CHAPTER THREE

PROPERTIES OF PURE SUBSTANCES

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).

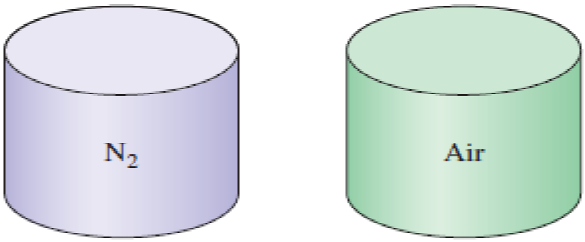
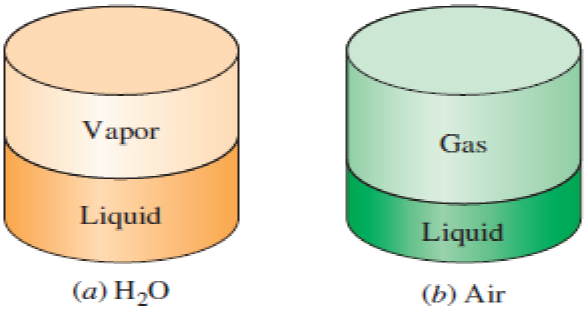


FIGURE 3–1
Nitrogen and gaseous air are pure substances.



(a) H_2O (b) Air

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

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 H2O 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. This is why 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).

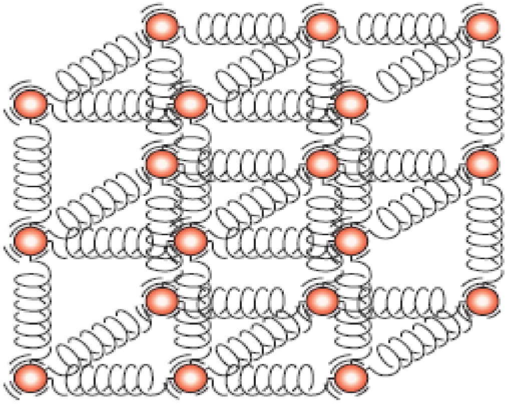


FIGURE 3–3
The molecules in a solid are kept at their positions by the large springlike intermolecular forces.

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. 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. 3–4).

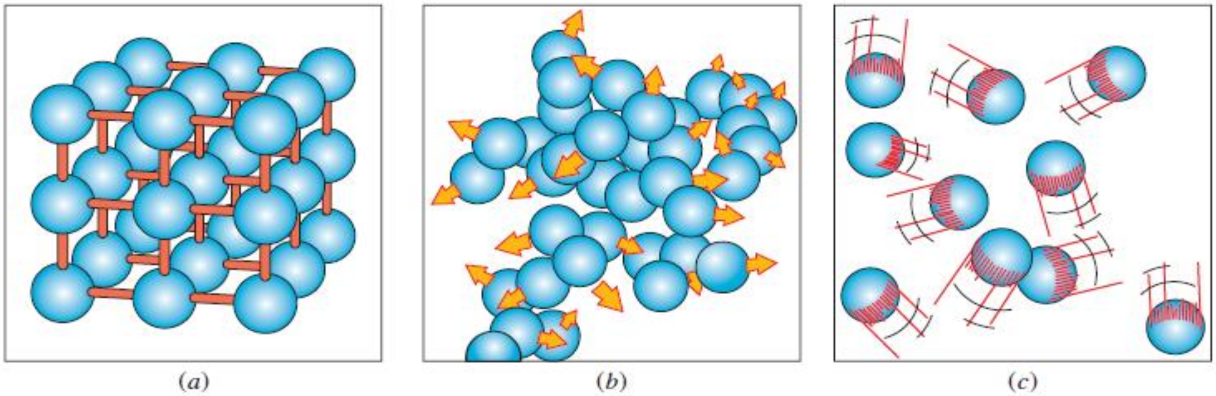


FIGURE 3–4
The arrangement of atoms in different phases: (*a*) molecules are at relatively fixed positions in a solid, (*b*) groups of molecules move about each other in the liquid phase, and (*c*) molecules move about at random in the gas phase.

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.

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 homeowners consider the freezing of water in underground pipes to be the most 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. 3–5). 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. 3–6). 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.

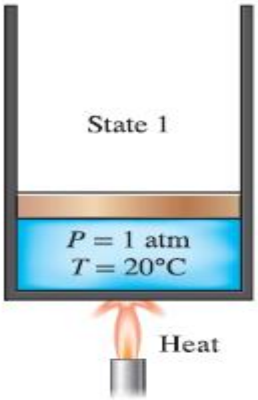


FIGURE 3–5
At 1 atm and 20°C, water exists in the liquid phase (*compressed liquid*).

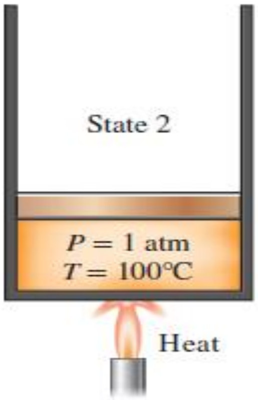


FIGURE 3–6
At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (*saturated liquid*).

Saturated Vapor and Superheated Vapor

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. 3–7), the cylinder contains equal amounts of liquid and vapor.

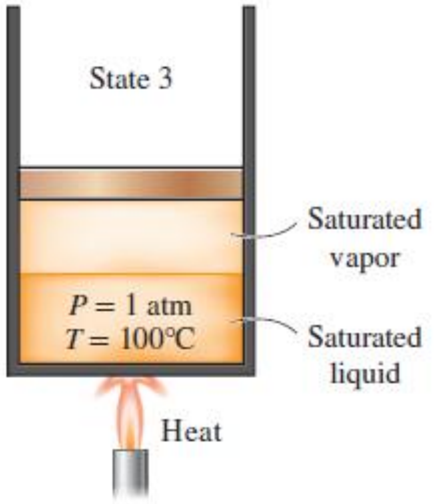


FIGURE 3–7
As more heat is transferred, part of the saturated liquid vaporizes (*saturated liquid–vapor mixture*).

As we continue transferring heat, the vaporization process continues until the last drop of liquid is vaporized (state 4, Fig. 3–8). 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. 3–9).

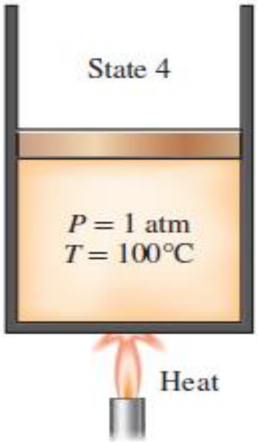


FIGURE 3–8
At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (*saturated vapor*).

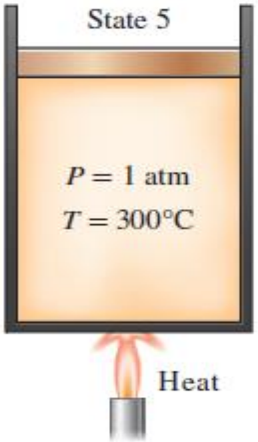


FIGURE 3–9
As more heat is transferred, the temperature of the vapor starts to rise (*superheated vapor*).

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 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. 3–10.

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: H_2O.

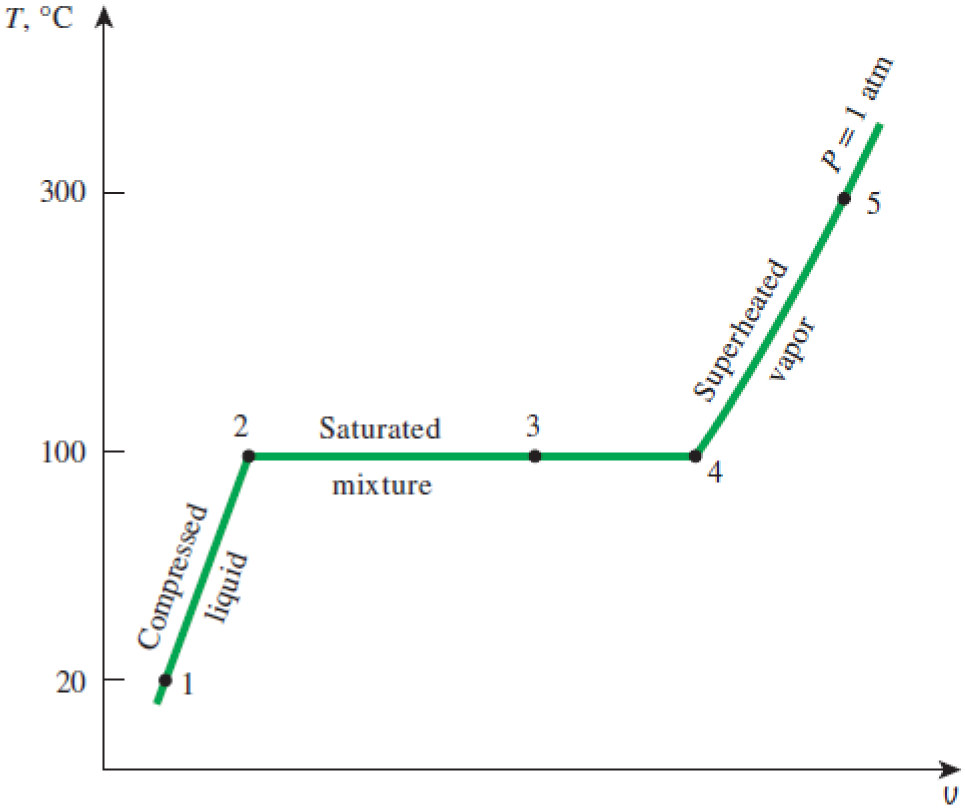


FIGURE 3–10 *T*-*v* diagram for the heating process of water at constant pressure.

