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# PROPERTIES OF PURE SUBSTANCES

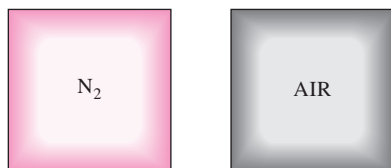
We start this chapter with the introduction of the concept of a *pure substance* and a discussion of the physics of phase-change processes. We then illustrate the various property diagrams and  $P$ - $v$ - $T$  surfaces of pure substances. After demonstrating the use of the property tables, the hypothetical substance *ideal gas* and the *ideal-gas equation of state* are discussed. The *compressibility factor*, which accounts for the deviation of real gases from ideal-gas behavior, is introduced, and some of the best-known equations of state such as the van der Waals, Beattie-Bridgeman, and Benedict-Webb-Rubin equations are presented.

## Objectives

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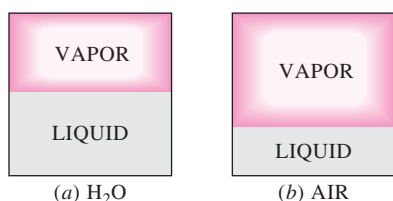
The objectives of Chapter 3 are to:

- 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.



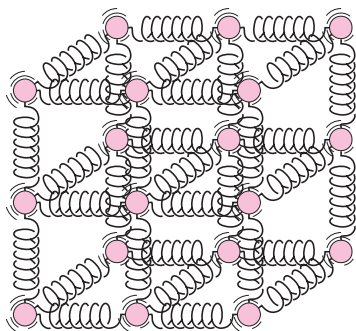
**FIGURE 3-1**

Nitrogen and gaseous air are pure substances.



**FIGURE 3-2**

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



**FIGURE 3-3**

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

### 3-1 ■ PURE SUBSTANCE

A substance that has a fixed chemical composition throughout is called a **pure substance**. Water, nitrogen, helium, and carbon dioxide, for example, are all pure substances.

A pure substance does not have to be of a single chemical element or compound, however. A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous. Air, for example, is a mixture of several gases, but it is often considered to be a pure substance because it has a uniform chemical composition (Fig. 3-1). However, a mixture of oil and water is not a pure substance. Since oil is not soluble in water, it will collect on top of the water, forming two chemically dissimilar regions.

A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same (Fig. 3-2). A mixture of ice and liquid water, for example, is a pure substance because both phases have the same chemical composition. A mixture of liquid air and gaseous air, however, is not a pure substance since the composition of liquid air is different from the composition of gaseous air, and thus the mixture is no longer chemically homogeneous. This is due to different components in air condensing at different temperatures at a specified pressure.

### 3-2 ■ PHASES OF A PURE SUBSTANCE

We all know from experience that substances exist in different phases. At room temperature and pressure, copper is a solid, mercury is a liquid, and nitrogen is a gas. Under different conditions, each may appear in a different phase. Even though there are three principal phases—solid, liquid, and gas—a substance may have several phases within a principal phase, each with a different molecular structure. Carbon, for example, may exist as graphite or diamond in the solid phase. Helium has two liquid phases; iron has three solid phases. Ice may exist at seven different phases at high pressures. A phase is identified as having a distinct molecular arrangement that is homogeneous throughout and separated from the others by easily identifiable boundary surfaces. The two phases of  $H_2O$  in iced water represent a good example of this.

When studying phases or phase changes in thermodynamics, one does not need to be concerned with the molecular structure and behavior of different phases. However, it is very helpful to have some understanding of the molecular phenomena involved in each phase, and a brief discussion of phase transformations follows.

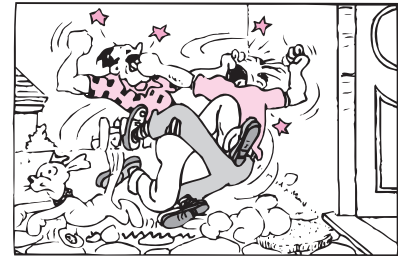
Intermolecular bonds are strongest in solids and weakest in gases. One reason is that molecules in solids are closely packed together, whereas in gases they are separated by relatively large distances.

The molecules in a **solid** are arranged in a three-dimensional pattern (lattice) that is repeated throughout (Fig. 3-3). Because of the small distances between molecules in a solid, the attractive forces of molecules on each other are large and keep the molecules at fixed positions (Fig. 3-4). Note that the attractive forces between molecules turn to repulsive forces as the

distance between the molecules approaches zero, thus preventing the molecules from piling up on top of each other. Even though the molecules in a solid cannot move relative to each other, they continually oscillate about their equilibrium positions. The velocity of the molecules during these oscillations depends on the temperature. At sufficiently high temperatures, the velocity (and thus the momentum) of the molecules may reach a point where the intermolecular forces are partially overcome and groups of molecules break away (Fig. 3–5). This is the beginning of the melting process.

The molecular spacing in the **liquid** phase is not much different from that of the solid phase, except the molecules are no longer at fixed positions relative to each other and they can rotate and translate freely. In a liquid, the intermolecular forces are weaker relative to solids, but still relatively strong compared with gases. The distances between molecules generally experience a slight increase as a solid turns liquid, with water being a notable exception.

In the **gas** phase, the molecules are far apart from each other, and a molecular order is nonexistent. Gas molecules move about at random, continually colliding with each other and the walls of the container they are in. Particularly at low densities, the intermolecular forces are very small, and collisions are the only mode of interaction between the molecules. Molecules in the gas phase are at a considerably higher energy level than they are in the liquid or solid phases. Therefore, the gas must release a large amount of its energy before it can condense or freeze.

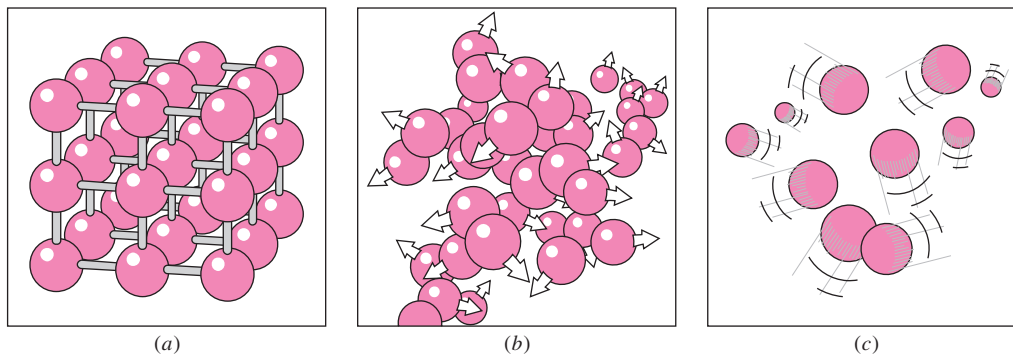


**FIGURE 3–4**

In a solid, the attractive and repulsive forces between the molecules tend to maintain them at relatively constant distances from each other.

### 3–3 ■ PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

There are many practical situations where two phases of a pure substance coexist in equilibrium. Water exists as a mixture of liquid and vapor in the boiler and the condenser of a steam power plant. The refrigerant turns from liquid to vapor in the freezer of a refrigerator. Even though many home owners consider the freezing of water in underground pipes as the most



**FIGURE 3–5**

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.

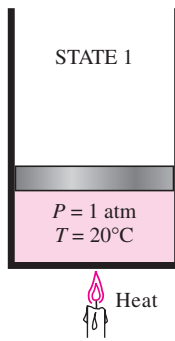


FIGURE 3-6

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

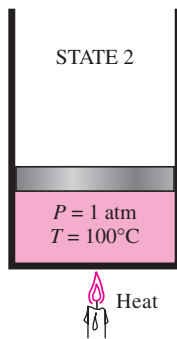


FIGURE 3-7

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

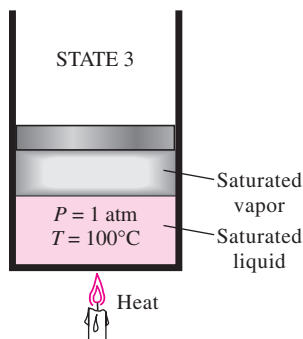


FIGURE 3-8

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

important phase-change process, attention in this section is focused on the liquid and vapor phases and their mixture. As a familiar substance, water is used to demonstrate the basic principles involved. Remember, however, that all pure substances exhibit the same general behavior.

## Compressed Liquid and Saturated Liquid

Consider a piston–cylinder device containing liquid water at 20°C and 1 atm pressure (state 1, Fig. 3–6). Under these conditions, water exists in the liquid phase, and it is called a **compressed liquid**, or a **subcooled liquid**, meaning that it is *not about to vaporize*. Heat is now transferred to the water until its temperature rises to, say, 40°C. As the temperature rises, the liquid water expands slightly, and so its specific volume increases. To accommodate this expansion, the piston moves up slightly. The pressure in the cylinder remains constant at 1 atm during this process since it depends on the outside barometric pressure and the weight of the piston, both of which are constant. Water is still a compressed liquid at this state since it has not started to vaporize.

As more heat is transferred, the temperature keeps rising until it reaches 100°C (state 2, Fig. 3–7). At this point water is still a liquid, but any heat addition will cause some of the liquid to vaporize. That is, a phase-change process from liquid to vapor is about to take place. A liquid that is *about to vaporize* is called a **saturated liquid**. Therefore, state 2 is a saturated liquid state.

## Saturated Vapor and Superheated Vapor

Once boiling starts, the temperature stops rising until the liquid is completely vaporized. That is, the temperature will remain constant during the entire phase-change process if the pressure is held constant. This can easily be verified by placing a thermometer into boiling pure water on top of a stove. At sea level ( $P = 1$  atm), the thermometer will always read 100°C if the pan is uncovered or covered with a light lid. During a boiling process, the only change we will observe is a large increase in the volume and a steady decline in the liquid level as a result of more liquid turning to vapor.

Midway about the vaporization line (state 3, Fig. 3–8), the cylinder contains equal amounts of liquid and vapor. As we continue transferring heat, the vaporization process continues until the last drop of liquid is vaporized (state 4, Fig. 3–9). At this point, the entire cylinder is filled with vapor that is on the borderline of the liquid phase. Any heat loss from this vapor will cause some of the vapor to condense (phase change from vapor to liquid). A vapor that is *about to condense* is called a **saturated vapor**. Therefore, state 4 is a saturated vapor state. A substance at states between 2 and 4 is referred to as a **saturated liquid–vapor mixture** since the *liquid and vapor phases coexist in equilibrium* at these states.

Once the phase-change process is completed, we are back to a single-phase region again (this time vapor), and further transfer of heat results in an increase in both the temperature and the specific volume (Fig. 3–10). At state 5, the temperature of the vapor is, let us say, 300°C; and if we transfer some heat from the vapor, the temperature may drop somewhat but no condensation will take place as long as the temperature remains above 100°C

(for  $P = 1 \text{ atm}$ ). A vapor that is *not about to condense* (i.e., not a saturated vapor) is called a **superheated vapor**. Therefore, water at state 5 is a superheated vapor. This constant-pressure phase-change process is illustrated on a  $T$ - $v$  diagram in Fig. 3–11.

If the entire process described here 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.

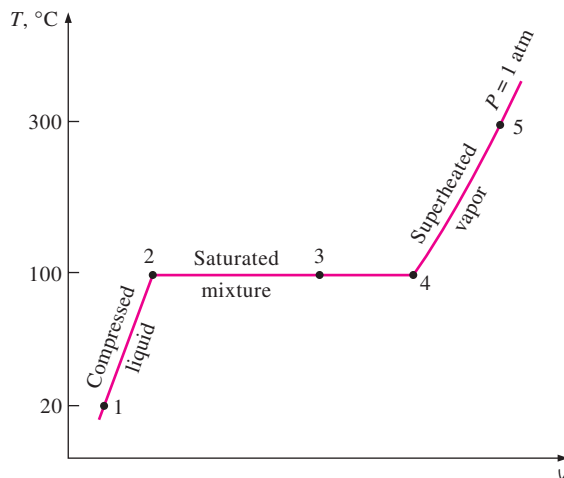
In our daily life, water implies liquid water and steam implies water vapor. In thermodynamics, however, both water and steam usually mean only one thing:  $\text{H}_2\text{O}$ .

### Saturation Temperature and Saturation Pressure

It probably came as no surprise to you that water started to boil at  $100^\circ\text{C}$ . Strictly speaking, the statement “water boils at  $100^\circ\text{C}$ ” is incorrect. The correct statement is “water boils at  $100^\circ\text{C}$  at 1 atm pressure.” The only reason water started boiling at  $100^\circ\text{C}$  was because we held the pressure constant at 1 atm (101.325 kPa). If the pressure inside the cylinder were raised to 500 kPa by adding weights on top of the piston, water would start boiling at  $151.8^\circ\text{C}$ . That is, *the temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.*

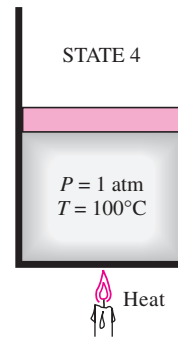
At a given pressure, the temperature at which a pure substance changes phase is called the **saturation temperature**  $T_{\text{sat}}$ . Likewise, at a given temperature, the pressure at which a pure substance changes phase is called the **saturation pressure**  $P_{\text{sat}}$ . At a pressure of 101.325 kPa,  $T_{\text{sat}}$  is  $99.97^\circ\text{C}$ . Conversely, at a temperature of  $99.97^\circ\text{C}$ ,  $P_{\text{sat}}$  is 101.325 kPa. (At  $100.00^\circ\text{C}$ ,  $P_{\text{sat}}$  is 101.42 kPa in the ITS-90 discussed in Chap. 1.)

Saturation tables that list the saturation pressure against the temperature (or the saturation temperature against the pressure) are available for



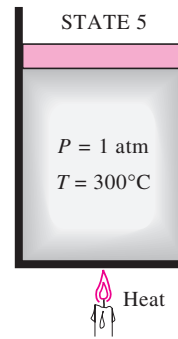
**FIGURE 3–11**

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



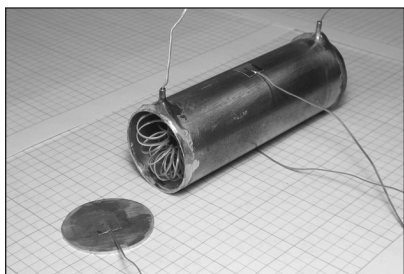
**FIGURE 3–9**

At 1 atm pressure, the temperature remains constant at  $100^\circ\text{C}$  until the last drop of liquid is vaporized (*saturated vapor*).



**FIGURE 3–10**

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



Use actual data from the experiment shown here to obtain the **latent heat of fusion** of water. See end-of-chapter problem 3–146.

