  (Latent heat of vaporization):** The amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure.

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



## Some more examples

- What is the pressure and specific volume for a saturated liquid at 70°C?

$$P_{\text{sat}} = 31.202 \text{ kPa} \quad v_f = 0.001023 \text{ m}^3/\text{kg}$$

- At what temperature does a container with liquid water and water vapor at 200 psia exist?

$$T_{\text{sat}} = 381.80 \text{ }^\circ\text{F}$$

- Determine the amount of energy (per mass) needed to boil water at 80°C and 47.416 kPa.

$$h_{fg} = 2308 \text{ kJ/kg}$$

- What is the pressure of a container that contains 2 kg of a saturated liquid of refrigerant-134a (R-134a) at -10°C?

$$P_{\text{sat}} = 200.74 \text{ kPa}$$

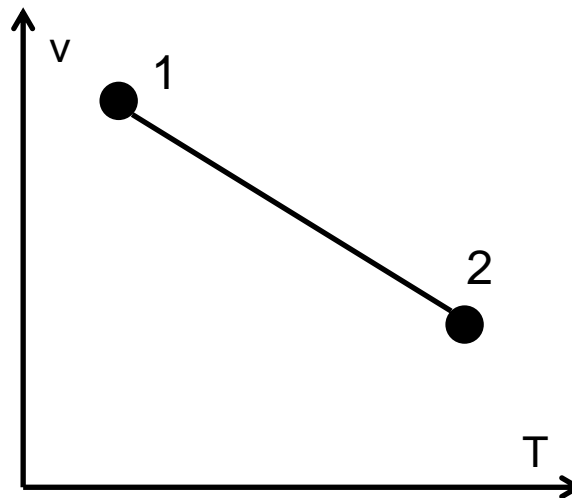
Determine the specific volume of a saturated vapor of water at  $93^{\circ}\text{C}$ .

There's no data for it. How can we determine the specific volume?

We use interpolation.

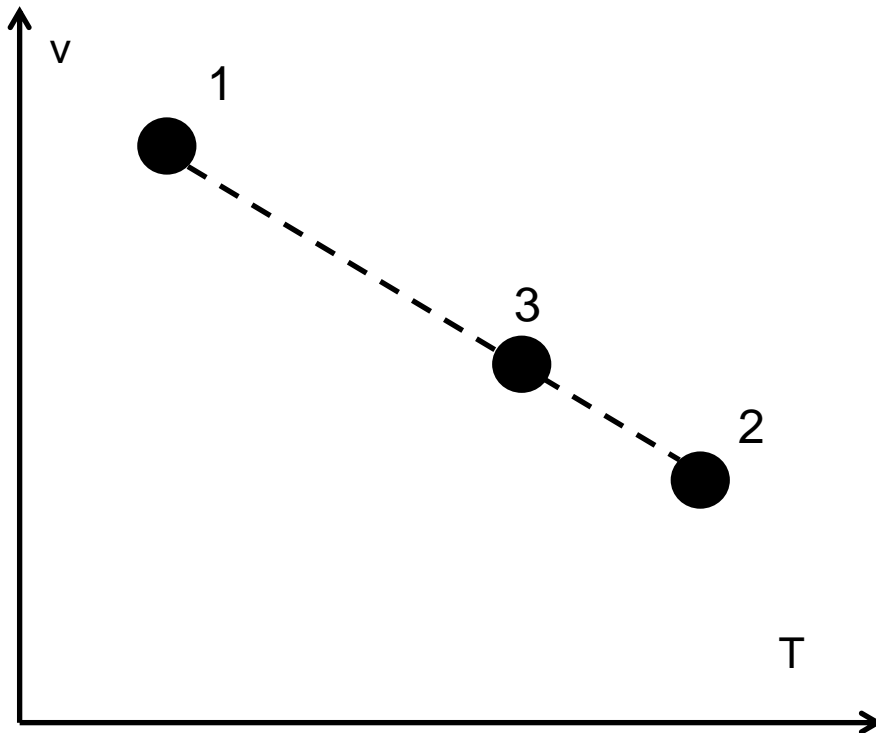
Find two points (one on each side of the value we are examining). So in this case we want to look at  $90^{\circ}\text{C}$  and  $95^{\circ}\text{C}$ .