Saturation Temperature and Saturation Pressure

It probably came as no surprise to you that water started to boil at 100°C. Strictly speaking, the statement "water boils at 100°C" is incorrect. The correct statement is "water boils at 100°C at 1 atm pressure." The only reason water started boiling at 100 °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°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_{sat}. Likewise, at a given temperature, the pressure at which a pure substance changes phase is called the **saturation pressure** P_{sat}.

At a pressure of 101.325 kPa, T_{sat} is 99.97°C. Conversely, at a temperature of 99.97°C, P_{sat} is 101.325 kPa. (At 100.00°C, P_{sat} is 101.42 kPa) . Saturation tables that list the saturation pressure against the temperature (or the saturation temperature against the pressure) are available for practically all substances. A partial listing of such a table is given in Table 3–1 for water.

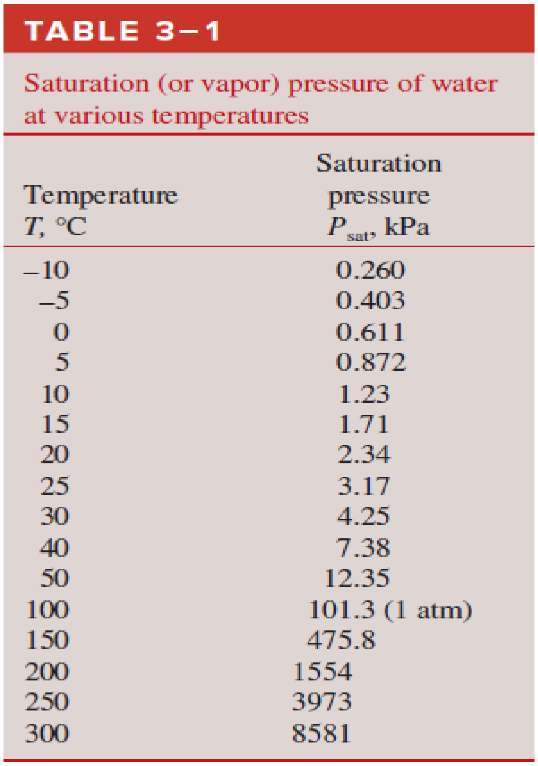


TABLE 3–1

Saturation (or vapor) pressure of water at various temperatures

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

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, $P_{sat} = f(T_{sat})$. A plot of P_{sat} versus T_{sat}, such as the one given for water in Fig. 3–11, is called a **liquid–vapor saturation curve**.

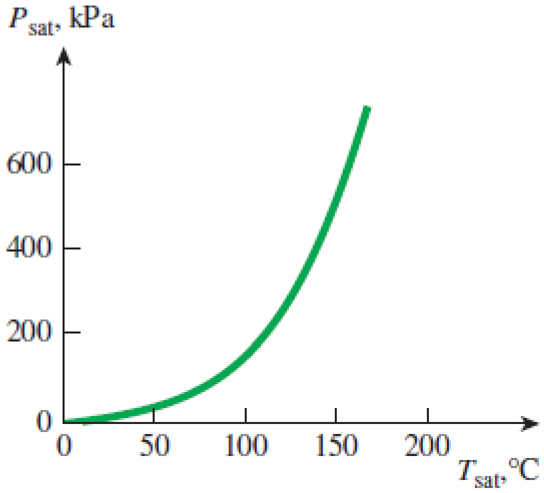


FIGURE 3–11
The liquid–vapor saturation curve of a pure substance (numerical values are for water).

A curve of this kind is characteristic of all pure substances. It is clear from Fig. 3–11 that T_{sat} increases with P_{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 1C.

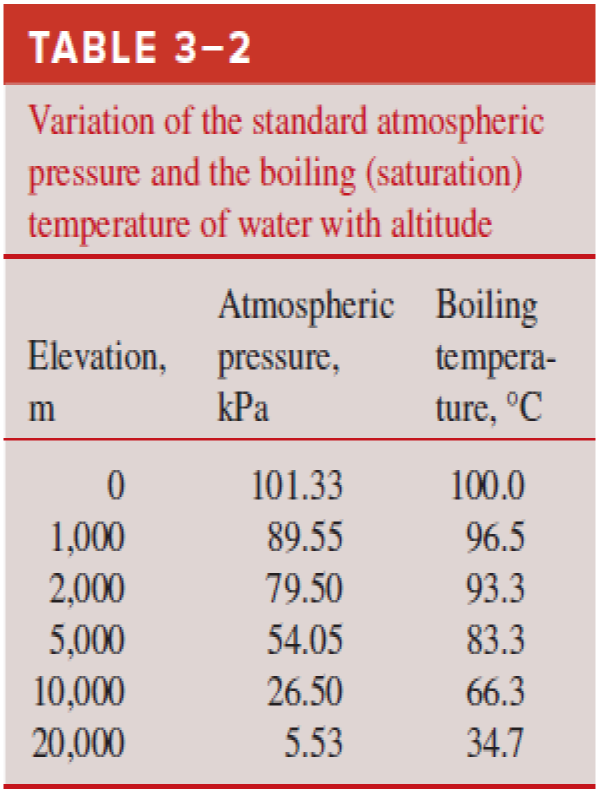


TABLE 3–2

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

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

Some Consequences of T_{sat} and P_{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. In this section 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°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°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°C indefinitely. The boiling temperature of *nitrogen* at atmospheric pressure is −196°C (see Table A–3*a*). This means the temperature of liquid nitrogen exposed to the atmosphere must be −196°C since some nitrogen will be evaporating.

The temperature of liquid nitrogen remains constant at −196°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°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°C (Fig. 3–12).

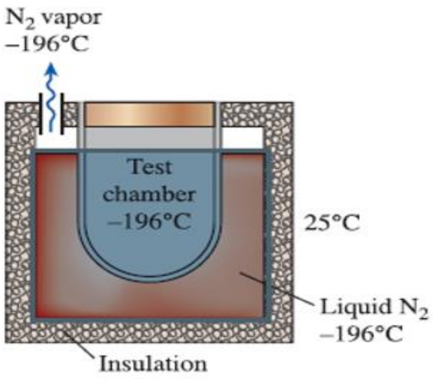


FIGURE 3–12
The temperature of liquid nitrogen exposed to the atmosphere remains constant at −196°C, and thus it maintains the test chamber at −196°C.

The 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 swab 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 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. 3–13).

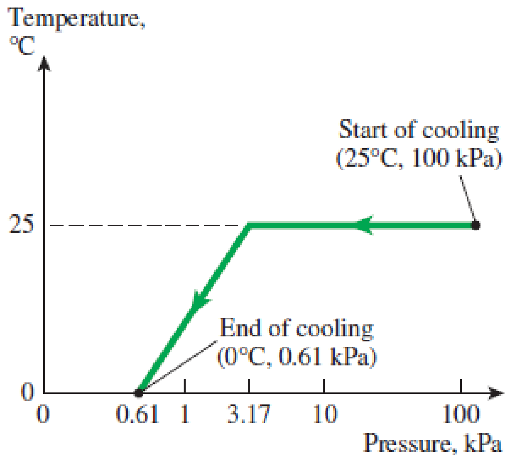


FIGURE 3–13
The variation of the temperature of fruits and vegetables with pressure during vacuum cooling from 25°C to 0°C.

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 a 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. 3–14).

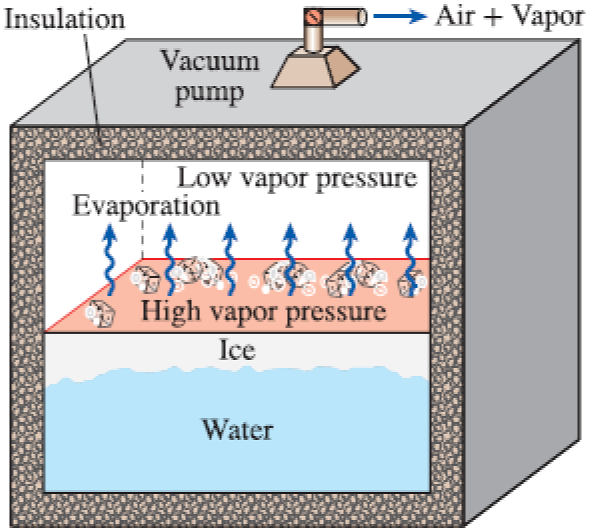


FIGURE 3–14
In 1775, ice was made by evacuating the airspace in a water tank.

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. 3–10. 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. 3–15, but there are some noticeable differences. First, water starts boiling at a much higher temperature (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.

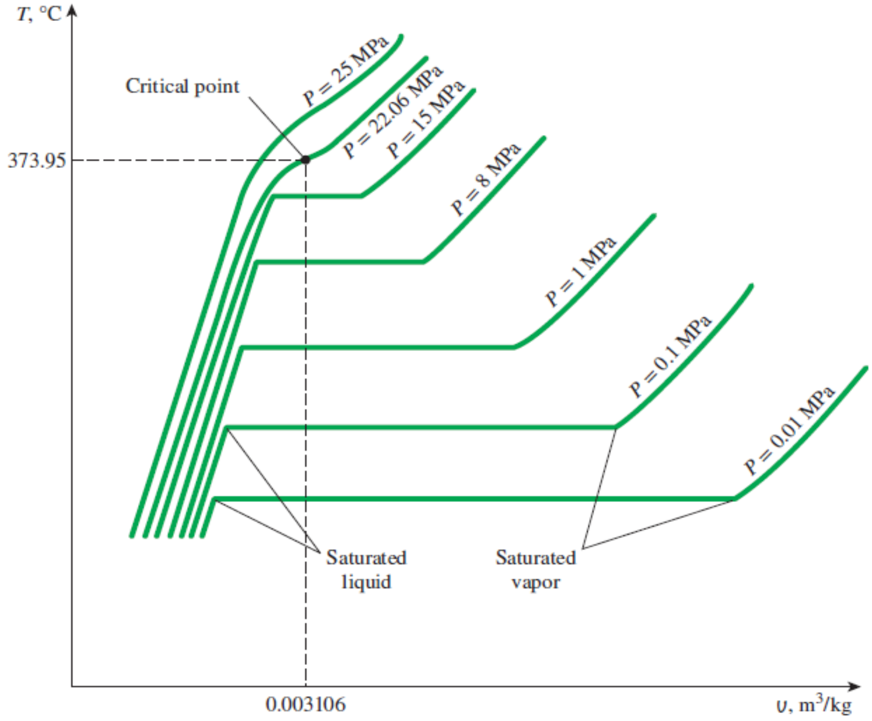


FIGURE 3–15
T-*υ* diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

As the pressure is increased further, this saturation line continues to shrink, as shown in Fig. 3–15, 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°C, and *v*cr = 0.003106 m3/kg. For helium, they are 0.23 MPa, −267.85°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. 3–16).