**TABLE 3–1**

Saturation (boiling) pressure of water at various temperatures

Temperature, $T_i$ , °C	Saturation pressure, $P_{\text{sat}}$ , 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

**FIGURE 3–12**

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

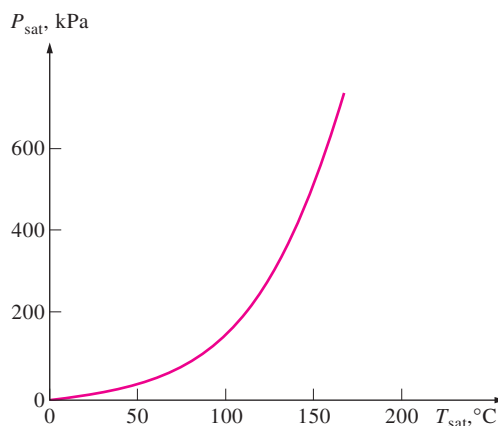
practically all substances. A partial listing of such a table is given in Table 3–1 for water. This table indicates that the pressure of water changing phase (boiling or condensing) at 25°C must be 3.17 kPa, and the pressure of water must be maintained at 3976 kPa (about 40 atm) to have it boil at 250°C. Also, water can be frozen by dropping its pressure below 0.61 kPa.

It takes a large amount of energy to melt a solid or vaporize a liquid. The amount of energy absorbed or released during a phase-change process is called the **latent heat**. More specifically, the amount of energy absorbed during melting is called the **latent heat of fusion** and is equivalent to the amount of energy released during freezing. Similarly, the amount of energy absorbed during vaporization is called the **latent heat of vaporization** and 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.

During a phase-change process, pressure and temperature are obviously dependent properties, and there is a definite relation between them, that is,  $T_{\text{sat}} = f(P_{\text{sat}})$ . A plot of  $T_{\text{sat}}$  versus  $P_{\text{sat}}$ , such as the one given for water in Fig. 3–12, is called a **liquid–vapor saturation curve**. A curve of this kind is characteristic of all pure substances.

It is clear from Fig. 3–12 that  $T_{\text{sat}}$  increases with  $P_{\text{sat}}$ . Thus, a substance at higher pressures boils at higher temperatures. In the kitchen, higher boiling temperatures mean shorter cooking times and energy savings. A beef stew, for example, may take 1 to 2 h to cook in a regular pan that operates at 1 atm pressure, but only 20 min in a pressure cooker operating at 3 atm absolute pressure (corresponding boiling temperature: 134°C).

The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation. Therefore, it takes longer to cook at higher altitudes than it does at sea level (unless a pressure cooker is used). For example, the standard atmospheric pressure at an elevation of 2000 m is 79.50 kPa, which corresponds to a boiling temperature of 93.3°C as opposed to 100°C at sea level (zero elevation). The variation of the boiling temperature of water with altitude at standard atmospheric conditions is given in Table 3–2. For each 1000 m increase in elevation, the boiling temperature



drops by a little over 3°C. Note that the atmospheric pressure at a location, and thus the boiling temperature, changes slightly with the weather conditions. But the corresponding change in the boiling temperature is no more than about 1°C.

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

We mentioned earlier that a substance at a specified pressure boils at the saturation temperature corresponding to that pressure. This phenomenon allows us to control the boiling temperature of a substance by simply controlling the pressure, and it has numerous applications in practice. Below we give some examples. The natural drive to achieve phase equilibrium by allowing some liquid to evaporate is at work behind the scenes.

Consider a sealed can of *liquid refrigerant-134a* in a room at 25°C. If the can has been in the room long enough, the temperature of the refrigerant in the can is also 25°C. Now, if the lid is opened slowly and some refrigerant is allowed to escape, the pressure in the can will start dropping until it reaches the atmospheric pressure. If you are holding the can, you will notice its temperature dropping rapidly, and even ice forming outside the can if the air is humid. A thermometer inserted in the can will register  $-26^\circ\text{C}$  when the pressure drops to 1 atm, which is the saturation temperature of refrigerant-134a at that pressure. The temperature of the liquid refrigerant will remain at  $-26^\circ\text{C}$  until the last drop of it vaporizes.

Another aspect of this interesting physical phenomenon is that a liquid cannot vaporize unless it absorbs energy in the amount of the latent heat of vaporization, which is 217 kJ/kg for refrigerant-134a at 1 atm. Therefore, the rate of vaporization of the refrigerant depends on the rate of heat transfer to the can: the larger the rate of heat transfer, the higher the rate of vaporization. The rate of heat transfer to the can and thus the rate of vaporization of the refrigerant can be minimized by insulating the can heavily. In the limiting case of no heat transfer, the refrigerant will remain in the can as a liquid at  $-26^\circ\text{C}$  indefinitely.

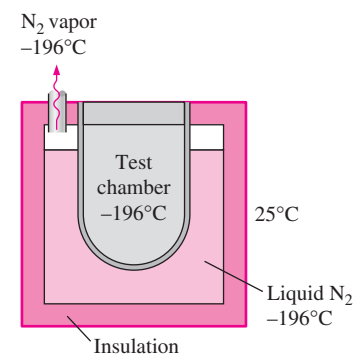
The boiling temperature of *nitrogen* at atmospheric pressure is  $-196^\circ\text{C}$  (see Table A-3a). This means the temperature of liquid nitrogen exposed to the atmosphere must be  $-196^\circ\text{C}$  since some nitrogen will be evaporating. The temperature of liquid nitrogen remains constant at  $-196^\circ\text{C}$  until it is depleted. For this reason, nitrogen is commonly used in low-temperature scientific studies (such as superconductivity) and cryogenic applications to maintain a test chamber at a constant temperature of  $-196^\circ\text{C}$ . This is done by placing the test chamber into a liquid nitrogen bath that is open to the atmosphere. Any heat transfer from the environment to the test section is absorbed by the nitrogen, which evaporates isothermally and keeps the test chamber temperature constant at  $-196^\circ\text{C}$  (Fig. 3-13). The entire test section must be insulated heavily to minimize heat transfer and thus liquid nitrogen consumption. Liquid nitrogen is also used for medical purposes to burn off unsightly spots on the skin. This is done by soaking a cotton swap in liquid nitrogen and wetting the target area with it. As the nitrogen evaporates, it freezes the affected skin by rapidly absorbing heat from it.

A practical way of cooling leafy vegetables is **vacuum cooling**, which is based on *reducing the pressure* of the sealed cooling chamber to the saturation pressure at the desired low temperature, and evaporating some water

**TABLE 3-2**

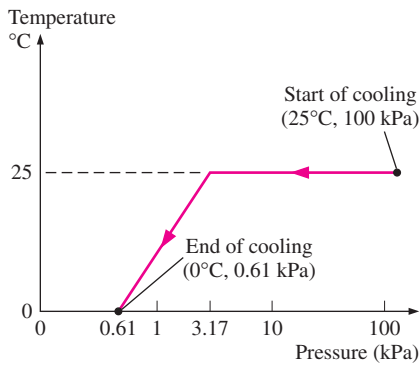
Variation of the standard atmospheric pressure and the boiling (saturation) temperature of water with altitude

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



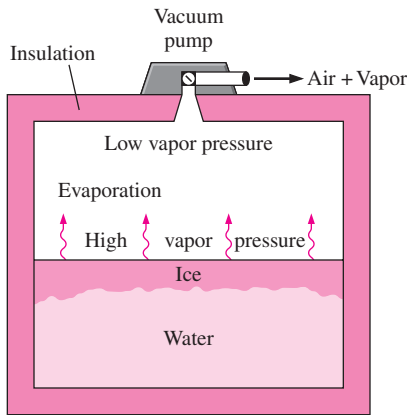
**FIGURE 3-13**

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



**FIGURE 3-14**

The variation of the temperature of fruits and vegetables with pressure during vacuum cooling from 25°C to 0°C.



**FIGURE 3-15**

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

from the products to be cooled. The heat of vaporization during evaporation is absorbed from the products, which lowers the product temperature. The saturation pressure of water at 0°C is 0.61 kPa, and the products can be cooled to 0°C by lowering the pressure to this level. The cooling rate can be increased by lowering the pressure below 0.61 kPa, but this is not desirable because of the danger of freezing and the added cost.

In vacuum cooling, there are two distinct stages. In the first stage, the products at ambient temperature, say at 25°C, are loaded into the chamber, and the operation begins. The temperature in the chamber remains constant until the *saturation pressure* is reached, which is 3.17 kPa at 25°C. In the second stage that follows, saturation conditions are maintained inside at progressively *lower pressures* and the corresponding *lower temperatures* until the desired temperature is reached (Fig. 3-14).

Vacuum cooling is usually more expensive than the conventional refrigerated cooling, and its use is limited to applications that result in much faster cooling. Products with large surface area per unit mass and a high tendency to release moisture such as lettuce and spinach are well-suited for vacuum cooling. Products with low surface area to mass ratio are not suitable, especially those that have relatively impervious peels such as tomatoes and cucumbers. Some products such as mushrooms and green peas can be vacuum cooled successfully by wetting them first.

The vacuum cooling just described becomes **vacuum freezing** if the vapor pressure in the vacuum chamber is dropped below 0.61 kPa, the saturation pressure of water at 0°C. The idea of making ice by using a vacuum pump is nothing new. Dr. William Cullen actually made ice in Scotland in 1775 by evacuating the air in a water tank (Fig. 3-15).

**Package icing** is commonly used in small-scale cooling applications to remove heat and keep the products cool during transit by taking advantage of the large latent heat of fusion of water, but its use is limited to products that are not harmed by contact with ice. Also, ice provides *moisture* as well as *refrigeration*.

### 3-4 ■ PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

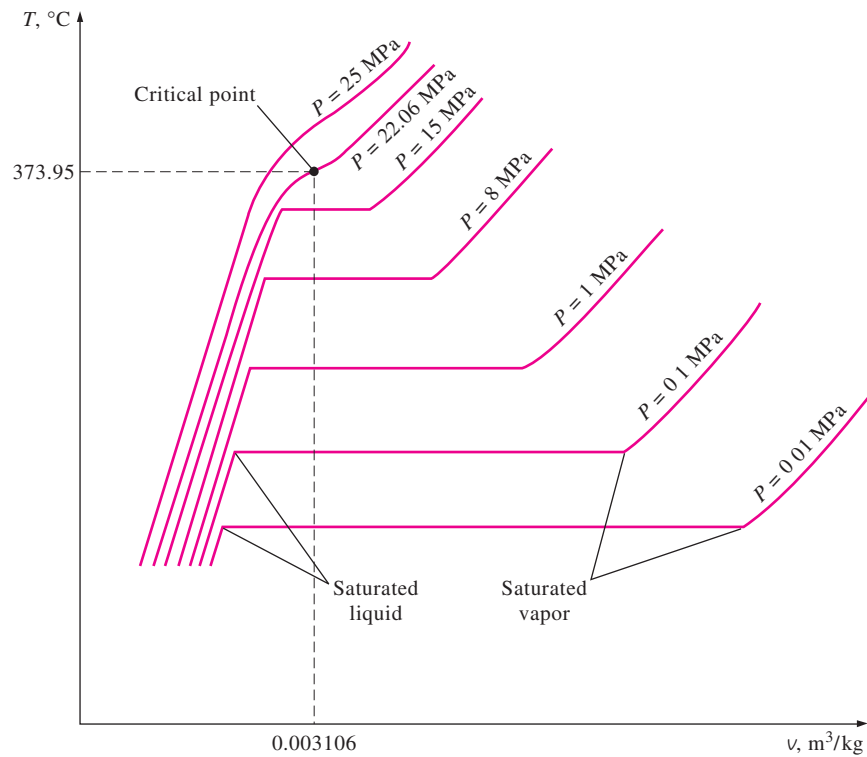
The variations of properties during phase-change processes are best studied and understood with the help of property diagrams. Next, we develop and discuss the  $T$ - $v$ ,  $P$ - $v$ , and  $P$ - $T$  diagrams for pure substances.

#### 1 The $T$ - $v$ Diagram

The phase-change process of water at 1 atm pressure was described in detail in the last section and plotted on a  $T$ - $v$  diagram in Fig. 3-11. Now we repeat this process at different pressures to develop the  $T$ - $v$  diagram.

Let us add weights on top of the piston until the pressure inside the cylinder reaches 1 MPa. At this pressure, water has a somewhat smaller specific volume than it does at 1 atm pressure. As heat is transferred to the water at this new pressure, the process follows a path that looks very much like the process path at 1 atm pressure, as shown in Fig. 3-16, but there are some noticeable differences. First, water starts boiling at a much higher tempera-





**FIGURE 3–16**

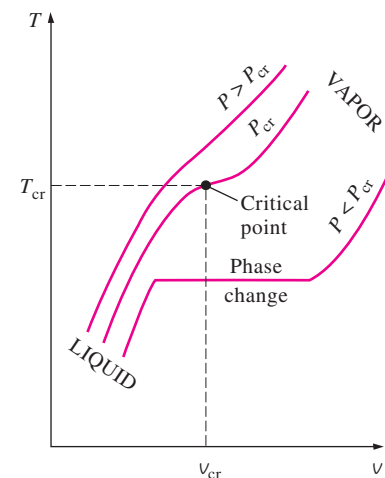
*T-v* diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

ture (179.9°C) at this pressure. Second, the specific volume of the saturated liquid is larger and the specific volume of the saturated vapor is smaller than the corresponding values at 1 atm pressure. That is, the horizontal line that connects the saturated liquid and saturated vapor states is much shorter.

As the pressure is increased further, this saturation line continues to shrink, as shown in Fig. 3–16, and it becomes a point when the pressure reaches 22.06 MPa for the case of water. This point is called the **critical point**, and it is defined as *the point at which the saturated liquid and saturated vapor states are identical*.

The temperature, pressure, and specific volume of a substance at the critical point are called, respectively, the *critical temperature*  $T_{cr}$ , *critical pressure*  $P_{cr}$ , and *critical specific volume*  $v_{cr}$ . The critical-point properties of water are  $P_{cr} = 22.06$  MPa,  $T_{cr} = 373.95^\circ\text{C}$ , and  $v_{cr} = 0.003106$  m³/kg. For helium, they are 0.23 MPa,  $-267.85^\circ\text{C}$ , and 0.01444 m³/kg. The critical properties for various substances are given in Table A–1 in the appendix.

At pressures above the critical pressure, there is not a distinct phase-change process (Fig. 3–17). Instead, the specific volume of the substance continually increases, and at all times there is only one phase present. Eventually, it resembles a vapor, but we can never tell when the change



**FIGURE 3–17**

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

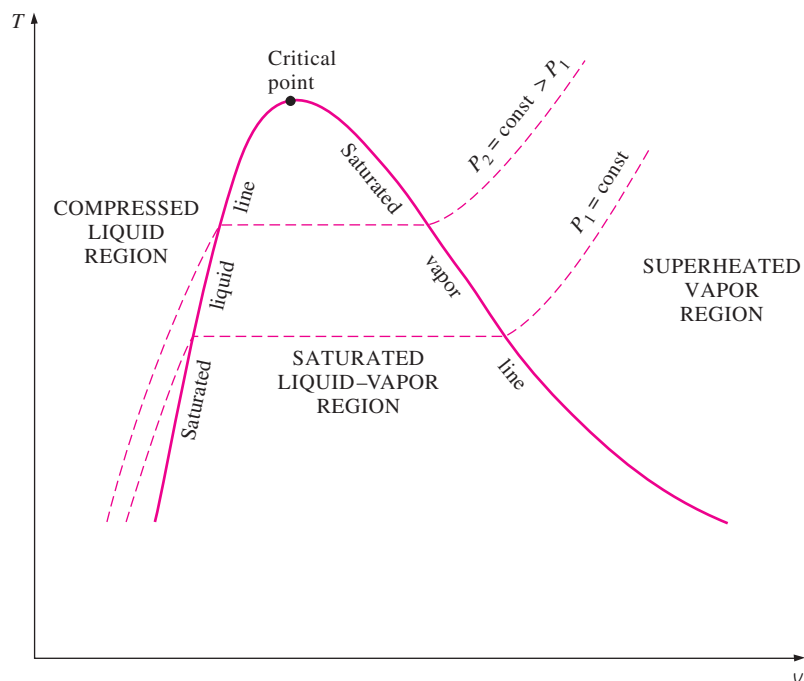
has occurred. Above the critical state, there is no line that separates the compressed liquid region and the superheated vapor region. However, it is customary to refer to the substance as superheated vapor at temperatures above the critical temperature and as compressed liquid at temperatures below the critical temperature.