Let's plot the temperatures and specific volumes and assume that the two points can be connected by a line.



# Interpolation

- If we assume that our third point (the point we are interested in) is located on the line, then the slope of the line from 1 to 2 is the same as 2 to 3 (or 1 to 3)



$$m_{12} = \frac{v_2 - v_1}{T_2 - T_1}$$

$$m_{23} = \frac{v_3 - v_2}{T_3 - T_2}$$

$$m_{12} = m_{23}$$

$$\frac{v_2 - v_1}{T_2 - T_1} = \frac{v_3 - v_2}{T_3 - T_2}$$

$$v_3 = \frac{v_2 - v_1}{T_2 - T_1} (T_3 - T_2) + v_2$$

Determine the specific volume of a saturated vapor of water at 93°C.

- At 90°C,  $v_g = 2.3593 \text{ m}^3/\text{kg}$
- At 95°C  $v_g = 1.9808 \text{ m}^3/\text{kg}$

$$v_3 = \frac{v_2 - v_1}{T_2 - T_1} (T_3 - T_2) + v_2$$

$$v_3 = \frac{2.3593 - 1.9808}{90 - 95} (93 - 90) + 2.3593$$

$$v_3 = 2.1322 \frac{\text{m}^3}{\text{kg}}$$

Notice that the value is between the two specific volumes at 90°C and 95°C. Check to make sure your answer is reasonable.

# Saturated Liquid–Vapor Mixture

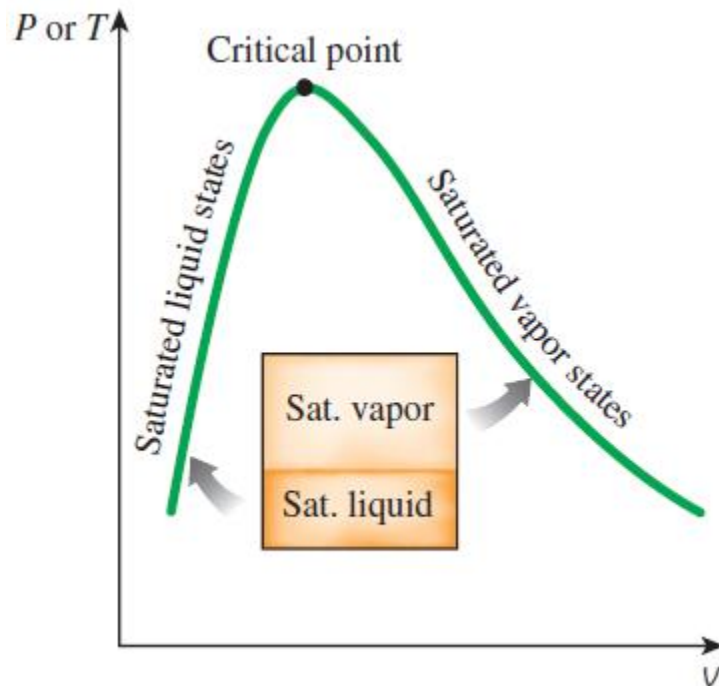
**Quality,  $x$** : The ratio of the mass of vapor to the total mass of the mixture.