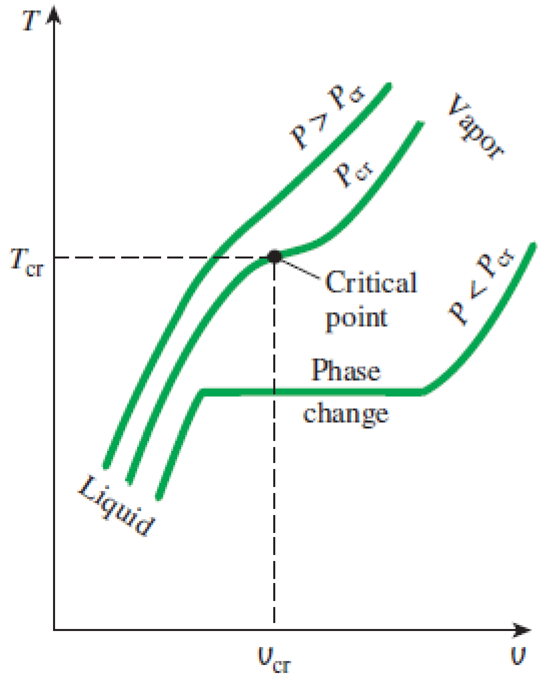


FIGURE 3–16
At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.

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 has occurred.

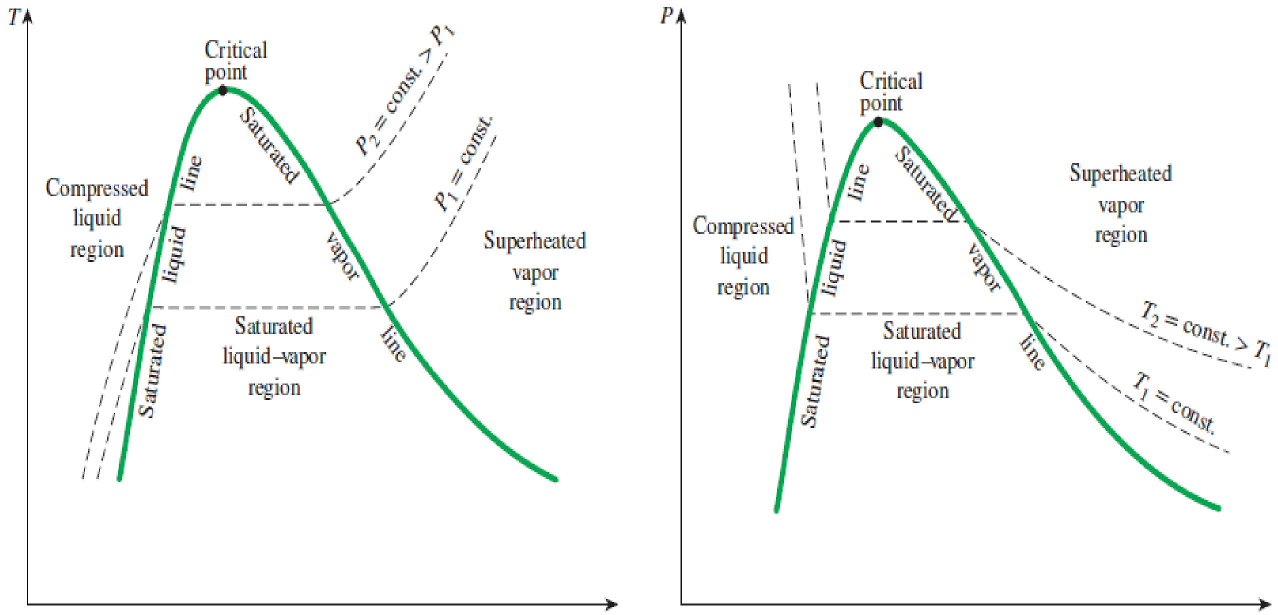
Above the critical state, there is no line that separates the compressed liquid region and the superheated vapor region. However, it is customary to refer to the substance as superheated vapor at temperatures above the critical temperature and as compressed liquid at temperatures below the critical temperature.

The saturated liquid states in Fig. 3–15 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. 3–17*a*.

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**.



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

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

FIGURE 3–17
Property diagrams of a pure substance.

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* = constant lines on this diagram have a downward trend, as shown in Fig. 3–17*b*.

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. 3–18).

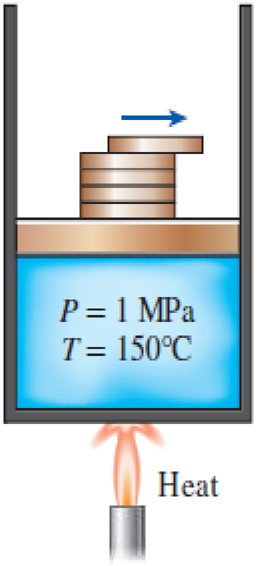


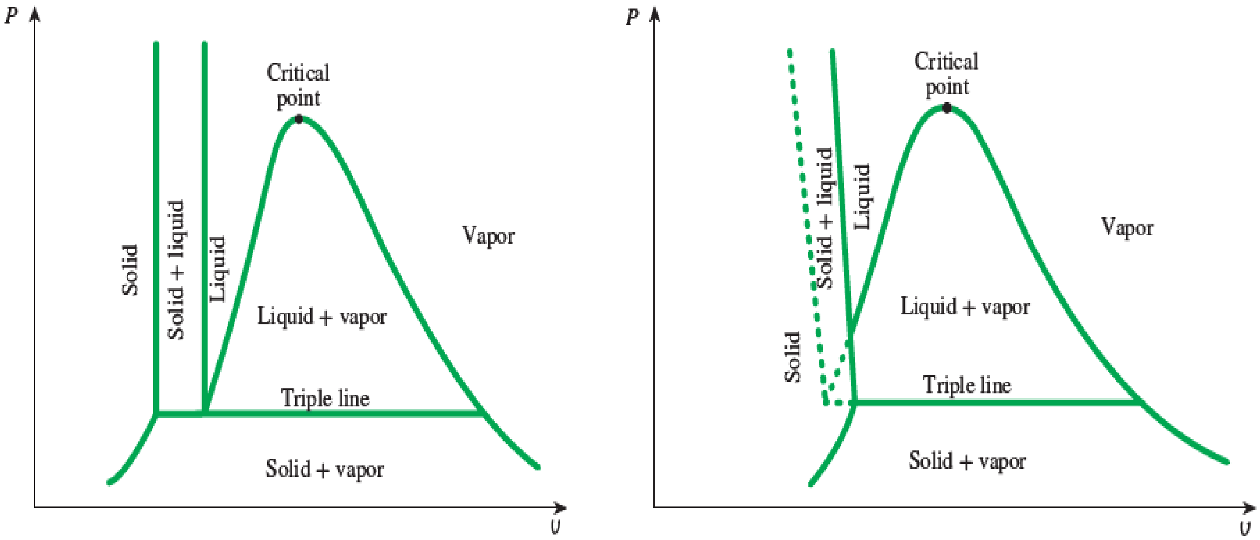
FIGURE 3–18
The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

The water is allowed to exchange heat with the surroundings so its temperature remains constant. As 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 $T_{sat} = f(P_{sat})$], 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. 3–17*b*.

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. 3–19*a* and 3–19*b*. These two diagrams differ only in the solid–liquid saturation region. The *T*-*v* diagrams look very much like the *P*-*v* diagrams, especially for substances that contract on freezing.



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

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

FIGURE 3–19
P-*υ* diagrams of different substances.

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. 3–20).

FIGURE 3–20
At triple-point pressure and temperature, a substance exists in three phases in equilibrium.

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°C and 0.6117 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, substances at high pressures can exist in the liquid phase at temperatures below the triple-point temperature.