The saturated liquid states in Fig. 3–16 can be connected by a line called the **saturated liquid line**, and saturated vapor states in the same figure can be connected by another line, called the **saturated vapor line**. These two lines meet at the critical point, forming a dome as shown in Fig. 3–18. All the compressed liquid states are located in the region to the left of the saturated liquid line, called the **compressed liquid region**. All the superheated vapor states are located to the right of the saturated vapor line, called the **superheated vapor region**. In these two regions, the substance exists in a single phase, a liquid or a vapor. All the states that involve both phases in equilibrium are located under the dome, called the **saturated liquid–vapor mixture region**, or the **wet region**.

## 2 The $P$ - $v$ Diagram

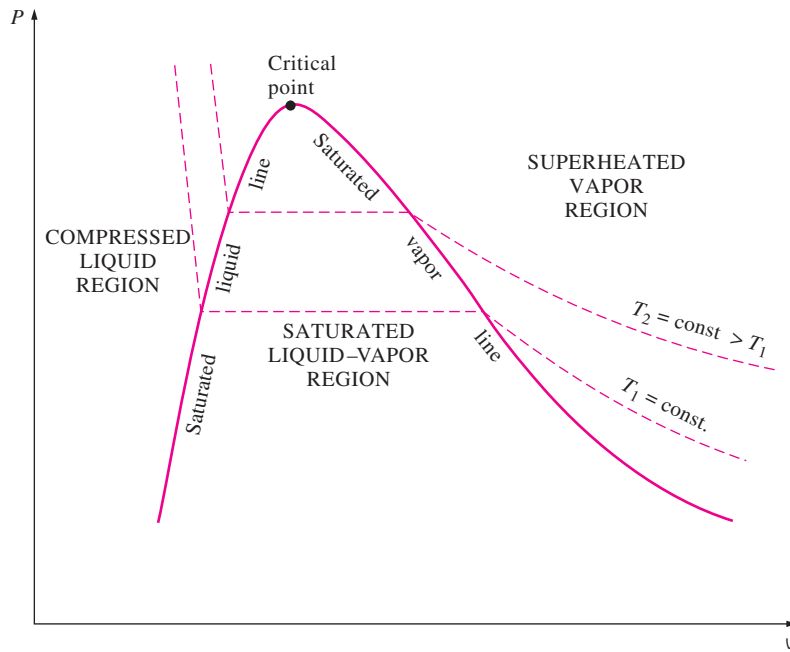
The general shape of the  $P$ - $v$  diagram of a pure substance is very much like the  $T$ - $v$  diagram, but the  $T = \text{constant}$  lines on this diagram have a downward trend, as shown in Fig. 3–19.

Consider again a piston–cylinder device that contains liquid water at 1 MPa and 150°C. Water at this state exists as a compressed liquid. Now the weights on top of the piston are removed one by one so that the pressure inside the cylinder decreases gradually (Fig. 3–20). The water is allowed to exchange heat with the surroundings so its temperature remains constant. As



**FIGURE 3–18**

$T$ - $v$  diagram of a pure substance.



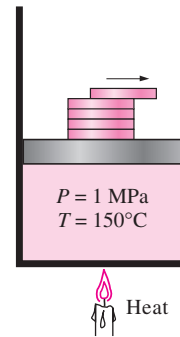
**FIGURE 3-19**  
P-v diagram of a pure substance.

the pressure decreases, the volume of the water increases slightly. When the pressure reaches the saturation-pressure value at the specified temperature (0.4762 MPa), the water starts to boil. During this vaporization process, both the temperature and the pressure remain constant, but the specific volume increases. Once the last drop of liquid is vaporized, further reduction in pressure results in a further increase in specific volume. Notice that during the phase-change process, we did not remove any weights. Doing so would cause the pressure and therefore the temperature to drop [since  $T_{\text{sat}} = f(P_{\text{sat}})$ ], and the process would no longer be isothermal.

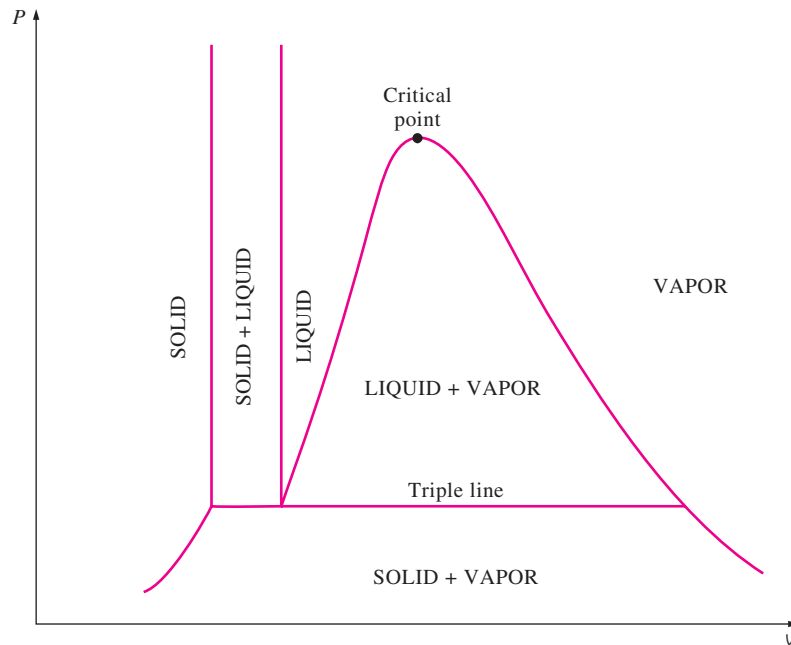
When the process is repeated for other temperatures, similar paths are obtained for the phase-change processes. Connecting the saturated liquid and the saturated vapor states by a curve, we obtain the P-v diagram of a pure substance, as shown in Fig. 3-19.

### Extending the Diagrams to Include the Solid Phase

The two equilibrium diagrams developed so far represent the equilibrium states involving the liquid and the vapor phases only. However, these diagrams can easily be extended to include the solid phase as well as the solid-liquid and the solid-vapor saturation regions. The basic principles discussed in conjunction with the liquid-vapor phase-change process apply equally to the solid-liquid and solid-vapor phase-change processes. Most substances contract during a solidification (i.e., freezing) process. Others, like water, expand as they freeze. The P-v diagrams for both groups of substances are given in Figs. 3-21 and 3-22. These two diagrams differ only in

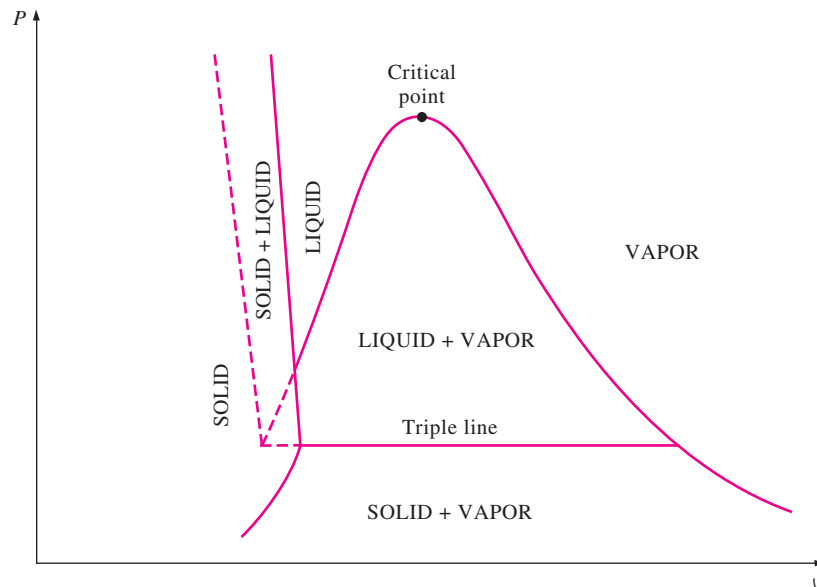


**FIGURE 3-20**  
The pressure in a piston-cylinder device can be reduced by reducing the weight of the piston.



**FIGURE 3-21**

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



**FIGURE 3-22**

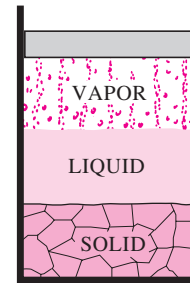
$P$ - $v$  diagram of a substance that expands on freezing (such as water).

the solid–liquid saturation region. The  $T$ - $v$  diagrams look very much like the  $P$ - $v$  diagrams, especially for substances that contract on freezing.

The fact that water expands upon freezing has vital consequences in nature. If water contracted on freezing as most other substances do, the ice formed would be heavier than the liquid water, and it would settle to the bottom of rivers, lakes, and oceans instead of floating at the top. The sun’s

rays would never reach these ice layers, and the bottoms of many rivers, lakes, and oceans would be covered with ice at times, seriously disrupting marine life.

We are all familiar with two phases being in equilibrium, but under some conditions all three phases of a pure substance coexist in equilibrium (Fig. 3–23). On  $P$ - $v$  or  $T$ - $v$  diagrams, these triple-phase states form a line called the **triple line**. The states on the triple line of a substance have the same pressure and temperature but different specific volumes. The triple line appears as a point on the  $P$ - $T$  diagrams and, therefore, is often called the **triple point**. The triple-point temperatures and pressures of various substances are given in Table 3–3. For water, the triple-point temperature and pressure are  $0.01^\circ\text{C}$  and  $0.6117\text{ kPa}$ , respectively. That is, all three phases of water coexist in equilibrium only if the temperature and pressure have precisely these values. No substance can exist in the liquid phase in stable equilibrium at pressures below the triple-point pressure. The same can be said for temperature for substances that contract on freezing. However,



**FIGURE 3–23**

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

**TABLE 3–3**

Triple-point temperatures and pressures of various substances

Substance	Formula	$T_{tp}$ , K	$P_{tp}$ , kPa
Acetylene	$\text{C}_2\text{H}_2$	192.4	120
Ammonia	$\text{NH}_3$	195.40	6.076
Argon	A	83.81	68.9
Carbon (graphite)	C	3900	10,100
Carbon dioxide	$\text{CO}_2$	216.55	517
Carbon monoxide	CO	68.10	15.37
Deuterium	$\text{D}_2$	18.63	17.1
Ethane	$\text{C}_2\text{H}_6$	89.89	$8 \times 10^{-4}$
Ethylene	$\text{C}_2\text{H}_4$	104.0	0.12
Helium 4 ( $\lambda$ point)	He	2.19	5.1
Hydrogen	$\text{H}_2$	13.84	7.04
Hydrogen chloride	HCl	158.96	13.9
Mercury	Hg	234.2	$1.65 \times 10^{-7}$
Methane	$\text{CH}_4$	90.68	11.7
Neon	Ne	24.57	43.2
Nitric oxide	NO	109.50	21.92
Nitrogen	$\text{N}_2$	63.18	12.6
Nitrous oxide	$\text{N}_2\text{O}$	182.34	87.85
Oxygen	$\text{O}_2$	54.36	0.152
Palladium	Pd	1825	$3.5 \times 10^{-3}$
Platinum	Pt	2045	$2.0 \times 10^{-4}$
Sulfur dioxide	$\text{SO}_2$	197.69	1.67
Titanium	Ti	1941	$5.3 \times 10^{-3}$
Uranium hexafluoride	$\text{UF}_6$	337.17	151.7
Water	$\text{H}_2\text{O}$	273.16	0.61
Xenon	Xe	161.3	81.5
Zinc	Zn	692.65	0.065

Source: Data from National Bureau of Standards (U.S.) Circ., 500 (1952).



**FIGURE 3–24**

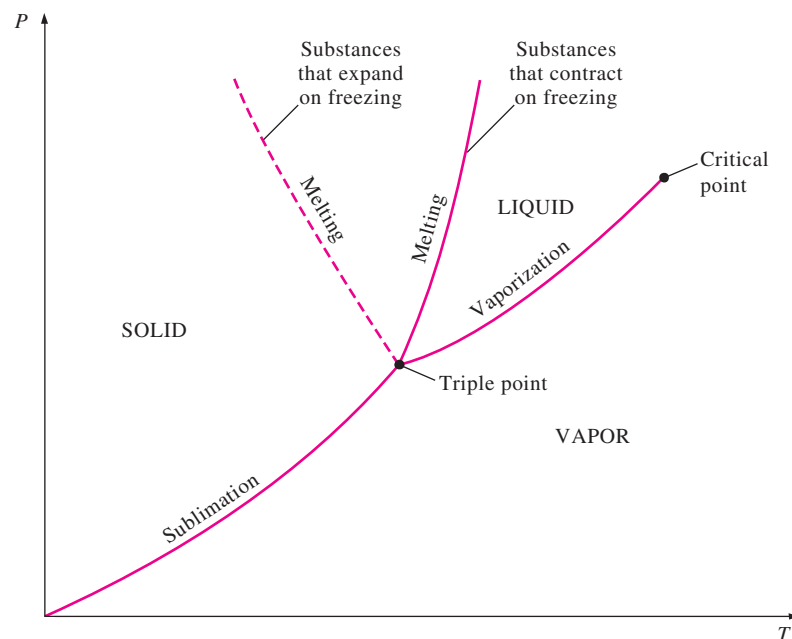
At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).

substances at high pressures can exist in the liquid phase at temperatures below the triple-point temperature. For example, water cannot exist in liquid form in equilibrium at atmospheric pressure at temperatures below 0°C, but it can exist as a liquid at –20°C at 200 MPa pressure. Also, ice exists at seven different solid phases at pressures above 100 MPa.

There are two ways a substance can pass from the solid to vapor phase: either it melts first into a liquid and subsequently evaporates, or it evaporates directly without melting first. The latter occurs at pressures below the triple-point value, since a pure substance cannot exist in the liquid phase at those pressures (Fig. 3–24). Passing from the solid phase directly into the vapor phase is called **sublimation**. For substances that have a triple-point pressure above the atmospheric pressure such as solid CO<sub>2</sub> (dry ice), sublimation is the only way to change from the solid to vapor phase at atmospheric conditions.

### 3 The *P-T* Diagram

Figure 3–25 shows the *P-T* diagram of a pure substance. This diagram is often called the **phase diagram** since all three phases are separated from each other by three lines. The sublimation line separates the solid and vapor regions, the vaporization line separates the liquid and vapor regions, and the melting (or fusion) line separates the solid and liquid regions. These three lines meet at the triple point, where all three phases coexist in equilibrium. The vaporization line ends at the critical point because no distinction can be made between liquid and vapor phases above the critical point. Substances that expand and contract on freezing differ only in the melting line on the *P-T* diagram.