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

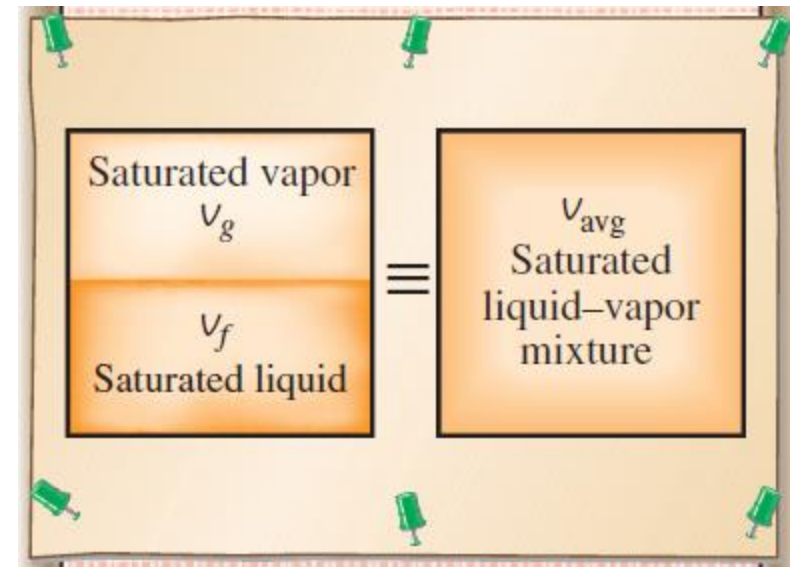
*The properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapor.*

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

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.