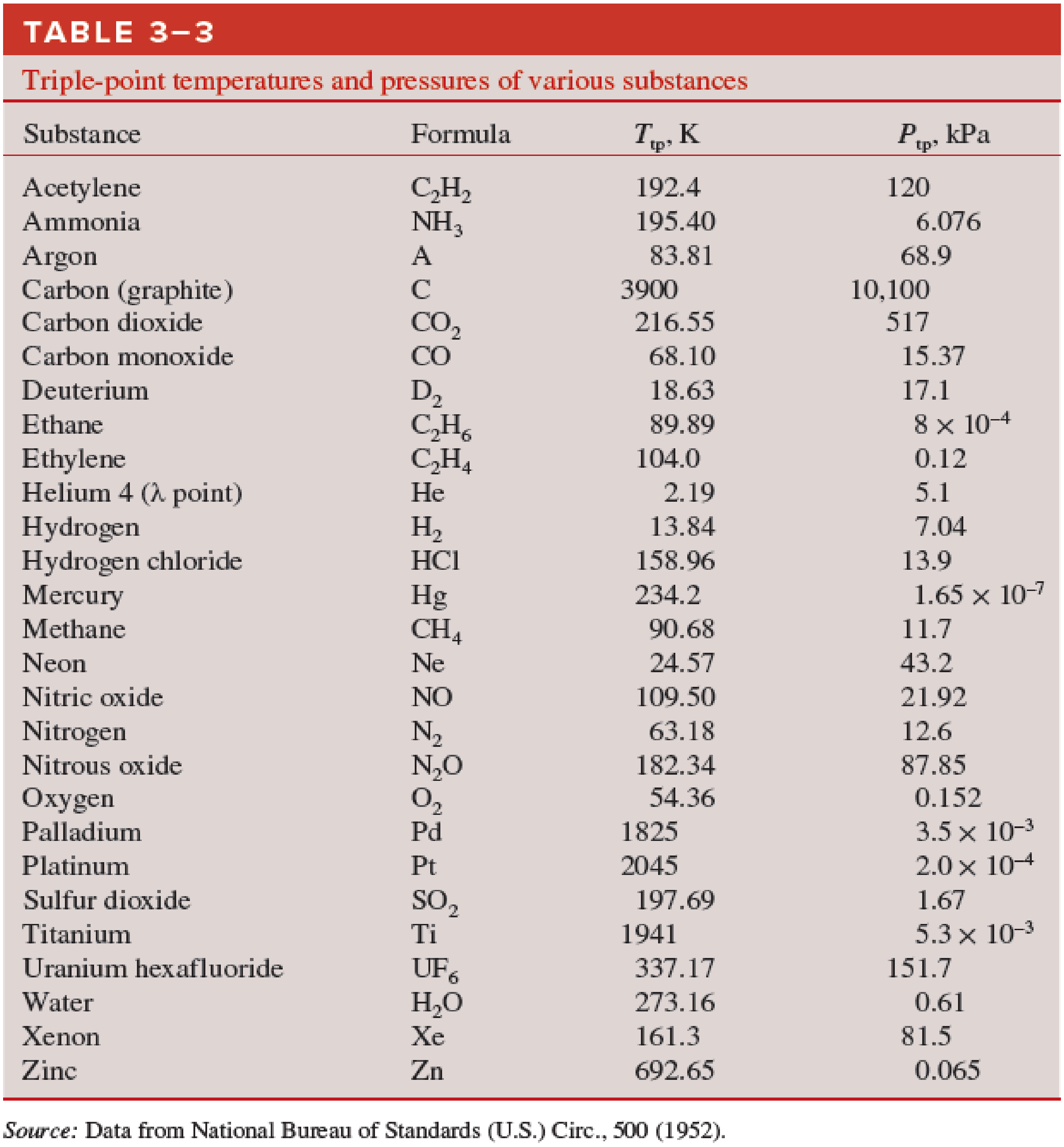


TABLE 3–3

Triple-point temperatures and pressures of various substances

Substance	Formula	T_{tp}, K	P_{tp}, kPa
Acetylene	C_2H_2	192.4	120
Ammonia	NH_3	195.40	6.076
Argon	A	83.81	68.9
Carbon (graphite)	C	3900	10,100
Carbon dioxide	CO_2	216.55	517
Carbon monoxide	CO	68.10	15.37
Deuterium	D_2	18.63	17.1
Ethane	C_2H_6	89.89	8×10^{-4}
Ethylene	C_2H_4	104.0	0.12
Helium 4 (λ point)	He	2.19	5.1
Hydrogen	H_2	13.84	7.04
Hydrogen chloride	HCl	158.96	13.9
Mercury	Hg	234.2	1.65×10^{-7}
Methane	CH_4	90.68	11.7
Neon	Ne	24.57	43.2
Nitric oxide	NO	109.50	21.92
Nitrogen	N_2	63.18	12.6
Nitrous oxide	N_2O	182.34	87.85
Oxygen	O_2	54.36	0.152
Palladium	Pd	1825	3.5×10^{-3}
Platinum	Pt	2045	2.0×10^{-4}
Sulfur dioxide	SO_2	197.69	1.67
Titanium	Ti	1941	5.3×10^{-3}
Uranium hexafluoride	UF_6	337.17	151.7
Water	H_2O	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).

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 the 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. 3–21).

FIGURE 3–21
At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).

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_2 (dry ice), sublimation is the only way to change from the solid to the vapor phase at atmospheric conditions.

3 The P-T Diagram

Figure 3–22 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.

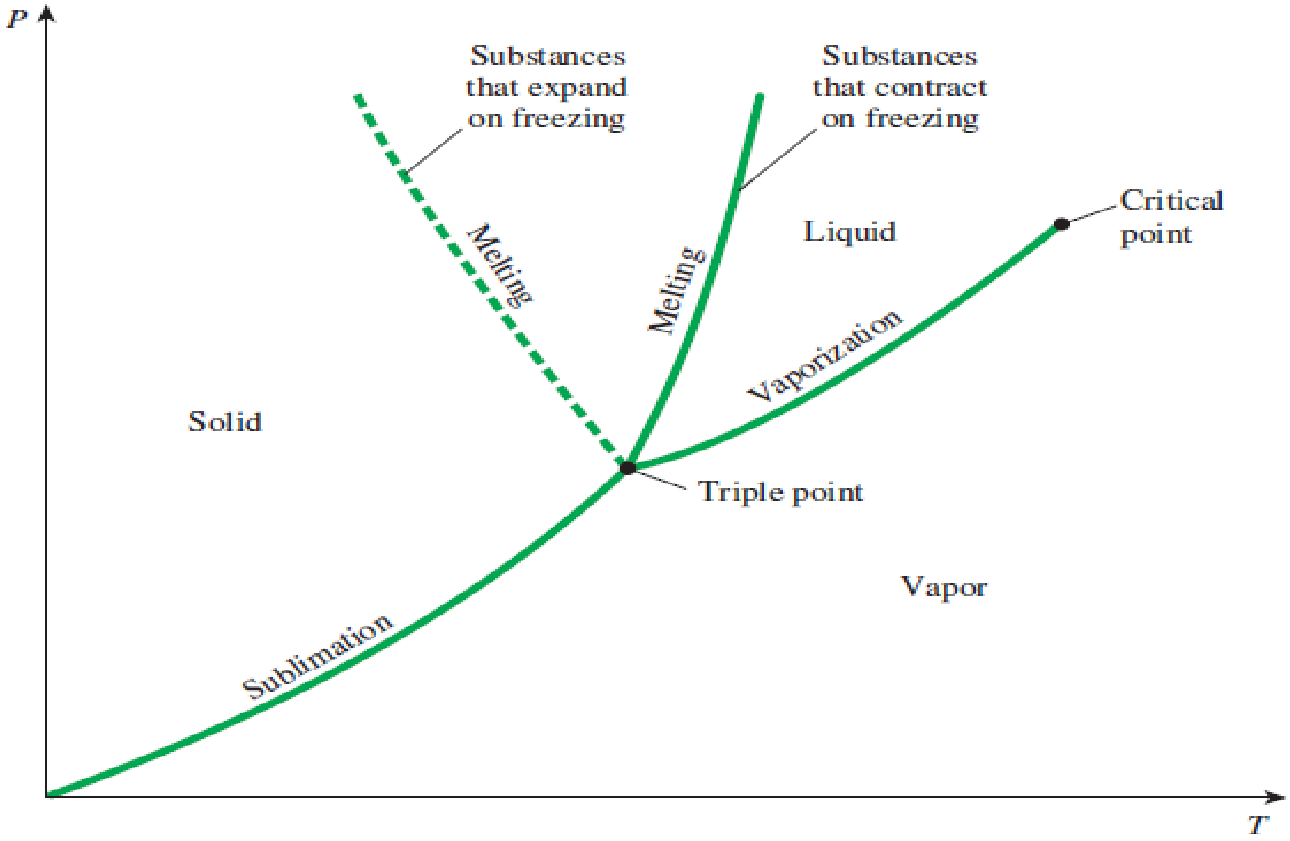


FIGURE 3–22 *P-T* diagram of pure substances.

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. 3–23 and 3–24. Here *T* and *v* may be 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.

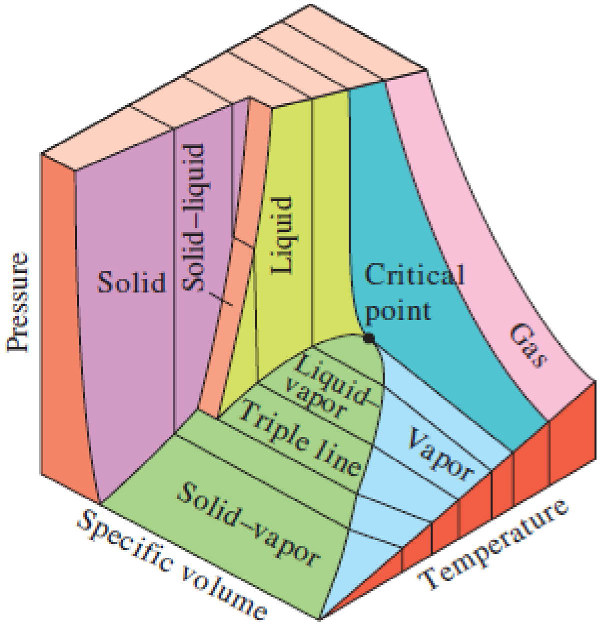


FIGURE 3–23
P-*v*-*T* surface of a substance that *contracts* on freezing.