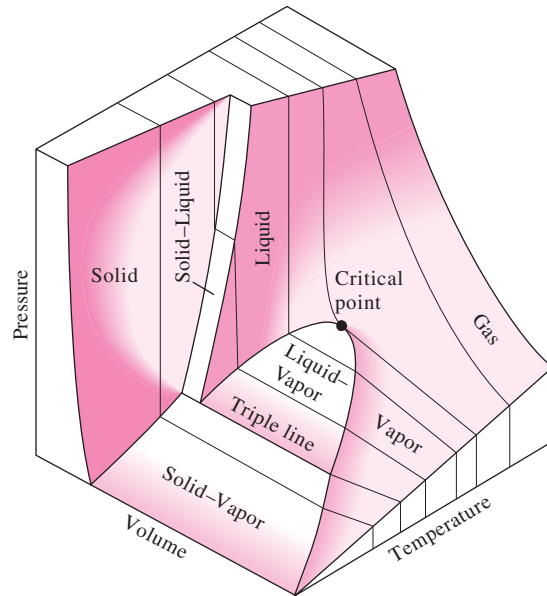


**FIGURE 3–25**

*P-T* diagram of pure substances.

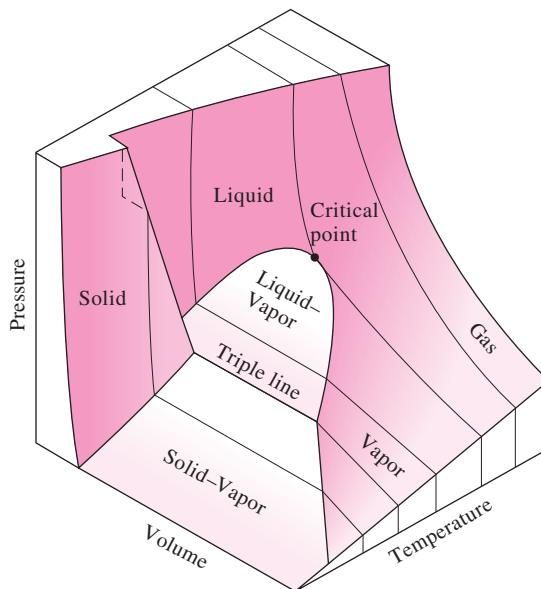
## The $P$ - $v$ - $T$ Surface

The state of a simple compressible substance is fixed by any two independent, intensive properties. Once the two appropriate properties are fixed, all the other properties become dependent properties. Remembering that any equation with two independent variables in the form  $z = z(x, y)$  represents a surface in space, we can represent the  $P$ - $v$ - $T$  behavior of a substance as a surface in space, as shown in Figs. 3–26 and 3–27. Here  $T$  and  $v$  may be



**FIGURE 3–26**

$P$ - $v$ - $T$  surface of a substance that contracts on freezing.



**FIGURE 3–27**

$P$ - $v$ - $T$  surface of a substance that expands on freezing (like water).

viewed as the independent variables (the base) and  $P$  as the dependent variable (the height).

All the points on the surface represent equilibrium states. All states along the path of a quasi-equilibrium process lie on the  $P$ - $v$ - $T$  surface since such a process must pass through equilibrium states. The single-phase regions appear as curved surfaces on the  $P$ - $v$ - $T$  surface, and the two-phase regions as surfaces perpendicular to the  $P$ - $T$  plane. This is expected since the projections of two-phase regions on the  $P$ - $T$  plane are lines.

All the two-dimensional diagrams we have discussed so far are merely projections of this three-dimensional surface onto the appropriate planes. A  $P$ - $v$  diagram is just a projection of the  $P$ - $v$ - $T$  surface on the  $P$ - $v$  plane, and a  $T$ - $v$  diagram is nothing more than the bird's-eye view of this surface. 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.

### 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. In the following discussion, the steam tables are used to demonstrate the use of thermodynamic property tables. Property tables of other substances are used in the same manner.

For each substance, the thermodynamic properties are listed in more than one table. In fact, a separate table is prepared for each region of interest such as the superheated vapor, compressed liquid, and saturated (mixture) regions. Property tables are given in the appendix in both SI and English units. The tables in English units carry the same number as the corresponding tables in SI, followed by an identifier E. Tables A-6 and A-6E, for example, list properties of superheated water vapor, the former in SI and the latter in English units. Before we get into the discussion of property tables, we define a new property called *enthalpy*.

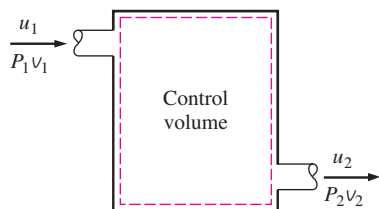


FIGURE 3-28

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

### Enthalpy—A Combination Property

A person looking at the tables will notice two new properties: enthalpy  $h$  and entropy  $s$ . Entropy is a property associated with the second law of thermodynamics, and we will not use it until it is properly defined in Chap. 7. However, it is appropriate to introduce enthalpy at this point.

In the analysis of certain types of processes, particularly in power generation and refrigeration (Fig. 3-28), we frequently encounter the combination of properties  $u + Pv$ . For the sake of simplicity and convenience, this combination is defined as a new property, **enthalpy**, and given the symbol  $h$ :

$$h = u + Pv \quad (\text{kJ/kg}) \quad (3-1)$$



or,

$$H = U + PV \quad (\text{kJ}) \quad (3-2)$$

Both the total enthalpy  $H$  and specific enthalpy  $h$  are simply referred to as enthalpy since the context clarifies which one is meant. Notice that the equations given above are dimensionally homogeneous. That is, the unit of the pressure–volume product may differ from the unit of the internal energy by only a factor (Fig. 3–29). For example, it can be easily shown that  $1 \text{ kPa} \cdot \text{m}^3 = 1 \text{ kJ}$ . In some tables encountered in practice, the internal energy  $u$  is frequently not listed, but it can always be determined from  $u = h - Pv$ .

The widespread use of the property enthalpy is due to Professor Richard Mollier, who recognized the importance of the group  $u + Pv$  in the analysis of steam turbines and in the representation of the properties of steam in tabular and graphical form (as in the famous Mollier chart). Mollier referred to the group  $u + Pv$  as *heat content* and *total heat*. These terms were not quite consistent with the modern thermodynamic terminology and were replaced in the 1930s by the term *enthalpy* (from the Greek word *enthalpien*, which means *to heat*).

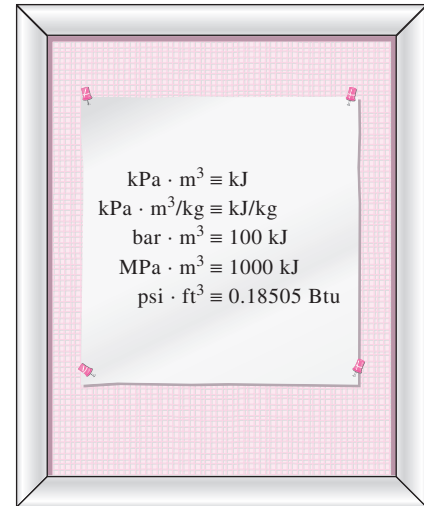


FIGURE 3–29

The product  $\text{pressure} \times \text{volume}$  has energy units.

## 1a Saturated Liquid and Saturated Vapor States

The properties of saturated liquid and saturated vapor for water are listed in Tables A–4 and A–5. Both tables give the same information. The only difference is that in Table A–4 properties are listed under temperature and in Table A–5 under pressure. Therefore, it is more convenient to use Table A–4 when *temperature* is given and Table A–5 when *pressure* is given. The use of Table A–4 is illustrated in Fig. 3–30.

The subscript  $f$  is used to denote properties of a saturated liquid, and the subscript  $g$  to denote the properties of saturated vapor. These symbols are commonly used in thermodynamics and originated from German. Another subscript commonly used is  $fg$ , which denotes the difference between the saturated vapor and saturated liquid values of the same property. For example,

$v_f$  = specific volume of saturated liquid

$v_g$  = specific volume of saturated vapor

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

The quantity  $h_{fg}$  is called the **enthalpy of vaporization** (or latent heat of vaporization). 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.

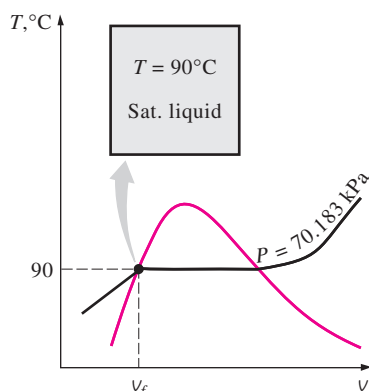
Temp. °C $T$	Sat. press. kPa $P_{\text{sat}}$	Specific volume $\text{m}^3/\text{kg}$	
		Sat. liquid $v_f$	Sat. vapor $v_g$
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

Annotations below the table:

- Arrows point from the labels "Specific temperature", "Corresponding saturation pressure", "Specific volume of saturated liquid", and "Specific volume of saturated vapor" to their respective values in the table.

FIGURE 3–30

A partial list of Table A–4.



**FIGURE 3-31**  
Schematic and  $T$ - $v$  diagram for Example 3-1.

**EXAMPLE 3-1 Pressure of Saturated Liquid in a Tank**

A rigid tank contains 50 kg of saturated liquid water at 90°C. Determine the pressure in the tank and the volume of the tank.

**Solution** A rigid tank contains saturated liquid water. The pressure and volume of the tank are to be determined.

**Analysis** The state of the saturated liquid water is shown on a  $T$ - $v$  diagram in Fig. 3-31. Since saturation conditions exist in the tank, the pressure must be the saturation pressure at 90°C:

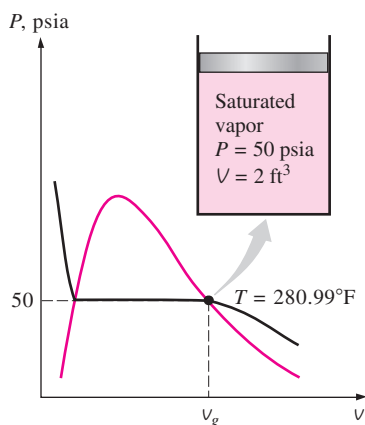
$$P = P_{\text{sat @ } 90^\circ\text{C}} = \mathbf{70.183 \text{ kPa}} \quad (\text{Table A-4})$$

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

$$v = v_f @ 90^\circ\text{C} = 0.001036 \text{ m}^3/\text{kg} \quad (\text{Table A-4})$$

Then the total volume of the tank becomes

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



**FIGURE 3-32**  
Schematic and  $P$ - $v$  diagram for Example 3-2.

**EXAMPLE 3-2 Temperature of Saturated Vapor in a Cylinder**

A piston-cylinder device contains 2 ft<sup>3</sup> of saturated water vapor at 50-psia pressure. Determine the temperature and the mass of the vapor inside the cylinder.

**Solution** A cylinder contains saturated water vapor. The temperature and the mass of vapor are to be determined.

**Analysis** The state of the saturated water vapor is shown on a  $P$ - $v$  diagram in Fig. 3-32. Since the cylinder contains saturated vapor at 50 psia, the temperature inside must be the saturation temperature at this pressure:

$$T = T_{\text{sat @ } 50 \text{ psia}} = \mathbf{280.99^\circ\text{F}} \quad (\text{Table A-5E})$$

The specific volume of the saturated vapor at 50 psia is

$$v = v_g @ 50 \text{ psia} = 8.5175 \text{ ft}^3/\text{lbm} \quad (\text{Table A-5E})$$

Then the mass of water vapor inside the cylinder becomes

$$m = \frac{V}{v} = \frac{2 \text{ ft}^3}{8.5175 \text{ ft}^3/\text{lbm}} = \mathbf{0.235 \text{ lbm}}$$

**EXAMPLE 3-3 Volume and Energy Change during Evaporation**

A mass of 200 g of saturated liquid water is completely vaporized at a constant pressure of 100 kPa. Determine (a) the volume change and (b) the amount of energy transferred to the water.

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

**Analysis** (a) The process described is illustrated on a  $P$ - $v$  diagram in Fig. 3-33. The volume change per unit mass during a vaporization process is  $v_{fg}$ , which

is the difference between  $v_g$  and  $v_f$ . Reading these values from Table A-5 at 100 kPa and substituting yield

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

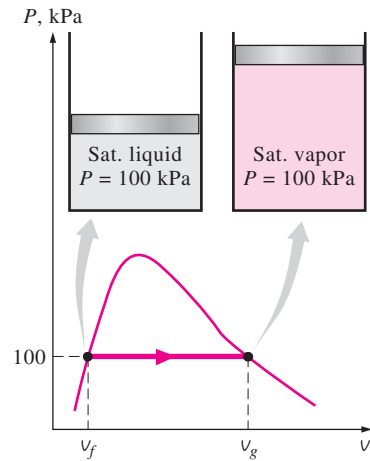
Thus,

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

(b) The amount of energy needed to vaporize a unit mass of a substance at a given pressure is the enthalpy of vaporization at that pressure, which is  $h_{fg} = 2257.5 \text{ kJ/kg}$  for water at 100 kPa. Thus, the amount of energy transferred is

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

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



**FIGURE 3-33**  
Schematic and  $P$ - $v$  diagram for Example 3-3.

## 1b Saturated Liquid–Vapor Mixture

During a vaporization process, a substance exists as part liquid and part vapor. That is, it is a mixture of saturated liquid and saturated vapor (Fig. 3-34). To analyze this mixture properly, we need to know the proportions of the liquid and vapor phases in the mixture. This is done by defining a new property called the **quality**  $x$  as the ratio of the mass of vapor to the total mass of the mixture:

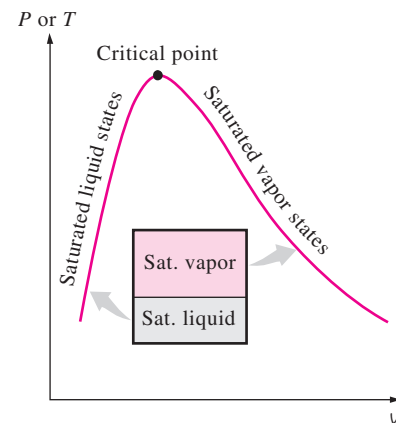
$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}} \quad (3-3)$$

where

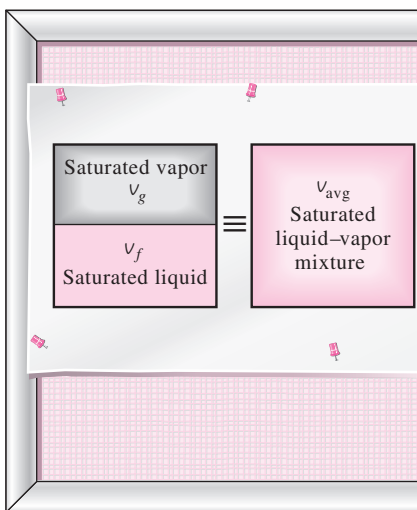
$$m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$

Quality has significance for *saturated mixtures* only. It has no meaning in the compressed liquid or superheated vapor regions. Its value is between 0 and 1. The quality of a system that consists of *saturated liquid* is 0 (or 0 percent), and the quality of a system consisting of *saturated vapor* is 1 (or 100 percent). In saturated mixtures, quality can serve as one of the two independent intensive properties needed to describe a state. Note that *the properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapor*. During the vaporization process, only the amount of saturated liquid changes, not its properties. The same can be said about a saturated vapor.