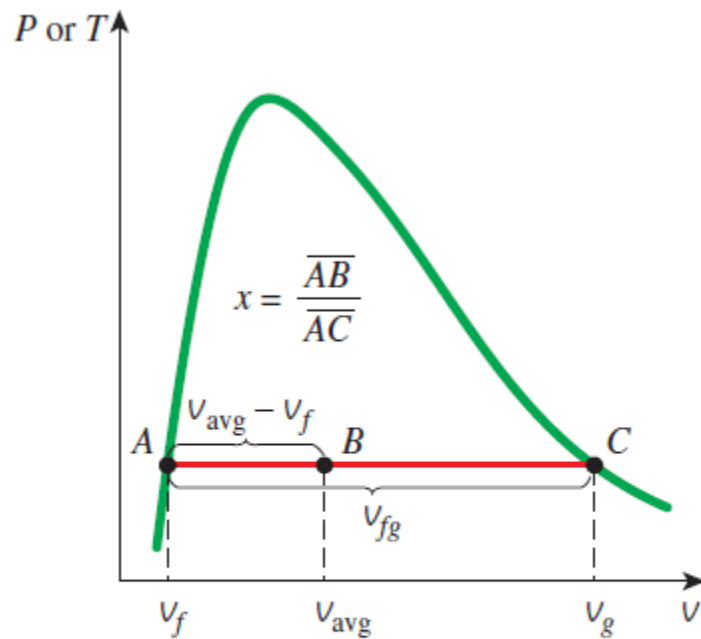


$$v_{\text{avg}} = v_f + x v_{fg} \quad (\text{m}^3/\text{kg})$$

$$x = m_g/m_t \quad x = \frac{v_{\text{avg}} - v_f}{v_{fg}}$$

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

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



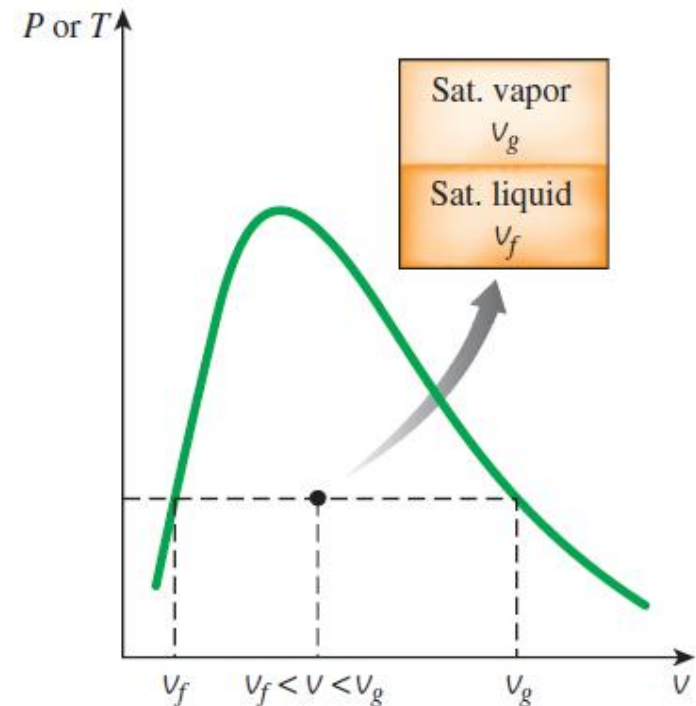
**FIGURE 3–33**

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

**y** → v, u, or h.

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

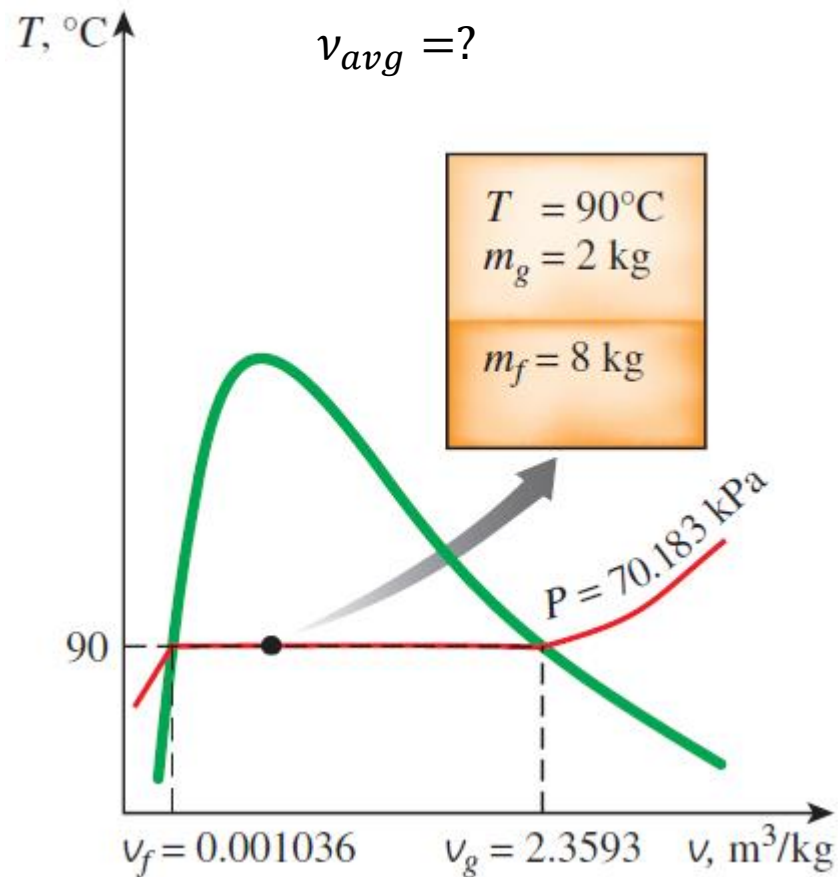
$$y_f \leq y_{\text{avg}} \leq y_g$$



**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  $P$ .

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



$$v_{avg} = 0.473 \frac{\text{m}^3}{\text{kg}}$$

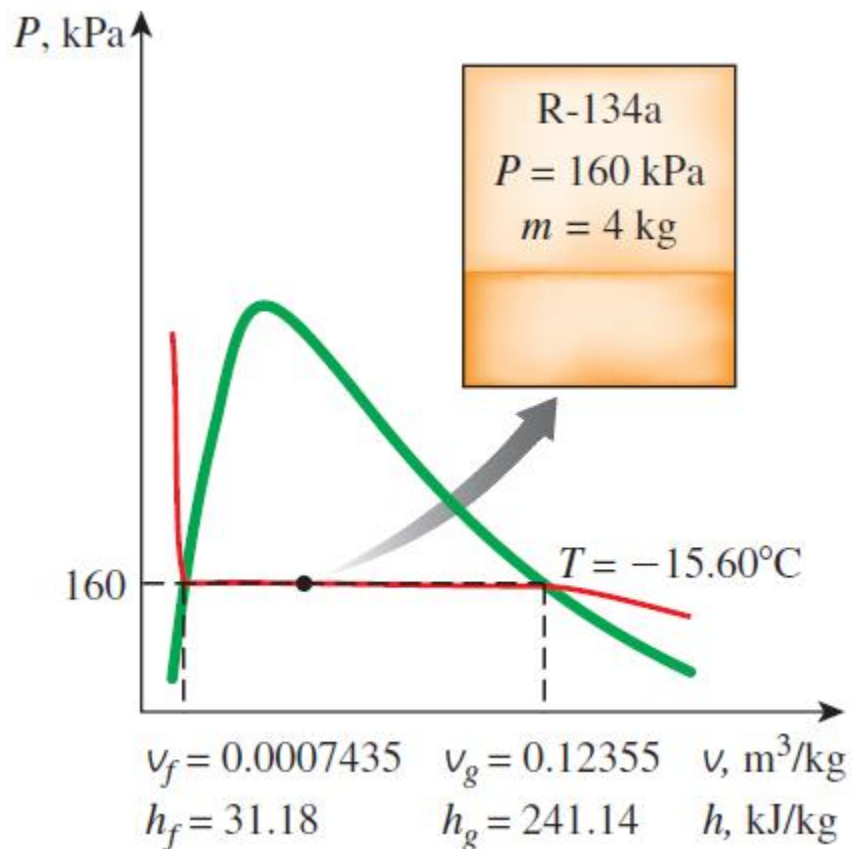
## Example

Determine the pressure and volume of a rigid container that contains 10 lbm of water at 150°F where water in the liquid form has a mass of 7 lbm.