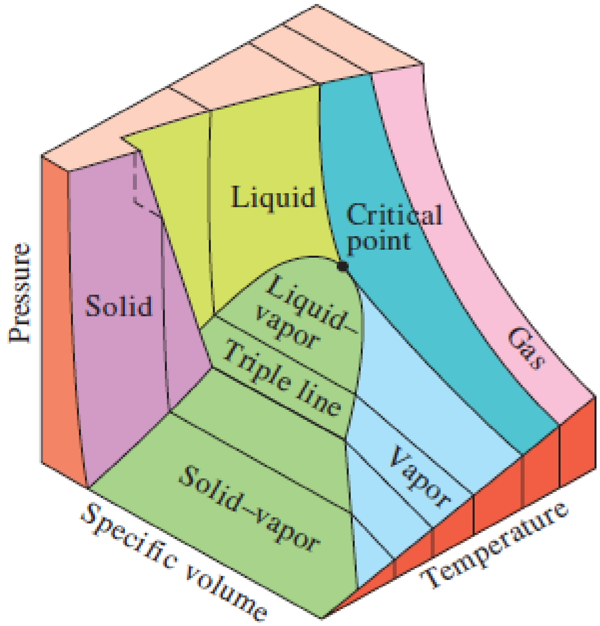


FIGURE 3–24
P-*v*-*T* surface of a substance that expands on freezing (like water).

3–5 PROPERTY TABLES

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 the latter 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*.

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. 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. 3–25), we often 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:

$$h = u + P\upsilon \qquad (\text{kJ/kg}) \tag{3–1}$$

or,

$$H = U + PV \qquad (\text{kJ}) \tag{3–2}$$

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. 3–26).

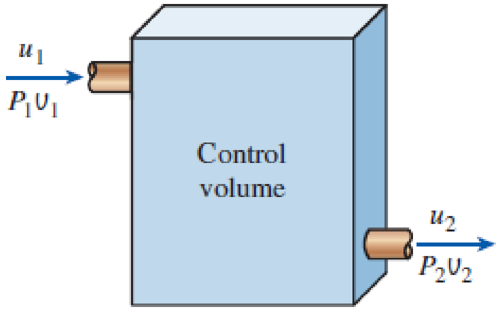
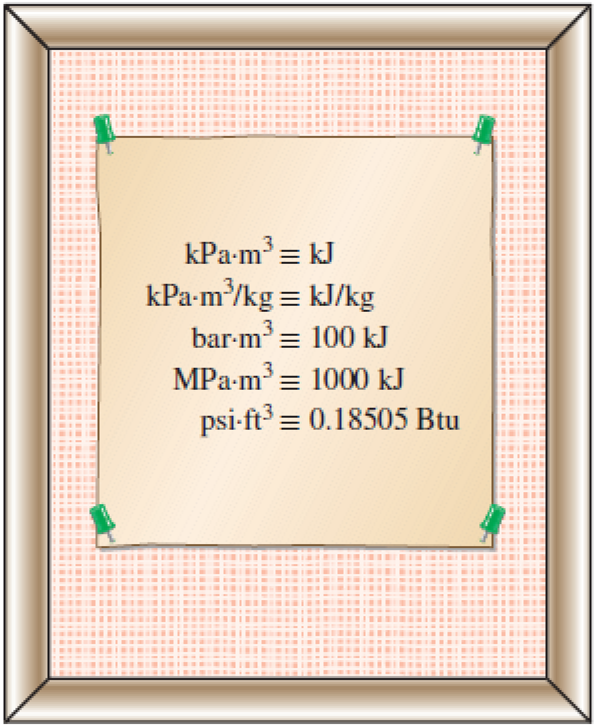


FIGURE 3–25
The combination $u + P\upsilon$ is often encountered in the analysis of control volumes.



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

FIGURE 3–26
The product *pressure* × *volume* has energy units.

For example, it can be easily shown that 1 $\text{kPa} \cdot \text{m}^3 = 1$ 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*).

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. 3–27.

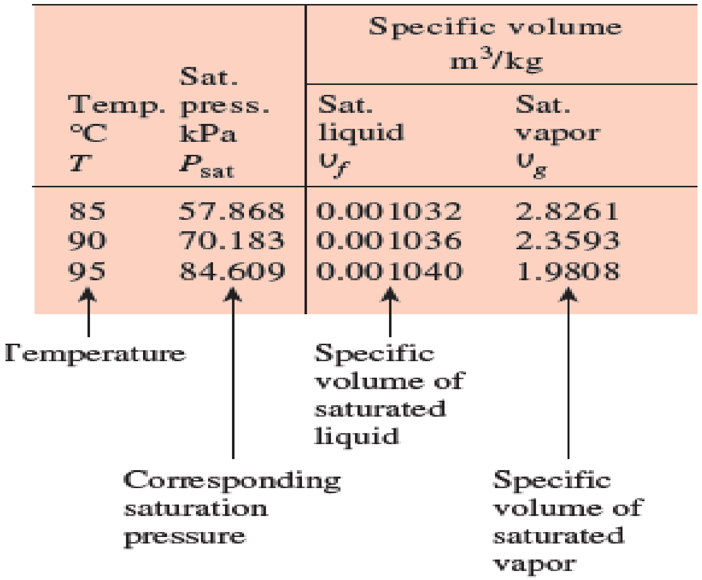
The subscript *f* is used to denote properties of a saturated liquid and the subscript *g* to denote the properties of saturated vapor. These symbols are commonly used in thermodynamics and originated from German. Another subscript commonly used is *fg*, which denotes the difference between the saturated 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 $\left(\text{that is } v_{fg} = v_g - v_f\right)$

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_{sat}	Specific volume m^3/kg Sat. liquid v_f	Specific volume m^3/kg Sat. vapor v_g
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

FIGURE 3–27
A partial list of Table A–4.

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-υ diagram in Fig. 3–28. Since saturation conditions exist in the tank, the pressure must be the saturation pressure at 90°C:

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

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

$$\upsilon = \upsilon_{f\text{ @ 90°C}} = 0.001036\ \text{m}^3/\text{kg} \qquad \text{(Table A-4)}$$

Then the total volume of the tank becomes

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

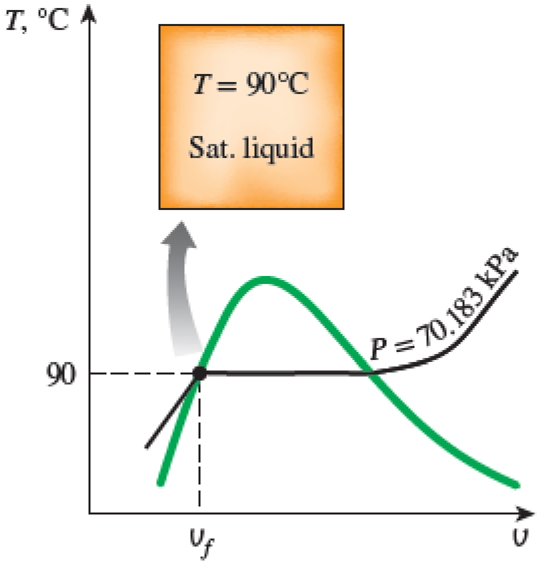


FIGURE 3–28
Schematic and T-υ diagram for Example 3–1.

EXAMPLE 3–2 Temperature of Saturated Vapor in a Cylinder

A piston–cylinder device contains 2 ft^3 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-υ diagram in Fig. 3–29. Since the cylinder contains saturated vapor at 50 psia, the temperature inside must be the saturation temperature at this pressure:

$$T = T_{\text{sat @ 50 psia}} = \mathbf{28.99°F} \qquad \text{(Table A–5E)}$$

The specific volume of the saturated vapor at 50 psia is

$$\upsilon = \upsilon_{g\text{ @ 50 psia}} = 8.5175\ \text{ft}^3/\text{lbm} \qquad \text{(Table A–5E)}$$

Then the mass of water vapor inside the cylinder becomes

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

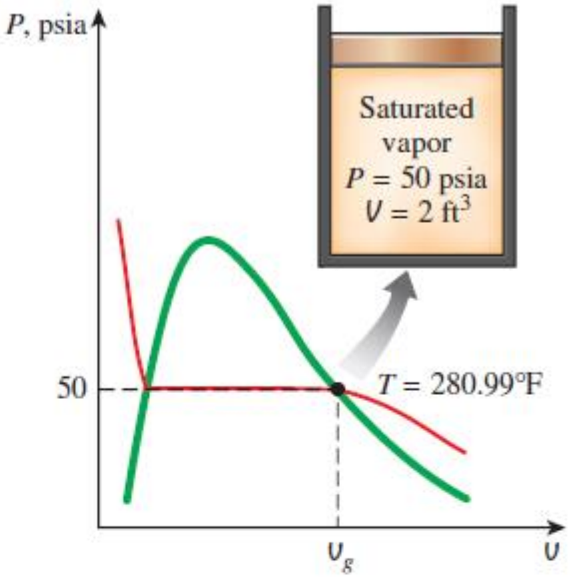


FIGURE 3–29
Schematic and P-υ diagram for Example 3–2.

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. 3–30. 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 $h_{fg} = 2257.5$ kJ/kg for water at 100 kPa. Thus, the amount of energy transferred is

$$m h_{fg} = (0.2 \text{ kg})(22575.5 \text{ kJ/kg}) = \mathbf{451.5 \text{ kJ}}$$

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.

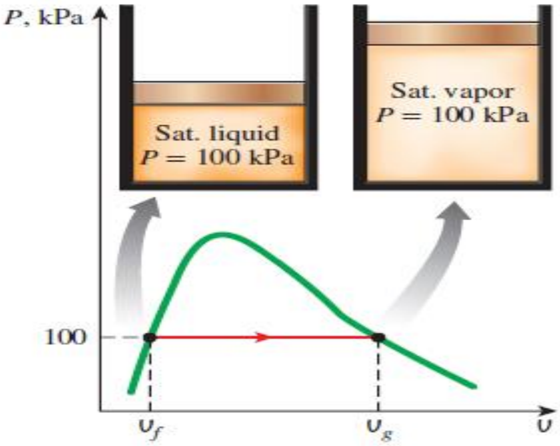


FIGURE 3–30
Schematic and *P*-v diagram for Example 3–3.