A saturated mixture can be treated as a combination of two subsystems: the saturated liquid and the saturated vapor. However, the amount of mass for each phase is usually not known. Therefore, it is often more convenient

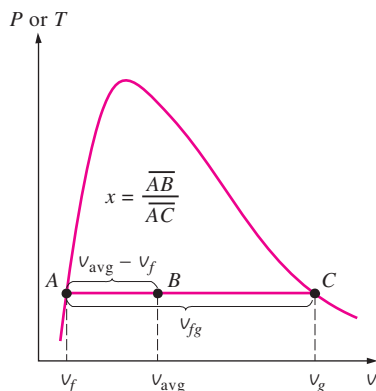


**FIGURE 3-34**  
The relative amounts of liquid and vapor phases in a saturated mixture are specified by the *quality*  $x$ .



**FIGURE 3-35**

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



**FIGURE 3-36**

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

to imagine that the two phases are mixed well, forming a homogeneous mixture (Fig. 3–35). Then the properties of this “mixture” will simply be the average properties of the saturated liquid–vapor mixture under consideration. Here is how it is done.

Consider a tank that contains a saturated liquid–vapor mixture. The volume occupied by saturated liquid is  $V_f$ , and the volume occupied by saturated vapor is  $V_g$ . The total volume  $V$  is the sum of the two:

$$V = V_f + V_g$$

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

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

Dividing by  $m_t$  yields

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

since  $x = m_g/m_t$ . This relation can also be expressed as

$$v_{\text{avg}} = v_f + x v_{fg} \quad (\text{m}^3/\text{kg}) \quad (3-4)$$

where  $v_{fg} = v_g - v_f$ . Solving for quality, we obtain

$$x = \frac{v_{\text{avg}} - v_f}{v_{fg}} \quad (3-5)$$

Based on this equation, quality can be related to the horizontal distances on a  $P$ - $v$  or  $T$ - $v$  diagram (Fig. 3–36). At a given temperature or pressure, the numerator of Eq. 3–5 is the distance between the actual state and the saturated liquid state, and the denominator is the length of the entire horizontal line that connects the saturated liquid and saturated vapor states. A state of 50 percent quality lies in the middle of this horizontal line.

The analysis given above can be repeated for internal energy and enthalpy with the following results:

$$u_{\text{avg}} = u_f + x u_{fg} \quad (\text{kJ}/\text{kg}) \quad (3-6)$$

$$h_{\text{avg}} = h_f + x h_{fg} \quad (\text{kJ}/\text{kg}) \quad (3-7)$$

All the results are of the same format, and they can be summarized in a single equation as

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

where  $y$  is  $v$ ,  $u$ , or  $h$ . The subscript “avg” (for “average”) is usually dropped for simplicity. The values of the average properties of the mixtures are always *between* the values of the saturated liquid and the saturated vapor properties (Fig. 3–37). That is,

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

Finally, all the saturated-mixture states are located under the saturation curve, and to analyze saturated mixtures, all we need are saturated liquid and saturated vapor data (Tables A–4 and A–5 in the case of water).

**EXAMPLE 3-4 Pressure and Volume of a Saturated Mixture**

A rigid tank contains 10 kg of water at 90°C. If 8 kg of the water is in the liquid form and the rest is in the vapor form, determine (a) the pressure in the tank and (b) the volume of the tank.

**Solution** A rigid tank contains saturated mixture. The pressure and the volume of the tank are to be determined.

**Analysis** (a) The state of the saturated liquid–vapor mixture is shown in Fig. 3–38. Since the two phases coexist in equilibrium, we have a saturated mixture, and the pressure must be the saturation pressure at the given temperature:

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

(b) At 90°C, we have  $v_f = 0.001036 \text{ m}^3/\text{kg}$  and  $v_g = 2.3593 \text{ m}^3/\text{kg}$  (Table A-4). One way of finding the volume of the tank is to determine the volume occupied by each phase and then add them:

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

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

$$\begin{aligned} x &= \frac{m_g}{m_t} = \frac{2 \text{ kg}}{10 \text{ kg}} = 0.2 \\ v &= v_f + x v_{fg} \\ &= 0.001036 \text{ m}^3/\text{kg} + (0.2)[(2.3593 - 0.001036) \text{ m}^3/\text{kg}] \\ &= 0.473 \text{ m}^3/\text{kg} \end{aligned}$$

and

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

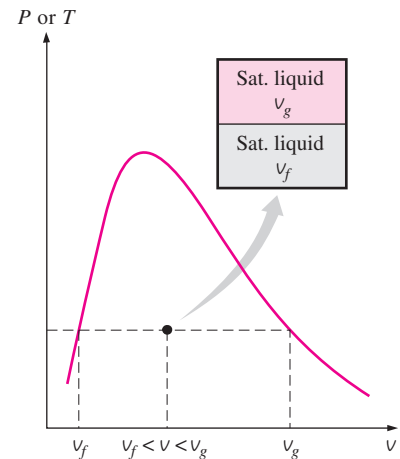
**Discussion** The first method appears to be easier in this case since the masses of each phase are given. In most cases, however, the masses of each phase are not available, and the second method becomes more convenient.

**EXAMPLE 3-5 Properties of Saturated Liquid–Vapor Mixture**

An 80-L vessel contains 4 kg of refrigerant-134a at a pressure of 160 kPa. Determine (a) the temperature, (b) the quality, (c) the enthalpy of the refrigerant, and (d) the volume occupied by the vapor phase.

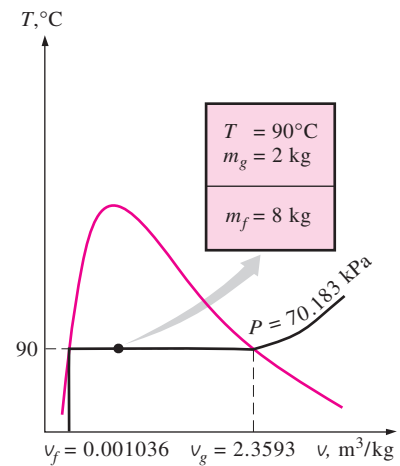
**Solution** A vessel is filled with refrigerant-134a. Some properties of the refrigerant are to be determined.

**Analysis** (a) The state of the saturated liquid–vapor mixture is shown in Fig. 3–39. At this point we do not know whether the refrigerant is in the compressed liquid, superheated vapor, or saturated mixture region. This can



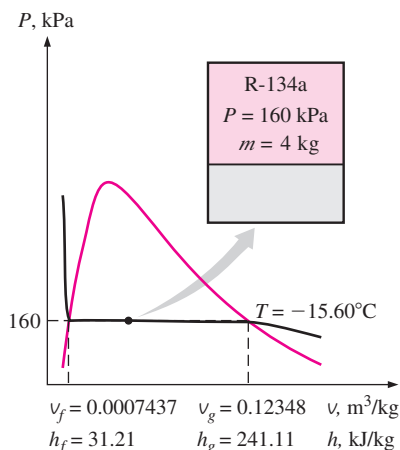
**FIGURE 3-37**

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



**FIGURE 3-38**

Schematic and  $T$ - $v$  diagram for Example 3–4.



**FIGURE 3-39**  
Schematic and  $P$ - $v$  diagram for Example 3-5.

be determined by comparing a suitable property to the saturated liquid and saturated vapor values. From the information given, we can determine the specific volume:

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

At 160 kPa, we read

$$\begin{aligned} v_f &= 0.0007437 \text{ m}^3/\text{kg} \\ v_g &= 0.12348 \text{ m}^3/\text{kg} \end{aligned} \quad (\text{Table A-12})$$

Obviously,  $v_f < v < v_g$ , and, the refrigerant is in the saturated mixture region. Thus, the temperature must be the saturation temperature at the specified pressure:

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

(b) Quality can be determined from

$$x = \frac{v - v_f}{v_{fg}} = \frac{0.02 - 0.0007437}{0.12348 - 0.0007437} = 0.157$$

(c) At 160 kPa, we also read from Table A-12 that  $h_f = 31.21 \text{ kJ/kg}$  and  $h_{fg} = 209.90 \text{ kJ/kg}$ . Then,

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

(d) The mass of the vapor is

$$m_g = xm_t = (0.157)(4 \text{ kg}) = 0.628 \text{ kg}$$

and the volume occupied by the vapor phase is

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

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

$T, ^\circ\text{C}$	$v$	$u$	$h$
	$\text{m}^3/\text{kg}$	$\text{kJ/kg}$	$\text{kJ/kg}$
$P = 0.1 \text{ MPa (99.61}^\circ\text{C)}$			
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

**FIGURE 3-40**  
A partial listing of Table A-6.

Property tables are also available for saturated solid–vapor mixtures. Properties of saturated ice–water vapor mixtures, for example, are listed in Table A-8. Saturated solid–vapor mixtures can be handled just as saturated liquid–vapor mixtures.

## 2 Superheated Vapor

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. Since the superheated region is a single-phase region (vapor phase only), temperature and pressure are no longer dependent properties and they can conveniently be used as the two independent properties in the tables. The format of the superheated vapor tables is illustrated in Fig. 3-40.

In these tables, the properties are listed against temperature for selected pressures starting with the saturated vapor data. The saturation temperature is given in parentheses following the pressure value.

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 ( $v > v_g$  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  $T$ )

**EXAMPLE 3-6 Internal Energy of Superheated Vapor**

Determine the internal energy of water at 20 psia and 400°F.

**Solution** The internal energy of water at a specified state is to be determined.

**Analysis** At 20 psia, the saturation temperature is 227.92°F. Since  $T > T_{\text{sat}}$ , 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 (Table A-6E) to be

$$u = 1145.1 \text{ Btu/lbm}$$

**EXAMPLE 3-7 Temperature of Superheated Vapor**

Determine the temperature of water at a state of  $P = 0.5 \text{ MPa}$  and  $h = 2890 \text{ kJ/kg}$ .

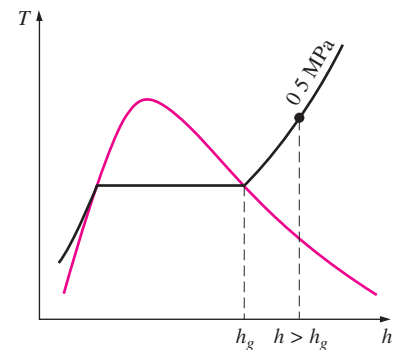
**Solution** The temperature of water at a specified state is to be determined.

**Analysis** At 0.5 MPa, the enthalpy of saturated water vapor is  $h_g = 2748.1 \text{ kJ/kg}$ . Since  $h > h_g$ , as shown in Fig. 3-41, we again have superheated vapor. Under 0.5 MPa in Table A-6 we read

$T, ^\circ\text{C}$	$h, \text{kJ/kg}$
200	2855.8
250	2961.0

Obviously, the temperature is between 200 and 250°C. By linear interpolation it is determined to be

$$T = 216.3^\circ\text{C}$$

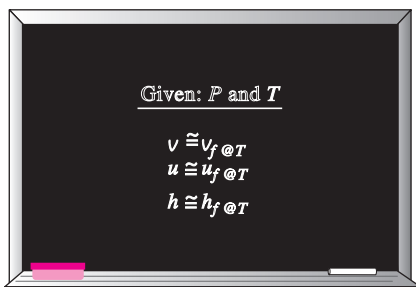


**FIGURE 3-41**

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

### 3 Compressed Liquid

Compressed liquid tables are not as commonly available, and Table A-7 is the only compressed liquid table in this text. The format of Table A-7 is very much like the format of the superheated vapor tables. One reason for the lack of compressed liquid data is the relative independence of compressed liquid properties from pressure. Variation of properties of compressed liquid with pressure is very mild. Increasing the pressure 100 times often causes properties to change less than 1 percent.



**FIGURE 3–42**

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

In the absence of compressed liquid data, a general approximation is to treat compressed liquid as saturated liquid at the given temperature (Fig. 3–42). This is because the compressed liquid properties depend on temperature much more strongly than they do on pressure. Thus,

$$y \cong y_{f@T} \quad (3-8)$$

for compressed liquids, where  $y$  is  $v$ ,  $u$ , or  $h$ . Of these three properties, the property whose value is most sensitive to variations in the pressure is the enthalpy  $h$ . Although the above approximation results in negligible error in  $v$  and  $u$ , the error in  $h$  may reach undesirable levels. However, the error in  $h$  at low to moderate pressures and temperatures can be reduced significantly by evaluating it from

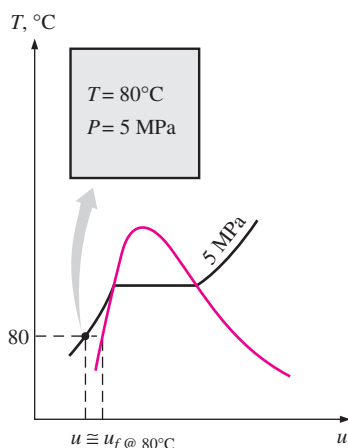
$$h \cong h_{f@T} + v_{f@T}(P - P_{\text{sat}@T}) \quad (3-9)$$

instead of taking it to be just  $h_f$ . Note, however, that the approximation in Eq. 3–9 does not yield any significant improvement at moderate to high temperatures and pressures, and it may even backfire and result in greater error due to overcorrection at very high temperatures and pressures (see Kostic, Ref. 4).

In general, a 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  $T$ )

But unlike superheated vapor, the compressed liquid properties are not much different from the corresponding saturated liquid values.



**FIGURE 3–43**

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

**EXAMPLE 3–8 Approximating Compressed Liquid as Saturated Liquid**

Determine the internal energy of compressed liquid water at 80°C and 5 MPa, using (a) data from the compressed liquid table and (b) saturated liquid data. What is the error involved in the second case?

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

**Analysis** At 80°C, the saturation pressure of water is 47.416 kPa, and since 5 MPa >  $P_{\text{sat}}$ , we obviously have compressed liquid, as shown in Fig. 3–43.

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

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

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

$$u \cong u_{f@80^\circ\text{C}} = 334.97 \text{ kJ/kg}$$

The error involved is

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

which is less than 1 percent.



## 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 thermodynamic 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. For water, the state of saturated liquid at  $0.01^\circ\text{C}$  is taken as the reference state, and the internal energy and entropy are assigned zero values at that state. For refrigerant-134a, the state of saturated liquid at  $-40^\circ\text{C}$  is taken as the reference state, and the enthalpy and entropy are assigned zero values at that state. Note that some properties may have negative values as a result of the reference state chosen.

It should be mentioned that 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 as long as we use values from a single consistent set of tables or charts.