Example 1

# Example

A 100 L container contains 4 kg of R-134a at a pressure 160 kPa. Determine the temperature, the quality, and the enthalpy of the refrigerant.



**Example 2**

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.

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

## Superheated Vapor

Compared to saturated vapor, superheated vapor is characterized by

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

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

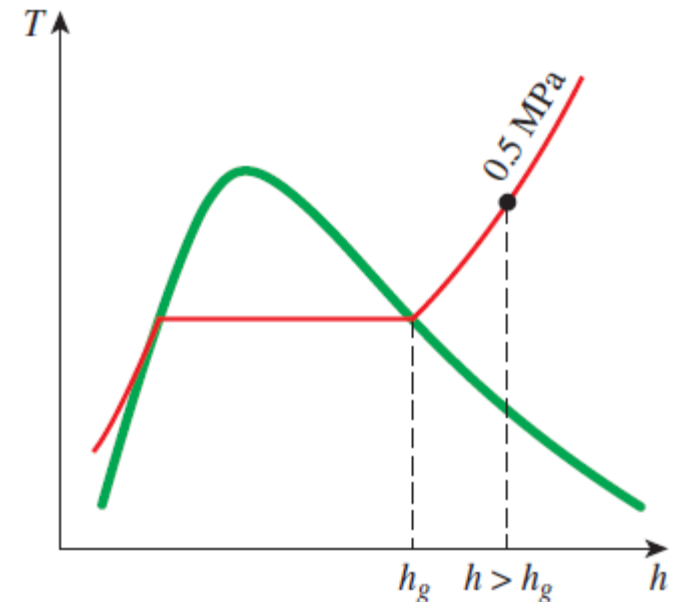
Higher specific volumes ( $\nu > \nu_g$  at a given  $P$  or  $T$ )

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

Higher enthalpies ( $h > h_g$  at a given  $P$  or  $T$ )

At a specified  $P$ , superheated vapor exists at a higher  $h$  than the saturated vapor.