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. 3–31). 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:

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}} \qquad (3\text{–}3)$$

where

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

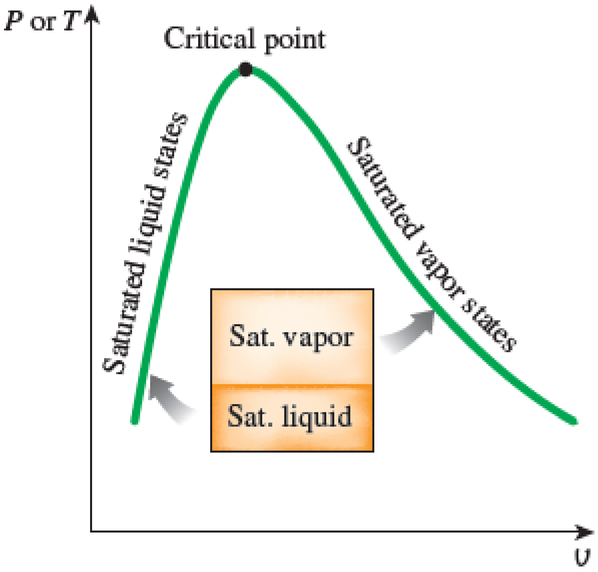


FIGURE 3–31
The relative amounts of liquid and vapor phases in a saturated mixture are specified by the *quality* x.

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 to imagine that the two phases are mixed well, forming a homogeneous mixture (Fig. 3–32). 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:

$$V = V_f + V_g$$

$$V = m\upsilon \longrightarrow m_t\upsilon_{\text{avg}} = m_f\upsilon_f + m_g\upsilon_g$$

$$m_f = m_t - m_g \longrightarrow m_t\upsilon_{\text{avg}} = (m_t - m_g)\upsilon_f + m_g\upsilon_g$$

Dividing by m_t yields

$$\upsilon_{\text{avg}} = (1 - x)\upsilon_f + x\upsilon_g$$

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

$$\upsilon_{\text{avg}} = \upsilon_f + x\upsilon_{fg} \qquad (\text{m}^3/\text{kg}) \tag{3–4}$$

where $\upsilon_{fg} = \upsilon_g - \upsilon_f$. Solving for quality, we obtain

$$x = \frac{\upsilon_{\text{avg}} - \upsilon_f}{\upsilon_{fg}} \tag{3–5}$$

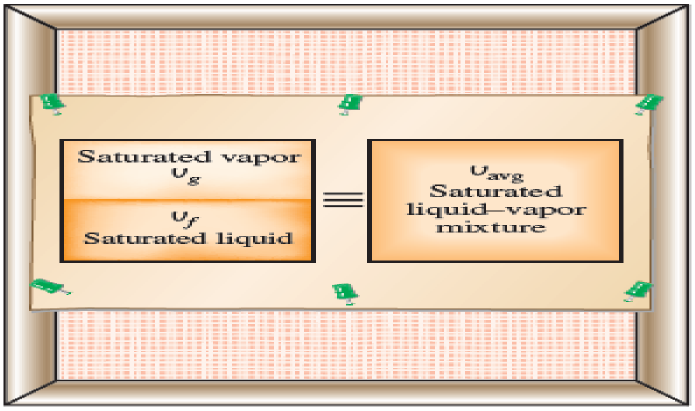


FIGURE 3–32
A two-phase system can be treated as a homogeneous mixture for convenience.

Based on this equation, quality can be related to the horizontal distances on a P-υ or T-υ diagram (Fig. 3–33). 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:

$$u_{\text{avg}} = u_f + xu_{fg} \qquad \text{(kJ/kg)} \tag{3–6}$$

$$h_{\text{avg}} = h_f + xh_{fg} \qquad \text{(kJ/kg)} \tag{3–7}$$

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

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

where y is υ, 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. 3–34). 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).

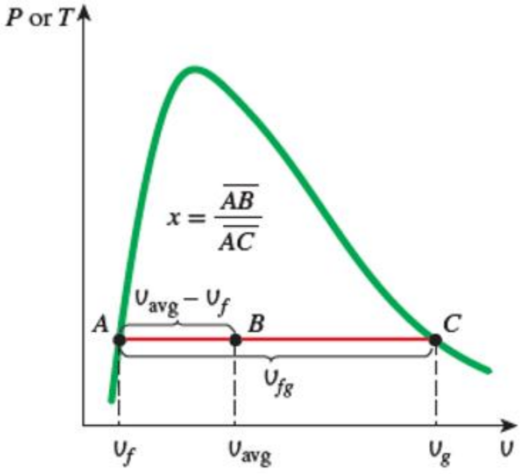


FIGURE 3–33
Quality is related to the horizontal distances on P-υ and T-υ diagrams.

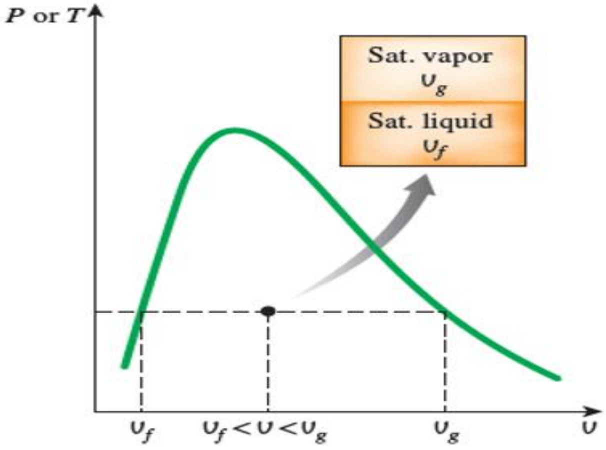


FIGURE 3–34
The υ value of a saturated liquid–vapor mixture lies between the υ_f and υ_g values at the specified T or P.

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. 3–35. Since the two phases coexist in equilibrium, we have a saturated mixture, and the pressure must be the saturation pressure at the given temperature:

$$P = P_{\text{sat @ 90°C}} = \mathbf{70.183\ kPa} \qquad \text{(Table A–4)}$$

(*b*) At 90°C, we have $\upsilon_f = 0.001036$ m³/kg and $\upsilon_g = 2.3593$ m³/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:

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

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

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

$$\begin{aligned} \upsilon &= \upsilon_f + x\upsilon_{fg} \\ &= 0.001036\ \text{m}^3/\text{kg} + (0.2)[(2.3593 - 0.001036)\ \text{m}^3/\text{kg}] \\ &= 0.473\ \text{m}^3/\text{kg} \end{aligned}$$

and

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

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.

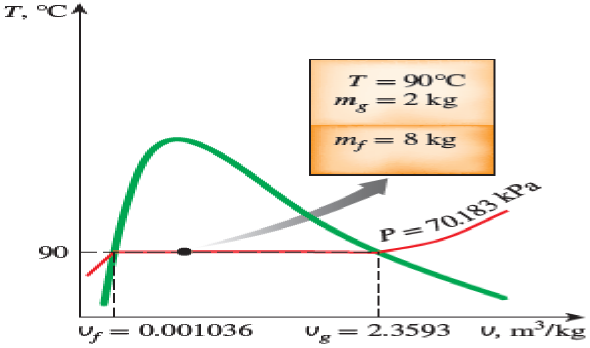


FIGURE 3–35
Schematic and T-υ diagram for Example 3–4.

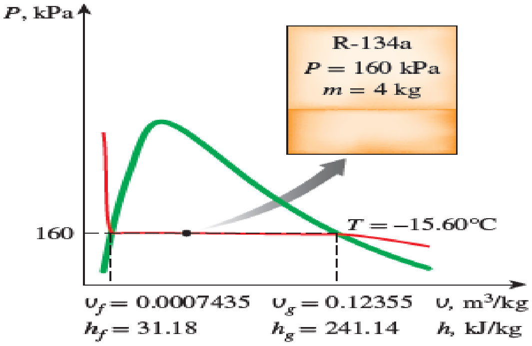
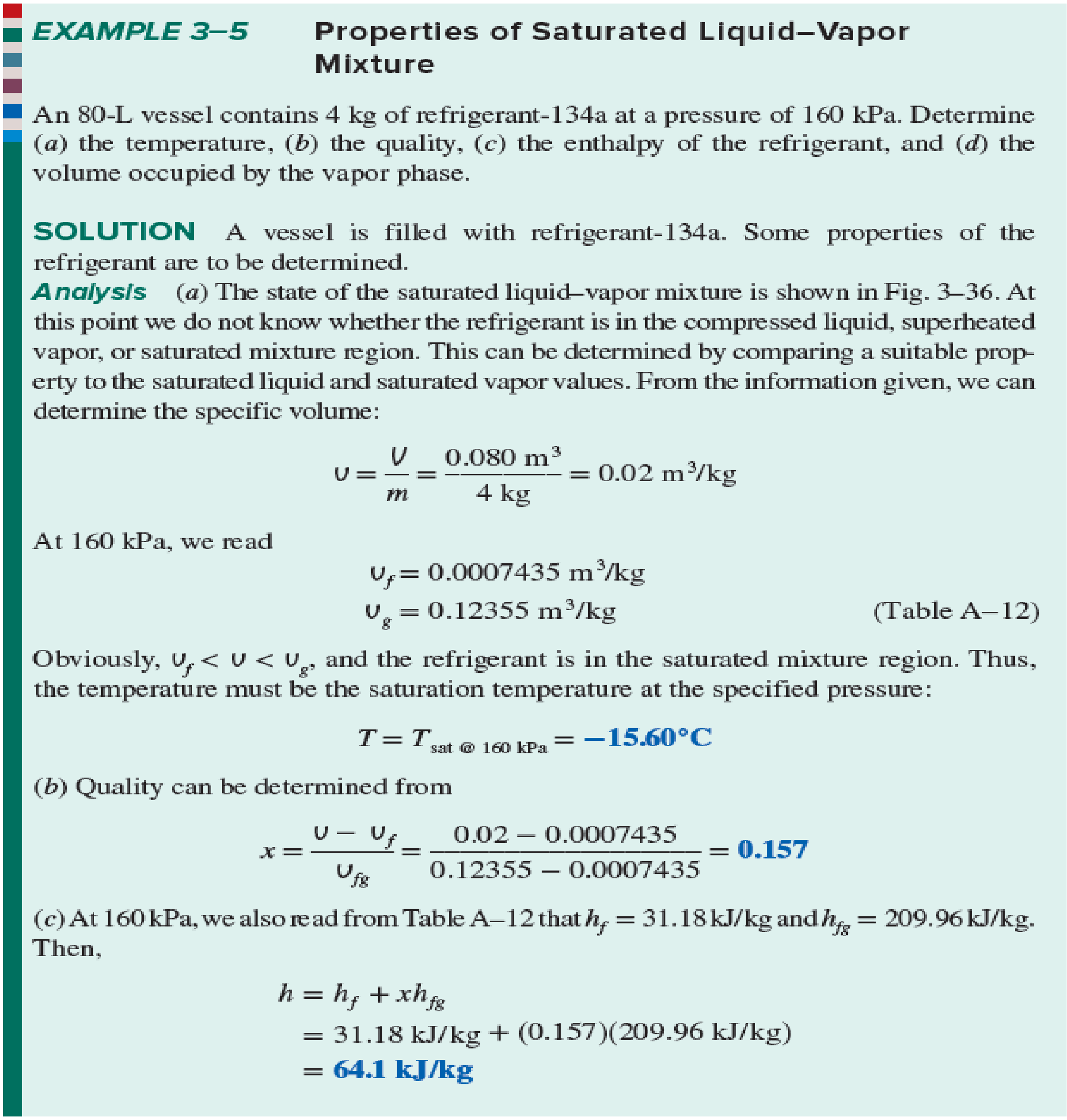