### EXAMPLE 3–9 The Use of Steam Tables to Determine Properties

Determine the missing properties and the phase descriptions in the following table for water:

	$T$ , $^\circ\text{C}$	$P$ , kPa	$u$ , kJ/kg	$x$	Phase description
(a)		200		0.6	
(b)	125		1600		
(c)		1000	2950		
(d)	75	500			
(e)		850		0.0	

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

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

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

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

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

(b) This time the temperature and the internal energy are given, but we do not know which table to use to determine the missing properties because we have no clue as to whether we have saturated mixture, compressed liquid, or superheated vapor. To determine the region we are in, we first go to the

saturation table (Table A-4) and determine the  $u_f$  and  $u_g$  values at the given temperature. At  $125^\circ\text{C}$ , we read  $u_f = 524.83 \text{ kJ/kg}$  and  $u_g = 2534.3 \text{ kJ/kg}$ . Next we 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*

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

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

The quality is determined from

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

The criteria above for determining whether we have compressed liquid, saturated mixture, or superheated vapor can also be used when enthalpy  $h$  or specific volume  $v$  is given instead of internal energy  $u$ , or when pressure is given instead of temperature.

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

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

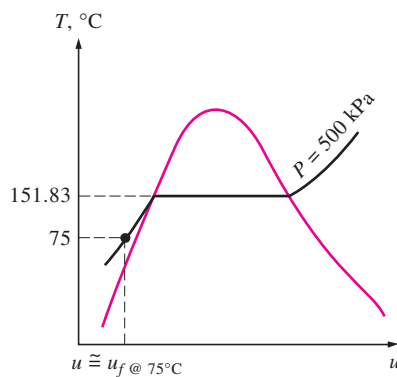
We would leave the quality column blank in this case since quality has no meaning for a superheated vapor.

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

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

In our case, the given  $T$  value is  $75^\circ\text{C}$ , which is less than the  $T_{\text{sat}}$  value at the specified pressure. Therefore, we have compressed liquid (Fig. 3-44), and normally we would determine the internal energy value from the compressed liquid table. But in this case the given pressure is much lower than the lowest pressure value in the compressed liquid table (which is 5 MPa), and therefore we are justified to treat the compressed liquid as saturated liquid at the given temperature (*not* pressure):

$$u \cong u_f@75^\circ\text{C} = \mathbf{313.99 \text{ kJ/kg}} \quad (\text{Table A-4})$$



**FIGURE 3-44**

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

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

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

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

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

### 3-6 ■ THE IDEAL-GAS EQUATION OF STATE

Property tables provide very accurate information about the properties, but they are bulky and vulnerable to typographical errors. A more practical and desirable approach would be to have some simple relations among the properties that are sufficiently general and accurate.

Any equation that relates the pressure, temperature, and specific volume of a substance is called an **equation of state**. Property relations that involve other properties of a substance at equilibrium states are also referred to as equations of state. There are several equations of state, some simple and others very complex. 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.

*Gas* and *vapor* are often used as synonymous words. The vapor phase of a substance is customarily called a *gas* when it is above the critical temperature. *Vapor* usually implies a gas that is not far from a state of condensation.

In 1662, Robert Boyle, an Englishman, observed during his experiments with a vacuum chamber that the pressure of gases is inversely proportional to their volume. In 1802, J. Charles and J. Gay-Lussac, Frenchmen, experimentally determined that at low pressures the volume of a gas is proportional to its temperature. That is,

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

or

$$Pv = RT \quad (3-10)$$

where the constant of proportionality  $R$  is called the **gas constant**. Equation 3-10 is called the **ideal-gas equation of state**, or simply the **ideal-gas relation**, and a gas that obeys this relation is called an **ideal gas**. In this equation,  $P$  is the absolute pressure,  $T$  is the absolute temperature, and  $v$  is the specific volume.

The gas constant  $R$  is different for each gas (Fig. 3-45) and is determined from

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

where  $R_u$  is the **universal gas constant** and  $M$  is the molar mass (also

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

FIGURE 3-45

Different substances have different gas constants.

called *molecular weight*) of the gas. The constant  $R_u$  is the same for all substances, and its value is

$$R_u = \begin{cases} 8.31447 \text{ kJ/kmol} \cdot \text{K} \\ 8.31447 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\ 0.0831447 \text{ bar} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\ 1.98588 \text{ Btu/lbmol} \cdot \text{R} \\ 10.7316 \text{ psia} \cdot \text{ft}^3/\text{lbmol} \cdot \text{R} \\ 1545.37 \text{ ft} \cdot \text{lbf/lbmol} \cdot \text{R} \end{cases} \quad (3-11)$$

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

FIGURE 3-46

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

The **molar mass**  $M$  can simply be defined as *the mass of one mole* (also called a *gram-mole*, abbreviated gmol) *of a substance in grams*, or *the mass of one kmol* (also called a *kilogram-mole*, abbreviated kgmol) *in kilograms*. In English units, it is the mass of 1 lbmol in lbm. Notice that the molar mass of a substance has the same numerical value in both unit systems because of the way it is defined. When we say the molar mass of nitrogen is 28, it simply means the mass of 1 kmol of nitrogen is 28 kg, or the mass of 1 lbmol of nitrogen is 28 lbm. That is,  $M = 28 \text{ kg/kmol} = 28 \text{ lbm/lbmol}$ . The mass of a system is equal to the product of its molar mass  $M$  and the mole number  $N$ :

$$m = MN \quad (\text{kg}) \quad (3-12)$$

The values of  $R$  and  $M$  for several substances are given in Table A-1.

The ideal-gas equation of state can be written in several different forms:

$$V = m v \longrightarrow PV = mRT \quad (3-13)$$

$$mR = (MN)R = NR_u \longrightarrow PV = NR_u T \quad (3-14)$$

$$V = N\bar{v} \longrightarrow P\bar{v} = R_u T \quad (3-15)$$

where  $\bar{v}$  is the molar specific volume, that is, the volume per unit mole (in  $\text{m}^3/\text{kmol}$  or  $\text{ft}^3/\text{lbmol}$ ). A bar above a property denotes values on a *unit-mole basis* throughout this text (Fig. 3-46).

By writing Eq. 3-13 twice for a fixed mass and simplifying, the properties of an ideal gas at two different states are related to each other by

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (3-16)$$

An ideal gas is an *imaginary* substance that obeys the relation  $Pv = RT$  (Fig. 3-47). It has been experimentally observed that the ideal-gas relation given closely approximates the  $P$ - $v$ - $T$  behavior of real gases at low densities. At low pressures and high temperatures, the density of a gas decreases, and the gas behaves as an ideal gas under these conditions. What constitutes low pressure and high temperature is explained later.

In the range of practical interest, many familiar gases such as air, nitrogen, oxygen, hydrogen, helium, argon, neon, krypton, and even heavier gases such as carbon dioxide can be treated as ideal gases with negligible error (often less than 1 percent). Dense gases such as water vapor in steam power plants and refrigerant vapor in refrigerators, however, should not be treated as ideal gases. Instead, the property tables should be used for these substances.

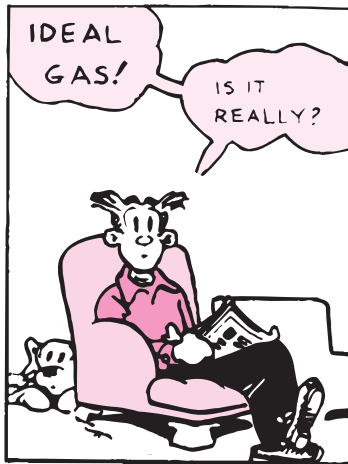


FIGURE 3-47

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

**EXAMPLE 3–10** Mass of Air in a Room

Determine the mass of the air in a room whose dimensions are 4 m × 5 m × 6 m at 100 kPa and 25°C.

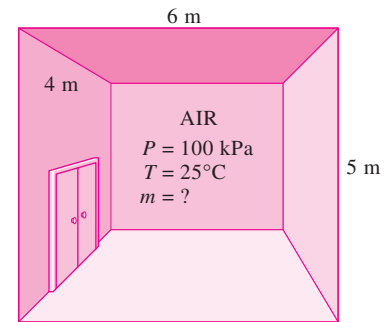
**Solution** The mass of air in a room is to be determined.

**Analysis** A sketch of the room is given in Fig. 3–48. Air at specified conditions can be treated as an ideal gas. From Table A–1, the gas constant of air is  $R = 0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}$ , and the absolute temperature is  $T = 25^\circ\text{C} + 273 = 298 \text{ K}$ . The volume of the room is

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

The mass of air in the room is determined from the ideal-gas relation to be

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

**FIGURE 3–48**

Schematic for Example 3–10.

## Is Water Vapor an Ideal Gas?

This question cannot be answered with a simple yes or no. The error involved in treating water vapor as an ideal gas is calculated and plotted in Fig. 3–49. It is clear from this figure that 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 (over 100 percent). Therefore, in air-conditioning applications, the water vapor in the air can be treated as an ideal gas with essentially no error since the pressure of the water vapor is very low. In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.

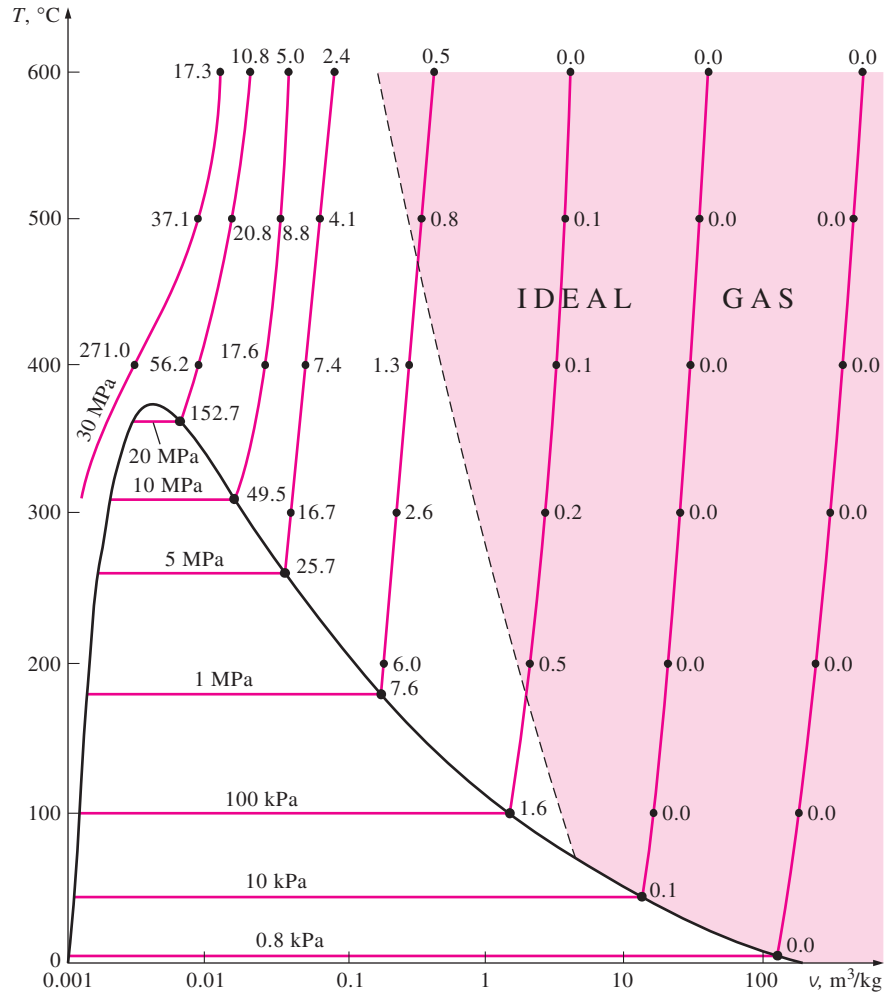
## 3–7 ■ COMPRESSIBILITY FACTOR—A MEASURE OF DEVIATION FROM IDEAL-GAS BEHAVIOR

The ideal-gas equation is very simple and thus very convenient to use. However, as illustrated in Fig. 3–49, gases deviate from ideal-gas behavior significantly at states near the saturation region and the critical point. This deviation from ideal-gas behavior at a given temperature and pressure can accurately be accounted for by the introduction of a correction factor called the **compressibility factor**  $Z$  defined as

$$Z = \frac{PV}{RT} \quad (3-17)$$

or

$$PV = ZRT \quad (3-18)$$

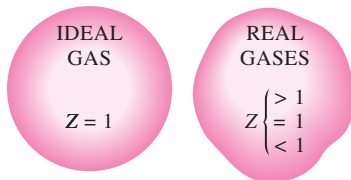


**FIGURE 3-49**  
 Percentage of error  
 $([v_{\text{table}} - v_{\text{ideal}}/v_{\text{table}}] \times 100)$   
 involved in assuming steam to be an  
 ideal gas, and the region where  
 steam can be treated as an ideal gas  
 with less than 1 percent error.

It can also be expressed as

$$Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}} \quad (3-19)$$

where  $v_{\text{ideal}} = RT/P$ . Obviously,  $Z = 1$  for ideal gases. For real gases  $Z$  can be greater than or less than unity (Fig. 3-50). The farther away  $Z$  is from unity, the more the gas deviates from ideal-gas behavior.



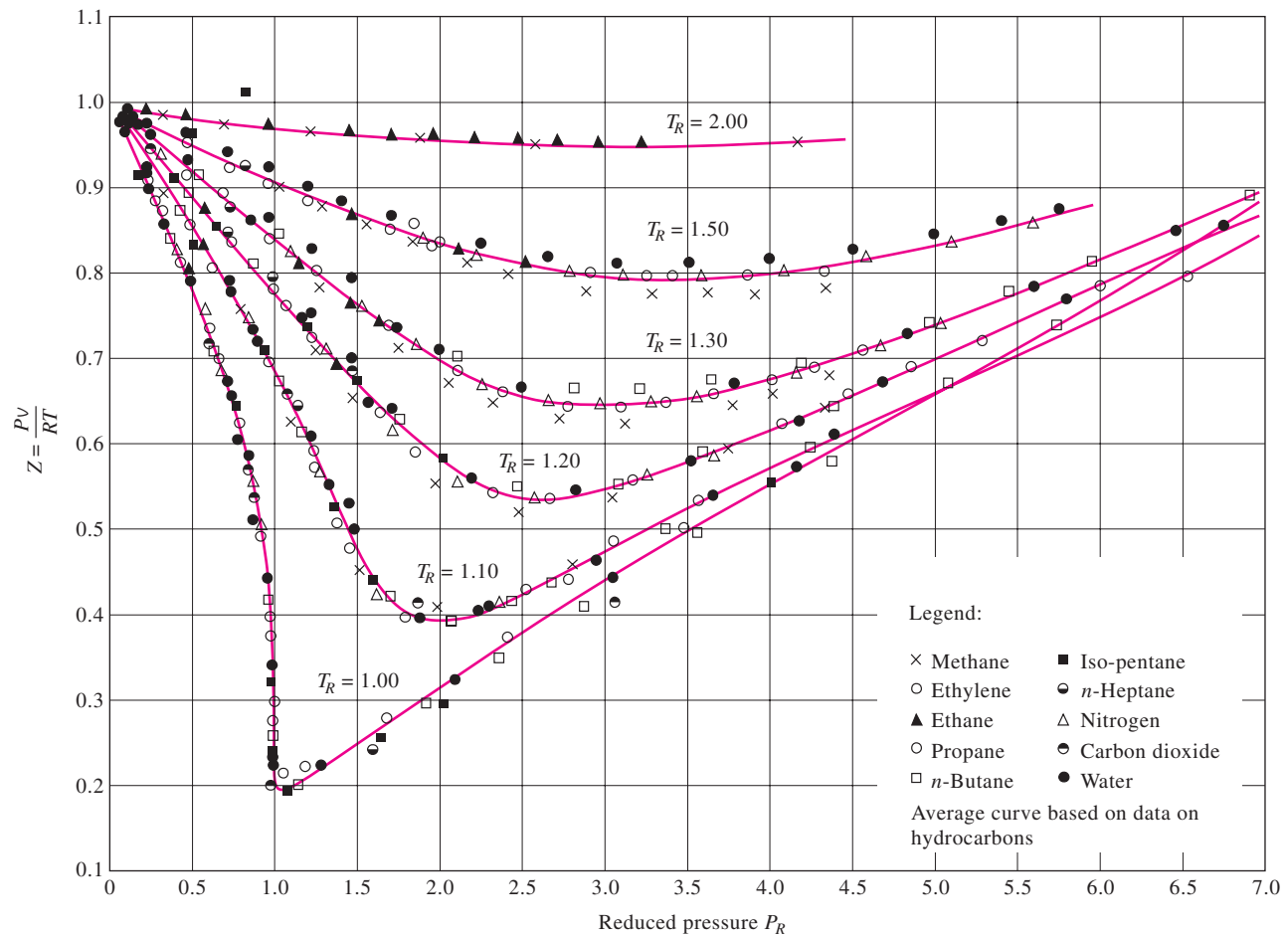
**FIGURE 3-50**  
 The compressibility factor is unity for  
 ideal gases.