A partial listing of Table A–6.



# Example

What is the specific volume for superheat water vapor at 500°F and 300 psia?

$$1.7670 \frac{ft^3}{lbm}$$

What is the pressure of 50 kg of superheated water vapor at a temperature of 200°C in a rigid container with a volume of 10,301L?

$$v = \frac{10301L}{50kg} = \frac{10.301m^3}{50kg} = 0.20602 \frac{m^3}{kg}$$

$$P = 1.00 MPa$$

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

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

A more accurate relation for  $h$

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

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.

## Compressed Liquid

Compressed liquid is characterized by

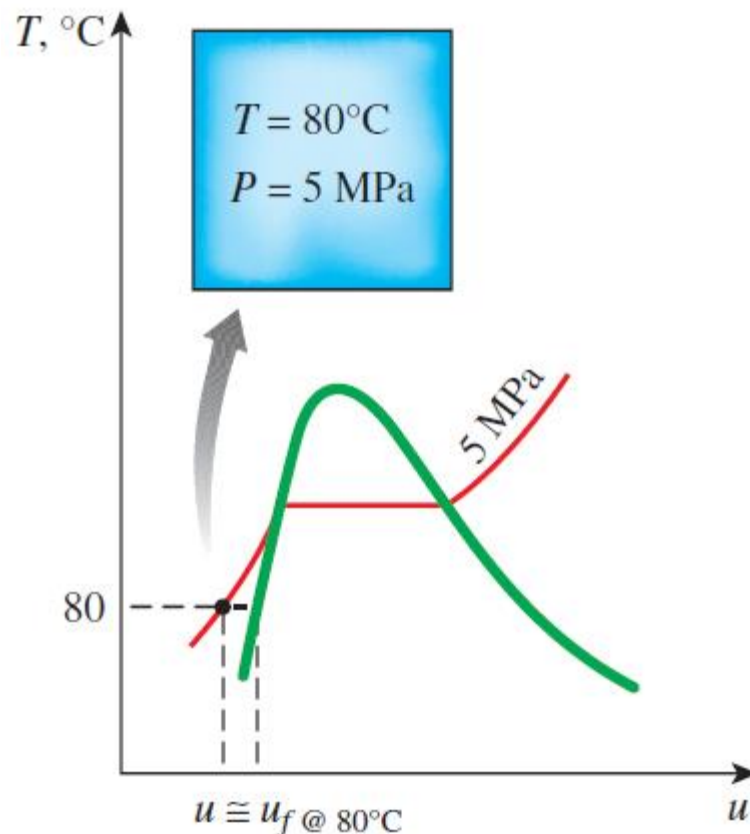
Higher pressures ( $P > P_{\text{sat}}$  at a given  $T$ )