FIGURE 3–36
Schematic and P-υ diagram for Example 3–5.



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. 3–36. At this point we do not know whether the refrigerant is in the compressed liquid, superheated vapor, or saturated mixture region. This can 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

$$v_f = 0.0007435 \text{ m}^3/\text{kg}$$
$$v_g = 0.12355 \text{ m}^3/\text{kg} \qquad \text{(Table A–12)}$$

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:

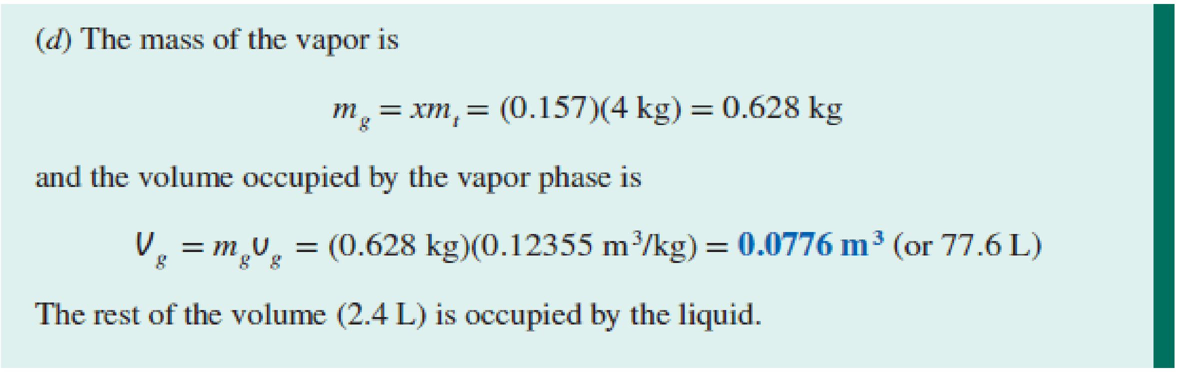
$$T = T_{\text{sat @ 160 kPa}} = \mathbf{-15.60°C}$$

(*b*) Quality can be determined from

$$x = \frac{v - v_f}{v_{fg}} = \frac{0.02 - 0.0007435}{0.12355 - 0.0007435} = \mathbf{0.157}$$

(*c*) At 160 kPa, we also read from Table A–12 that $h_f = 31.18$ kJ/kg and $h_{fg} = 209.96$ kJ/kg. Then,

$$\begin{aligned} h &= h_f + x h_{fg} \\ &= 31.18 \text{ kJ/kg} + (0.157)(209.96 \text{ kJ/kg}) \\ &= \mathbf{64.1 \text{ kJ/kg}} \end{aligned}$$



(*d*) The mass of the vapor is

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

and the volume occupied by the vapor phase is

$$V_g = m_g v_g = (0.628 \text{ kg})(0.12355 \text{ m}^3/\text{kg}) = \mathbf{0.0776 \text{ m}^3} \text{ (or 77.6 L)}$$

The rest of the volume (2.4 L) is occupied by the liquid.

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,

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

or

$$P\upsilon = RT \qquad (3\text{–}10)$$

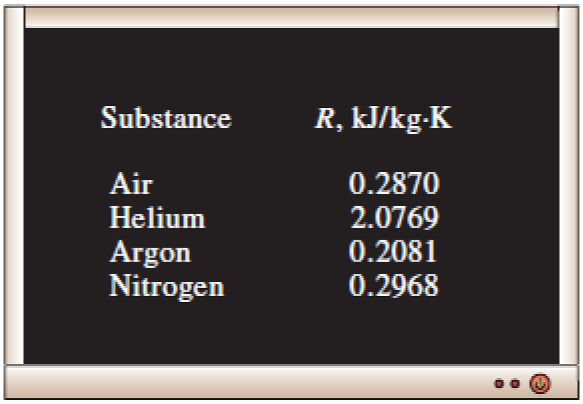
where the constant of proportionality *R* is called the **gas constant**. Equation 3–10 is called the **ideal-gas equation of state**, or simply the **ideal-gas relation**, and a gas that obeys this relation is called an **ideal gas**. In this equation, *P* is the absolute pressure, *T* is the absolute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

The gas constant *R* is different for each gas (Fig. 3–43) and is determined from

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

where *Ru* is the **universal gas constant** and *M* is the molar mass (also called *molecular weight)* of the gas. The constant *Ru* is the same for all substances, and its value is

$$R_u = \begin{cases} 8.31447 \text{ kJ/kmol·K} \\ 8.31447 \text{ kPa·m}^3\text{/kmol·K} \\ 0.0831447 \text{ bar·m}^3\text{/kmol·K} \\ 1.98588 \text{ Btu/lbmol·R} \\ 10.7316 \text{ psia·ft}^3\text{/lbmol·R} \\ 1545.37 \text{ ft·lbf/lbmol·R} \end{cases} \tag{3–11}$$



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

FIGURE 3–43
Different substances have different gas constants.

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, $M = 28$ kg/kmol $= 28$ lbm/lbmol.

The mass of a system is equal to the product of its molar mass M and the mole number N:

$$m = MN \qquad \text{(kg)} \tag{3–12}$$

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:

$$V = m\upsilon \longrightarrow PV = mRT \tag{3–13}$$

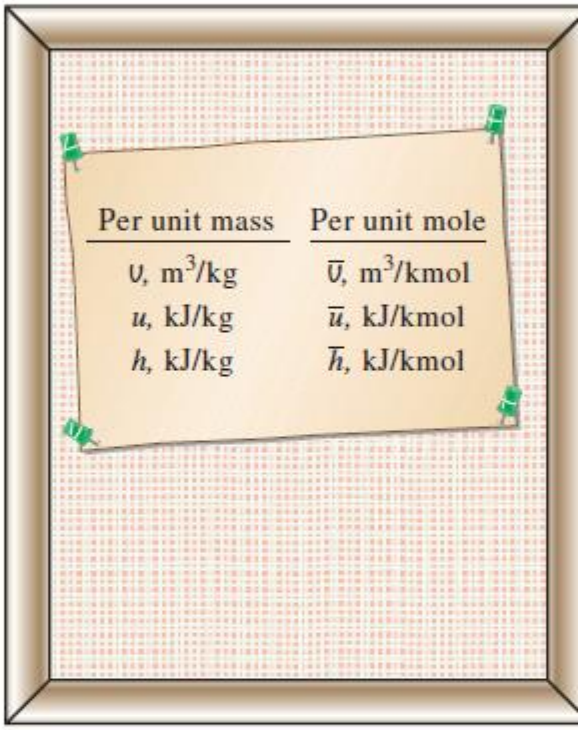
$$mR = (MN)R = NR_u \longrightarrow PV = NR_uT \tag{3–14}$$

$$V = N\bar{\upsilon} \longrightarrow P\bar{\upsilon} = R_uT \tag{3–15}$$

where $\bar{\upsilon}$ is the molar specific volume, that is, the volume per unit mole (in m^3/kmol or ft^3/lbmol). A bar above a property denotes values on a *unit-mole basis* throughout this text (Fig. 3–44).