We have said that gases follow the ideal-gas equation closely at low pressures and high temperatures. But what exactly constitutes low pressure or high temperature? Is  $-100^\circ\text{C}$  a low temperature? It definitely is for most substances but not for air. Air (or nitrogen) can be treated as an ideal gas at this temperature and atmospheric pressure with an error under 1 percent. This is because nitrogen is well over its critical temperature ( $-147^\circ\text{C}$ ) and away from the saturation region. At this temperature and pressure, however, most substances would exist in the solid phase. Therefore, the pressure or temperature of a substance is high or low relative to its critical temperature or pressure.

Gases behave differently at a given temperature and pressure, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures. The normalization is done as

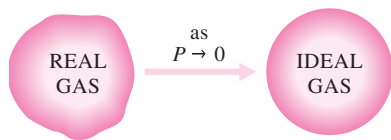
$$P_R = \frac{P}{P_{cr}} \quad \text{and} \quad T_R = \frac{T}{T_{cr}} \quad (3-20)$$

Here  $P_R$  is called the **reduced pressure** and  $T_R$  the **reduced temperature**. The  $Z$  factor for all gases is approximately the same at the same reduced pressure and temperature. This is called the **principle of corresponding states**. In Fig. 3-51, the experimentally determined  $Z$  values are plotted against  $P_R$  and  $T_R$  for several gases. The gases seem to obey the principle of corresponding states reasonably well. By curve-fitting all the data, we



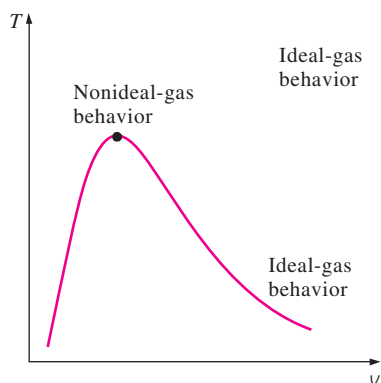
**FIGURE 3-51**

Comparison of  $Z$  factors for various gases.



**FIGURE 3–52**

At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).



**FIGURE 3–53**

Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

obtain the **generalized compressibility chart** that can be used for all gases (Fig. A–15).

The following observations can be made from the generalized compressibility chart:

1. At very low pressures ( $P_R \ll 1$ ), gases behave as an ideal gas regardless of temperature (Fig. 3–52),
2. At high temperatures ( $T_R > 2$ ), ideal-gas behavior can be assumed with good accuracy regardless of pressure (except when  $P_R \gg 1$ ).
3. The deviation of a gas from ideal-gas behavior is greatest in the vicinity of the critical point (Fig. 3–53).

### EXAMPLE 3–11 The Use of Generalized Charts

Determine the specific volume of refrigerant-134a at 1 MPa and 50°C, using (a) the ideal-gas equation of state and (b) the generalized compressibility chart. Compare the values obtained to the actual value of 0.021796 m<sup>3</sup>/kg and determine the error involved in each case.

**Solution** The specific volume of refrigerant-134a is to be determined assuming ideal- and nonideal-gas behavior.

**Analysis** The gas constant, the critical pressure, and the critical temperature of refrigerant-134a are determined from Table A–1 to be

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

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

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

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

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

Therefore, treating the refrigerant-134a vapor as an ideal gas would result in an error of  $(0.026325 - 0.021796)/0.021796 = \mathbf{0.208}$ , or 20.8 percent in this case.

(b) To determine the correction factor  $Z$  from the compressibility chart, we first need to calculate the reduced pressure and temperature:

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

Thus

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

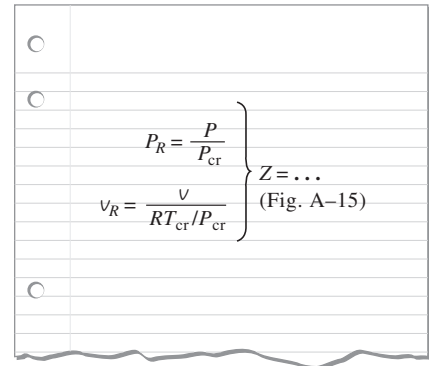
**Discussion** The error in this result is less than **2 percent**. Therefore, in the absence of tabulated data, the generalized compressibility chart can be used with confidence.



When  $P$  and  $v$ , or  $T$  and  $v$ , are given instead of  $P$  and  $T$ , the generalized compressibility chart can still be used to determine the third property, but it would involve tedious trial and error. Therefore, it is necessary to define one more reduced property called the **pseudo-reduced specific volume**  $v_R$  as

$$v_R = \frac{v_{\text{actual}}}{RT_{\text{cr}}/P_{\text{cr}}} \quad (3-21)$$

Note that  $v_R$  is defined differently from  $P_R$  and  $T_R$ . It is related to  $T_{\text{cr}}$  and  $P_{\text{cr}}$  instead of  $v_{\text{cr}}$ . Lines of constant  $v_R$  are also added to the compressibility charts, and this enables one to determine  $T$  or  $P$  without having to resort to time-consuming iterations (Fig. 3–54).



**FIGURE 3–54**

The compressibility factor can also be determined from a knowledge of  $P_R$  and  $v_R$ .

**EXAMPLE 3–12 Using Generalized Charts to Determine Pressure**

Determine the pressure of water vapor at 600°F and 0.51431 ft<sup>3</sup>/lbm, using (a) the steam tables, (b) the ideal-gas equation, and (c) the generalized compressibility chart.

**Solution** The pressure of water vapor is to be determined in three different ways.

**Analysis** A sketch of the system is given in Fig. 3–55. The gas constant, the critical pressure, and the critical temperature of steam are determined from Table A–1E to be

$$R = 0.5956 \text{ psia} \cdot \text{ft}^3/\text{lbm} \cdot \text{R}$$

$$P_{\text{cr}} = 3200 \text{ psia}$$

$$T_{\text{cr}} = 1164.8 \text{ R}$$

(a) The pressure at the specified state is determined from Table A–6E to be

$$\left. \begin{array}{l} v = 0.51431 \text{ ft}^3/\text{lbm} \\ T = 600^\circ\text{F} \end{array} \right\} P = \mathbf{1000 \text{ psia}}$$

This is the experimentally determined value, and thus it is the most accurate.

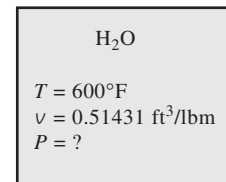
(b) The pressure of steam under the ideal-gas assumption is determined from the ideal-gas relation to be

$$P = \frac{RT}{v} = \frac{(0.5956 \text{ psia} \cdot \text{ft}^3/\text{lbm} \cdot \text{R})(1060 \text{ R})}{0.51431 \text{ ft}^3/\text{lbm}} = \mathbf{1228 \text{ psia}}$$

Therefore, treating the steam as an ideal gas would result in an error of  $(1228 - 1000)/1000 = 0.228$ , or 22.8 percent in this case.

(c) To determine the correction factor  $Z$  from the compressibility chart (Fig. A–15), we first need to calculate the pseudo-reduced specific volume and the reduced temperature:

$$\left. \begin{array}{l} v_R = \frac{v_{\text{actual}}}{RT_{\text{cr}}/P_{\text{cr}}} = \frac{(0.51431 \text{ ft}^3/\text{lbm})(3200 \text{ psia})}{(0.5956 \text{ psia} \cdot \text{ft}^3/\text{lbm} \cdot \text{R})(1164.8 \text{ R})} = 2.372 \\ T_R = \frac{T}{T_{\text{cr}}} = \frac{1060 \text{ R}}{1164.8 \text{ R}} = 0.91 \end{array} \right\} P_R = 0.33$$



**FIGURE 3–55**

Schematic for Example 3–12.

	$P$ , psia
Exact	1000
Z chart	1056
Ideal gas	1228

(from Example 3-12)

**FIGURE 3-56**

Results obtained by using the compressibility chart are usually within a few percent of actual values.

Thus,

$$P = P_R P_{cr} = (0.33)(3200 \text{ psia}) = \mathbf{1056 \text{ psia}}$$

**Discussion** Using the compressibility chart reduced the error from 22.8 to 5.6 percent, which is acceptable for most engineering purposes (Fig. 3-56). A bigger chart, of course, would give better resolution and reduce the reading errors. Notice that we did not have to determine  $Z$  in this problem since we could read  $P_R$  directly from the chart.

### 3-8 ■ OTHER EQUATIONS OF STATE

The ideal-gas equation of state is very simple, but its range of applicability is limited. It is desirable to have equations of state that represent the  $P$ - $v$ - $T$  behavior of substances accurately over a larger region with no limitations. Such equations are naturally more complicated. Several equations have been proposed for this purpose (Fig. 3-57), but we shall discuss only three: the *van der Waals* equation because it is one of the earliest, the *Beattie-Bridgeman* equation of state because it is one of the best known and is reasonably accurate, and the *Benedict-Webb-Rubin* equation because it is one of the more recent and is very accurate.

#### Van der Waals Equation of State

The van der Waals equation of state was proposed in 1873, and it has two constants that are determined from the behavior of a substance at the critical point. It is given by

$$\left( P + \frac{a}{v^2} \right) (v - b) = RT \tag{3-22}$$



**FIGURE 3-57**

Several equations of state have been proposed throughout history.

Van der Waals intended to improve the ideal-gas equation of state by including two of the effects not considered in the ideal-gas model: the *intermolecular attraction forces* and the *volume occupied by the molecules themselves*. The term  $a/v^2$  accounts for the intermolecular forces, and  $b$  accounts for the volume occupied by the gas molecules. In a room at atmospheric pressure and temperature, the volume actually occupied by molecules is only about one-thousandth of the volume of the room. As the pressure increases, the volume occupied by the molecules becomes an increasingly significant part of the total volume. Van der Waals proposed to correct this by replacing  $v$  in the ideal-gas relation with the quantity  $v - b$ , where  $b$  represents the volume occupied by the gas molecules per unit mass.

The determination of the two constants appearing in this equation is based on the observation that the critical isotherm on a  $P$ - $v$  diagram has a horizontal inflection point at the critical point (Fig. 3-58). Thus, the first and the second derivatives of  $P$  with respect to  $v$  at the critical point must be zero. That is,

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

By performing the differentiations and eliminating  $v_{cr}$ , the constants  $a$  and  $b$  are determined to be

$$a = \frac{27R^2T_{cr}^2}{64P_{cr}} \quad \text{and} \quad b = \frac{RT_{cr}}{8P_{cr}} \quad (3-23)$$

The constants  $a$  and  $b$  can be determined for any substance from the critical-point data alone (Table A-1).

The accuracy of the van der Waals equation of state is often inadequate, but it can be improved by using values of  $a$  and  $b$  that are based on the actual behavior of the gas over a wider range instead of a single point. Despite its limitations, the van der Waals equation of state has a historical value in that it was one of the first attempts to model the behavior of real gases. The van der Waals equation of state can also be expressed on a unit-mole basis by replacing the  $v$  in Eq. 3-22 by  $\bar{v}$  and the  $R$  in Eqs. 3-22 and 3-23 by  $R_u$ .

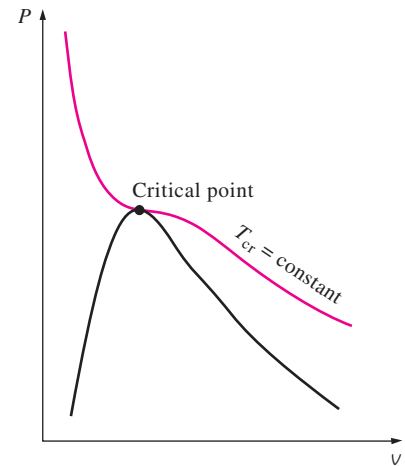


FIGURE 3-58

Critical isotherm of a pure substance has an inflection point at the critical state.

### Beattie-Bridgeman Equation of State

The Beattie-Bridgeman equation, proposed in 1928, is an equation of state based on five experimentally determined constants. It is expressed as

$$P = \frac{R_u T}{\bar{v}^2} \left( 1 - \frac{c}{\bar{v} T^3} \right) (\bar{v} + B) - \frac{A}{\bar{v}^2} \quad (3-24)$$

where

$$A = A_0 \left( 1 - \frac{a}{\bar{v}} \right) \quad \text{and} \quad B = B_0 \left( 1 - \frac{b}{\bar{v}} \right) \quad (3-25)$$

The constants appearing in the above equation are given in Table 3-4 for various substances. The Beattie-Bridgeman equation is known to be reasonably accurate for densities up to about  $0.8\rho_{cr}$ , where  $\rho_{cr}$  is the density of the substance at the critical point.

### Benedict-Webb-Rubin Equation of State

Benedict, Webb, and Rubin extended the Beattie-Bridgeman equation in 1940 by raising the number of constants to eight. It is expressed as

$$P = \frac{R_u T}{\bar{v}} + \left( B_0 R_u T - A_0 - \frac{C_0}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2} \left( 1 + \frac{\gamma}{\bar{v}^2} \right) e^{-\gamma/\bar{v}^2} \quad (3-26)$$

The values of the constants appearing in this equation are given in Table 3-4. This equation can handle substances at densities up to about  $2.5\rho_{cr}$ . In 1962, Strohbridge further extended this equation by raising the number of constants to 16 (Fig. 3-59).