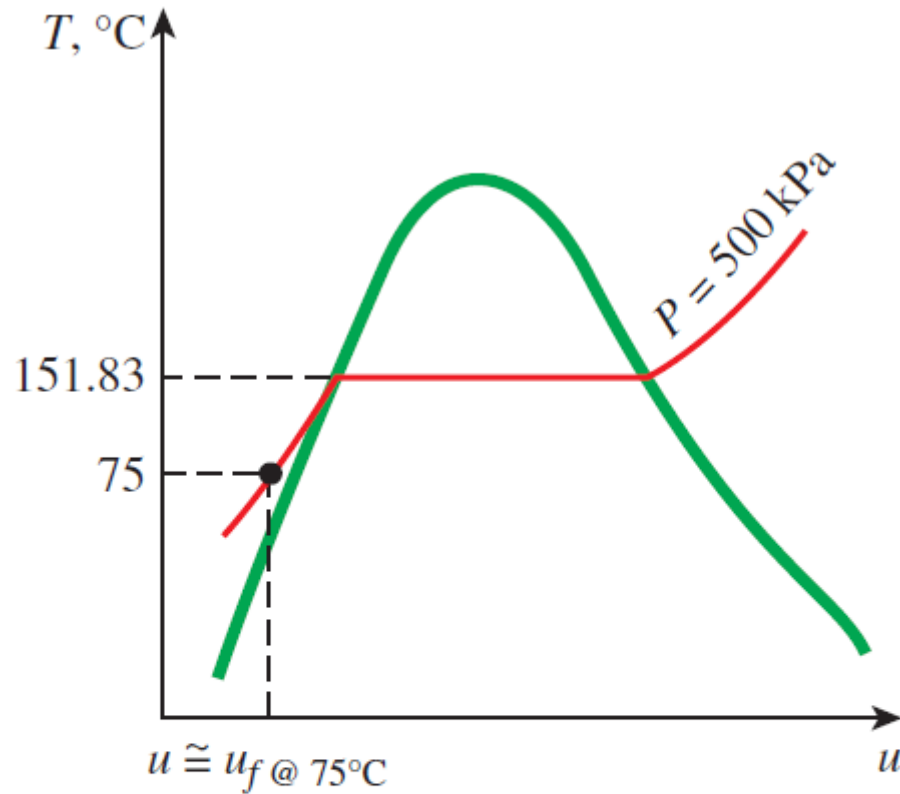
Lower temperatures ( $T < T_{\text{sat}}$  at a given  $P$ )

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  $T$ )





**FIGURE 3–41**

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.
- 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.

Saturated water—Temperature table

| Temp.,<br>$T$ °C | Sat.<br>press.,<br>$P_{\text{sat}}$ kPa | Specific volume,<br>$\text{m}^3/\text{kg}$ |                         | Internal energy,<br>$\text{kJ/kg}$ |                    |                         | Enthalpy,<br>$\text{kJ/kg}$ |                    |                         | Entropy,<br>$\text{kJ/kg} \cdot \text{K}$ |                    |                         |
|------------------|---|--|-------------------------|------------------------------------|--------------------|-------------------------|-----------------------------|--------------------|-------------------------|---|--------------------|-------------------------|
|                  |   | Sat.<br>liquid,<br>$v_f$                   | Sat.<br>vapor,<br>$v_g$ | Sat.<br>liquid,<br>$u_f$           | Evap.,<br>$u_{fg}$ | Sat.<br>vapor,<br>$u_g$ | Sat.<br>liquid,<br>$h_f$    | Evap.,<br>$h_{fg}$ | Sat.<br>vapor,<br>$h_g$ | Sat.<br>liquid,<br>$s_f$                  | Evap.,<br>$s_{fg}$ | Sat.<br>vapor,<br>$s_g$ |
| 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

| Temp.,<br>$T$ °C | Sat.<br>press.,<br>$P_{\text{sat}}$ kPa | Specific volume,<br>$\text{m}^3/\text{kg}$ |                         | Internal energy,<br>$\text{kJ/kg}$ |                    |                         | Enthalpy,<br>$\text{kJ/kg}$ |                    |                         | Entropy,<br>$\text{kJ/kg} \cdot \text{K}$ |                    |                         |
|------------------|---|--|-------------------------|------------------------------------|--------------------|-------------------------|-----------------------------|--------------------|-------------------------|---|--------------------|-------------------------|
|                  |   | Sat.<br>liquid,<br>$v_f$                   | Sat.<br>vapor,<br>$v_g$ | Sat.<br>liquid,<br>$u_f$           | Evap.,<br>$u_{fg}$ | Sat.<br>vapor,<br>$u_g$ | Sat.<br>liquid,<br>$h_f$    | Evap.,<br>$h_{fg}$ | Sat.<br>vapor,<br>$h_g$ | Sat.<br>liquid,<br>$s_f$                  | Evap.,<br>$s_{fg}$ | Sat.<br>vapor,<br>$s_g$ |
| -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                 |

# 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