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{3–16}$$

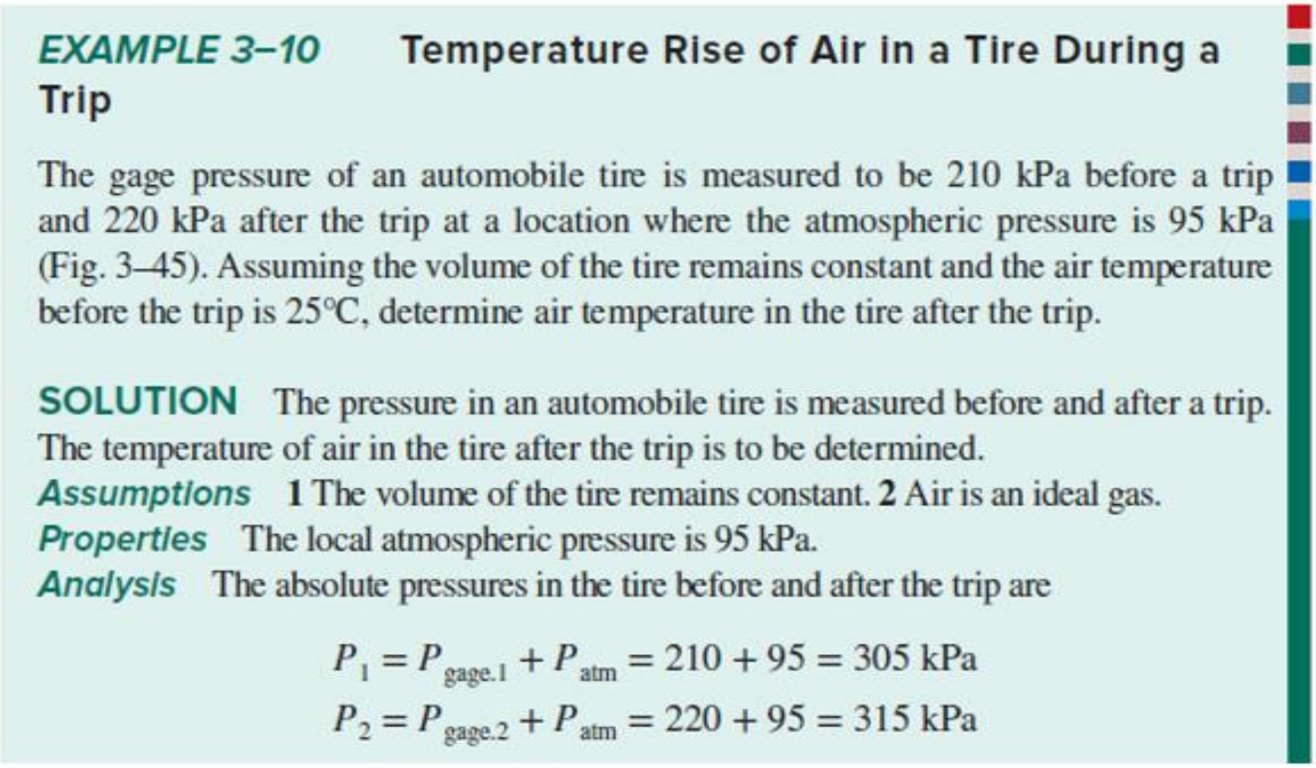


Per unit mass	Per unit mole
v, m^3/kg	$\bar{v}$, m^3/kmol
u, kJ/kg	$\bar{u}$, kJ/kmol
h, kJ/kg	$\bar{h}$, kJ/kmol

FIGURE 3–44
Properties per unit mole are denoted with a bar on the top.

An ideal gas is an *imaginary* substance that obeys the relation $Pv = RT$. 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, and carbon dioxide and even heavier gases such as krypton 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.



EXAMPLE 3–10 Temperature Rise of Air in a Tire During a Trip

The gage pressure of an automobile tire is measured to be 210 kPa before a trip and 220 kPa after the trip at a location where the atmospheric pressure is 95 kPa (Fig. 3–45). Assuming the volume of the tire remains constant and the air temperature before the trip is 25°C, determine air temperature in the tire after the trip.

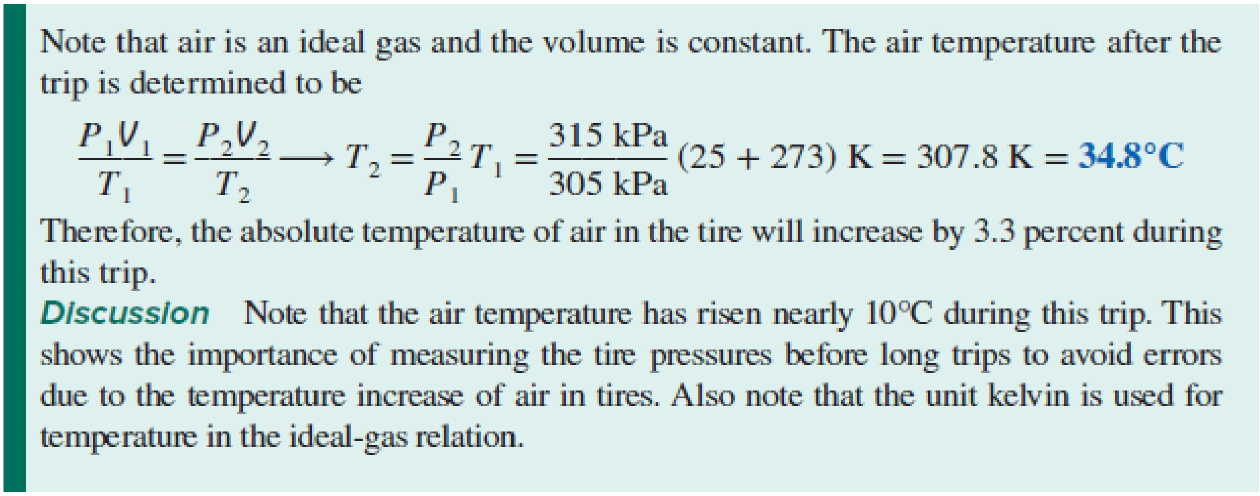
SOLUTION The pressure in an automobile tire is measured before and after a trip. The temperature of air in the tire after the trip is to be determined.

Assumptions **1** The volume of the tire remains constant. **2** Air is an ideal gas.

Properties The local atmospheric pressure is 95 kPa.

Analysis The absolute pressures in the tire before and after the trip are

$$P_1 = P_{\text{gage.1}} + P_{\text{atm}} = 210 + 95 = 305 \text{ kPa}$$
$$P_2 = P_{\text{gage.2}} + P_{\text{atm}} = 220 + 95 = 315 \text{ kPa}$$



Note that air is an ideal gas and the volume is constant. The air temperature after the trip is determined to be

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \longrightarrow T_2 = \frac{P_2}{P_1} T_1 = \frac{315 \text{ kPa}}{305 \text{ kPa}} (25 + 273) \text{ K} = 307.8 \text{ K} = \mathbf{34.8°C}$$

Therefore, the absolute temperature of air in the tire will increase by 3.3 percent during this trip.

Discussion Note that the air temperature has risen nearly 10°C during this trip. This shows the importance of measuring the tire pressures before long trips to avoid errors due to the temperature increase of air in tires. Also note that the unit kelvin is used for temperature in the ideal-gas relation.

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. 3–46. 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 (over 100 percent) and the saturated vapor line. 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, the ideal-gas relation should not be used.

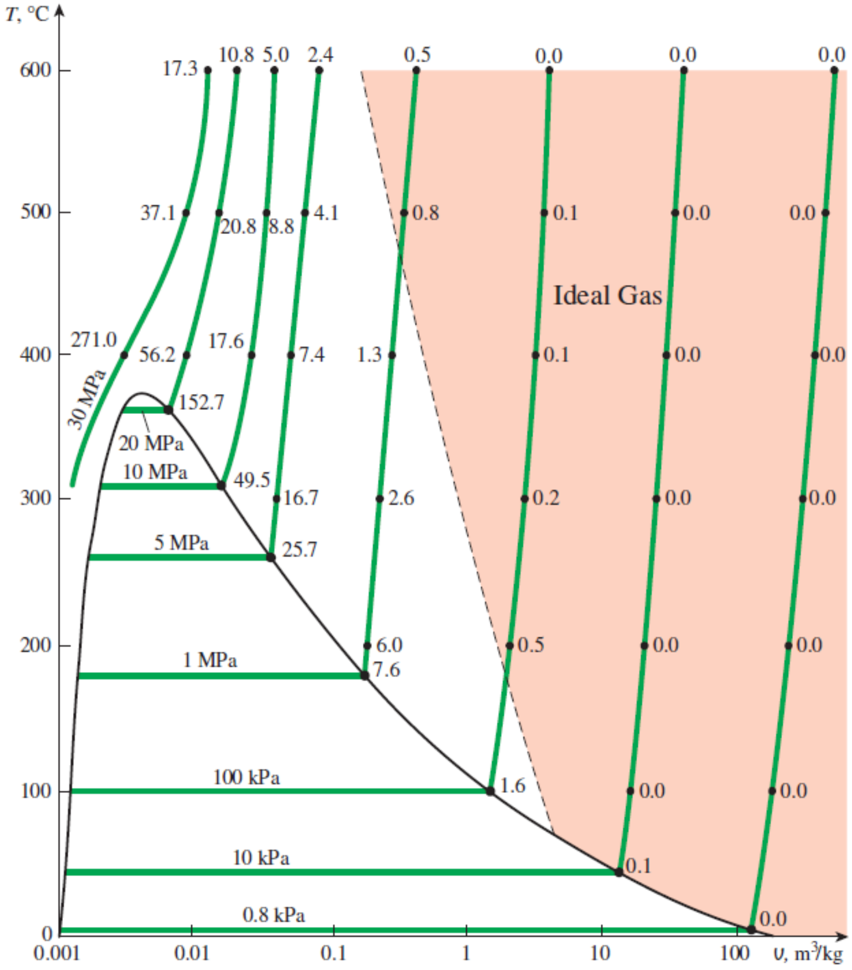


FIGURE 3–46
Percentage of error ($[|\upsilon_{table} - \upsilon_{ideal}|/\upsilon_{table}] \times 100$) involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with less than 1 percent error.