### Virial Equation of State

The equation of state of a substance can also be expressed in a series form as

$$P = \frac{RT}{v} + \frac{a(T)}{v^2} + \frac{b(T)}{v^3} + \frac{c(T)}{v^4} + \frac{d(T)}{v^5} + \dots \quad (3-27)$$

TABLE 3-4

Constants that appear in the Beattie-Bridgeman and the Benedict-Webb-Rubin equations of state

(a) When  $P$  is in kPa,  $\bar{v}$  is in  $\text{m}^3/\text{kmol}$ ,  $T$  is in K, and  $R_u = 8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K}$ , the five constants in the Beattie-Bridgeman equation are as follows:

Gas	$A_0$	$a$	$B_0$	$b$	$c$
Air	131.8441	0.01931	0.04611	-0.001101	$4.34 \times 10^4$
Argon, Ar	130.7802	0.02328	0.03931	0.0	$5.99 \times 10^4$
Carbon dioxide, $\text{CO}_2$	507.2836	0.07132	0.10476	0.07235	$6.60 \times 10^5$
Helium, He	2.1886	0.05984	0.01400	0.0	40
Hydrogen, $\text{H}_2$	20.0117	-0.00506	0.02096	-0.04359	504
Nitrogen, $\text{N}_2$	136.2315	0.02617	0.05046	-0.00691	$4.20 \times 10^4$
Oxygen, $\text{O}_2$	151.0857	0.02562	0.04624	0.004208	$4.80 \times 10^4$

Source: Gordon J. Van Wylen and Richard E. Sonntag, *Fundamentals of Classical Thermodynamics*, English/SI Version, 3rd ed. (New York: John Wiley & Sons, 1986), p. 46, table 3.3.

(b) When  $P$  is in kPa,  $\bar{v}$  is in  $\text{m}^3/\text{kmol}$ ,  $T$  is in K, and  $R_u = 8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K}$ , the eight constants in the Benedict-Webb-Rubin equation are as follows:

Gas	$a$	$A_0$	$b$	$B_0$	$c$	$C_0$	$\alpha$	$\gamma$
n-Butane, $\text{C}_4\text{H}_{10}$	190.68	1021.6	0.039998	0.12436	$3.205 \times 10^7$	$1.006 \times 10^8$	$1.101 \times 10^{-3}$	0.0340
Carbon dioxide, $\text{CO}_2$	13.86	277.30	0.007210	0.04991	$1.511 \times 10^6$	$1.404 \times 10^7$	$8.470 \times 10^{-5}$	0.00539
Carbon monoxide, CO	3.71	135.87	0.002632	0.05454	$1.054 \times 10^5$	$8.673 \times 10^5$	$1.350 \times 10^{-4}$	0.0060
Methane, $\text{CH}_4$	5.00	187.91	0.003380	0.04260	$2.578 \times 10^5$	$2.286 \times 10^6$	$1.244 \times 10^{-4}$	0.0060
Nitrogen, $\text{N}_2$	2.54	106.73	0.002328	0.04074	$7.379 \times 10^4$	$8.164 \times 10^5$	$1.272 \times 10^{-4}$	0.0053

Source: Kenneth Wark, *Thermodynamics*, 4th ed. (New York: McGraw-Hill, 1983), p. 815, table A-21M. Originally published in H. W. Cooper and J. C. Goldfrank, *Hydrocarbon Processing* 46, no. 12 (1967), p. 141.

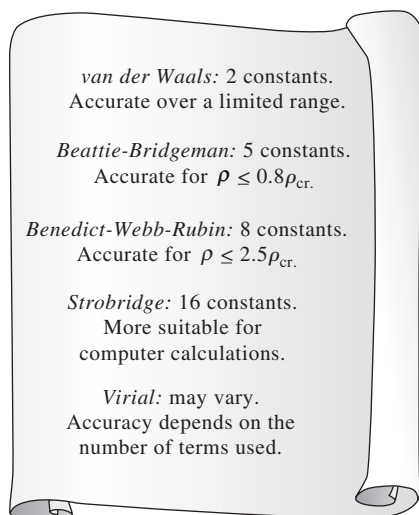
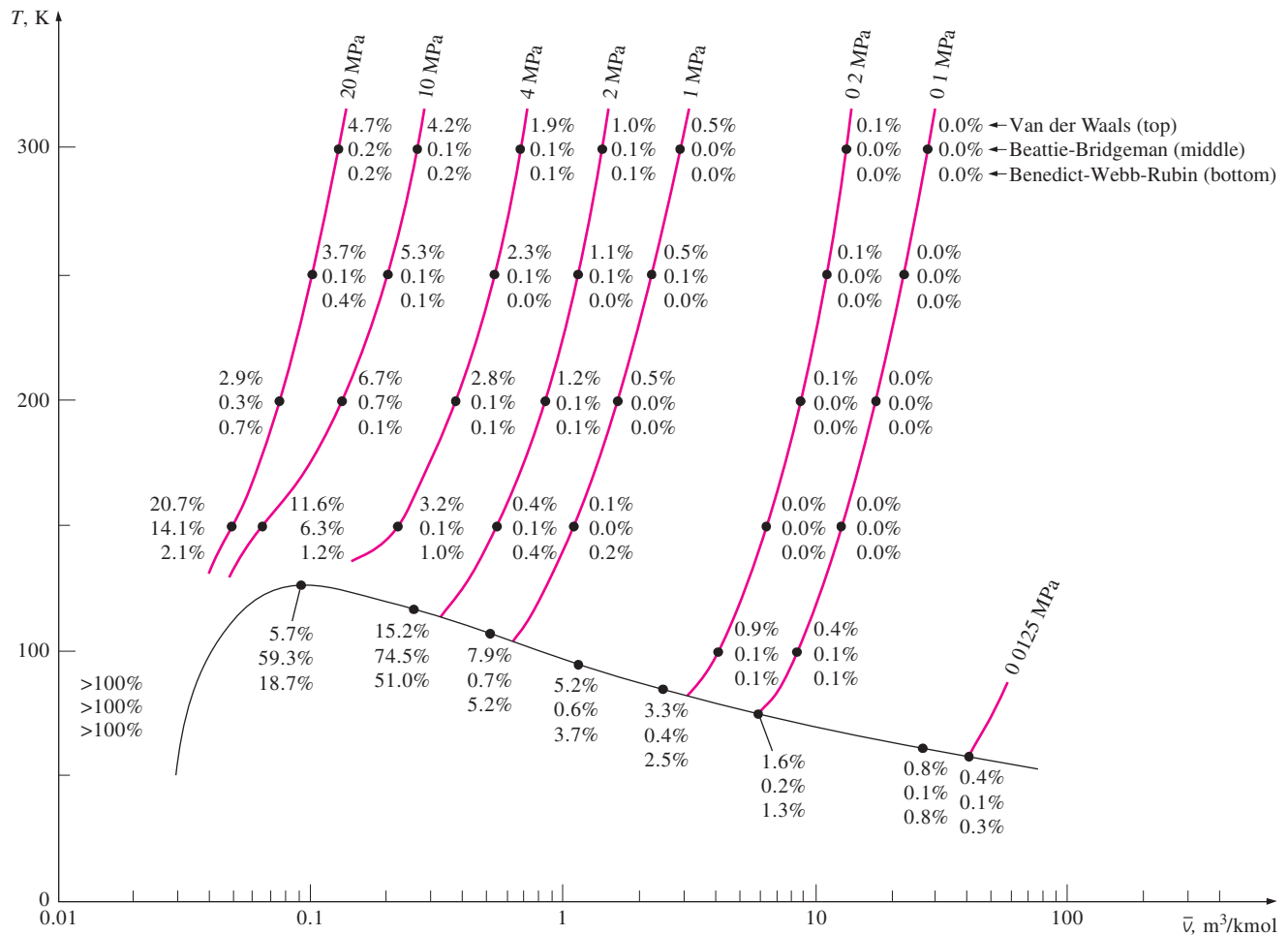


FIGURE 3-59

Complex equations of state represent the  $P$ - $v$ - $T$  behavior of gases more accurately over a wider range.

This and similar equations are called the *virial equations of state*, and the coefficients  $a(T)$ ,  $b(T)$ ,  $c(T)$ , and so on, that are functions of temperature alone are called *virial coefficients*. These coefficients can be determined experimentally or theoretically from statistical mechanics. Obviously, as the pressure approaches zero, all the virial coefficients will vanish and the equation will reduce to the ideal-gas equation of state. The  $P$ - $v$ - $T$  behavior of a substance can be represented accurately with the virial equation of state over a wider range by including a sufficient number of terms. The equations of state discussed here are applicable to the gas phase of the substances only, and thus should not be used for liquids or liquid-vapor mixtures.

Complex equations represent the  $P$ - $v$ - $T$  behavior of substances reasonably well and are very suitable for digital computer applications. For hand calculations, however, it is suggested that the reader use the property tables or the simpler equations of state for convenience. This is particularly true for specific-volume calculations since all the earlier equations are implicit in  $v$  and require a trial-and-error approach. The accuracy of the van der Waals,



**FIGURE 3-60** Percentage of error involved in various equations of state for nitrogen ( $\% \text{ error} = [(v_{\text{table}} - v_{\text{equation}})/v_{\text{table}}] \times 100$ ).

Beattie-Bridgeman, and Benedict-Webb-Rubin equations of state is illustrated in Fig. 3-60. It is apparent from this figure that the Benedict-Webb-Rubin equation of state is usually the most accurate.

**EXAMPLE 3-13 Different Methods of Evaluating Gas Pressure**

Predict the pressure of nitrogen gas at  $T = 175 \text{ K}$  and  $v = 0.00375 \text{ m}^3/\text{kg}$  on the basis of (a) the ideal-gas equation of state, (b) the van der Waals equation of state, (c) the Beattie-Bridgeman equation of state, and (d) the Benedict-Webb-Rubin equation of state. Compare the values obtained to the experimentally determined value of 10,000 kPa.

**Solution** The pressure of nitrogen gas is to be determined using four different equations of state.

**Properties** The gas constant of nitrogen gas is  $0.2968 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}$  (Table A-1).

**Analysis** (a) Using the ideal-gas equation of state, the pressure is found to be

$$P = \frac{RT}{v} = \frac{(0.2968 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(175 \text{ K})}{0.00375 \text{ m}^3/\text{kg}} = \mathbf{13,851 \text{ kPa}}$$

which is in error by 38.5 percent.

(b) The van der Waals constants for nitrogen are determined from Eq. 3-23 to be

$$a = 0.175 \text{ m}^6 \cdot \text{kPa}/\text{kg}^2$$

$$b = 0.00138 \text{ m}^3/\text{kg}$$

From Eq. 3-22,

$$P = \frac{RT}{v - b} - \frac{a}{v^2} = \mathbf{9471 \text{ kPa}}$$

which is in error by 5.3 percent.

(c) The constants in the Beattie-Bridgeman equation are determined from Table 3-4 to be

$$A = 102.29$$

$$B = 0.05378$$

$$c = 4.2 \times 10^4$$

Also,  $\bar{v} = Mv = (28.013 \text{ kg/mol})(0.00375 \text{ m}^3/\text{kg}) = 0.10505 \text{ m}^3/\text{kmol}$ . Substituting these values into Eq. 3-24, we obtain

$$P = \frac{R_u T}{\bar{v}^2} \left( 1 - \frac{c}{\bar{v} T^3} \right) (\bar{v} + B) - \frac{A}{\bar{v}^2} = \mathbf{10,110 \text{ kPa}}$$

which is in error by 1.1 percent.

(d) The constants in the Benedict-Webb-Rubin equation are determined from Table 3-4 to be

$$a = 2.54 \quad A_0 = 106.73$$

$$b = 0.002328 \quad B_0 = 0.04074$$

$$c = 7.379 \times 10^4 \quad C_0 = 8.164 \times 10^5$$

$$\alpha = 1.272 \times 10^{-4} \quad \gamma = 0.0053$$

Substituting these values into Eq. 3-26 gives

$$\begin{aligned} P &= \frac{R_u T}{\bar{v}} + \left( B_0 R_u T - A_0 - \frac{C_0}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} \\ &\quad + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2} \left( 1 + \frac{\gamma}{\bar{v}^2} \right) e^{-\gamma/\bar{v}^2} \\ &= \mathbf{10,009 \text{ kPa}} \end{aligned}$$

which is in error by only 0.09 percent. Thus, the accuracy of the Benedict-Webb-Rubin equation of state is rather impressive in this case.

## SUMMARY

A substance that has a fixed chemical composition throughout is called a *pure substance*. A pure substance exists in different phases depending on its energy level. In the liquid phase, a substance that is not about to vaporize is called a *compressed* or *subcooled liquid*. In the gas phase, a substance that is not about to condense is called a *superheated vapor*. During a phase-change process, the temperature and pressure of a pure substance are dependent properties. At a given pressure, a substance changes phase at a fixed temperature, called the *saturation temperature*. Likewise, at a given temperature, the pressure at which a substance changes phase is called the *saturation pressure*. During a boiling process, both the liquid and the vapor phases coexist in equilibrium, and under this condition the liquid is called *saturated liquid* and the vapor *saturated vapor*.

In a saturated liquid–vapor mixture, the mass fraction of vapor is called the *quality* and is expressed as

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

Quality may have values between 0 (saturated liquid) and 1 (saturated vapor). It has no meaning in the compressed liquid or superheated vapor regions. In the saturated mixture region, the average value of any intensive property  $y$  is determined from

$$y = y_f + xy_{fg}$$

where  $f$  stands for saturated liquid and  $g$  for saturated vapor.

In the absence of compressed liquid data, a general approximation is to treat a compressed liquid as a saturated liquid at the given *temperature*,

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

where  $y$  stands for  $v$ ,  $u$ , or  $h$ .

The state beyond which there is no distinct vaporization process is called the *critical point*. At supercritical pressures, a substance gradually and uniformly expands from the liquid to vapor phase. All three phases of a substance coexist in equilibrium at states along the *triple line* characterized by triple-line temperature and pressure. The compressed liquid has lower  $v$ ,  $u$ , and  $h$  values than the saturated liquid at the same  $T$  or  $P$ . Likewise, superheated vapor has higher  $v$ ,  $u$ , and  $h$  values than the saturated vapor at the same  $T$  or  $P$ .

Any relation among the pressure, temperature, and specific volume of a substance is called an *equation of state*. The simplest and best-known equation of state is the *ideal-gas equation of state*, given as

$$Pv = RT$$

where  $R$  is the gas constant. Caution should be exercised in using this relation since an ideal gas is a fictitious substance.

Real gases exhibit ideal-gas behavior at relatively low pressures and high temperatures.

The deviation from ideal-gas behavior can be properly accounted for by using the *compressibility factor*  $Z$ , defined as

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

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

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

where  $P_{\text{cr}}$  and  $T_{\text{cr}}$  are the critical pressure and temperature, respectively. This is known as the *principle of corresponding states*. When either  $P$  or  $T$  is unknown, it can be determined from the compressibility chart with the help of the *pseudo-reduced specific volume*, defined as

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

The  $P$ - $v$ - $T$  behavior of substances can be represented more accurately by more complex equations of state. Three of the best known are

$$\text{van der Waals:} \quad \left( P + \frac{a}{v^2} \right) (v - b) = RT$$

where

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

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

where

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

*Benedict-Webb-Rubin:*

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

where  $R_u$  is the universal gas constant and  $\bar{v}$  is the molar specific volume.