

PROPERTIES OF PURE SUBSTANCES

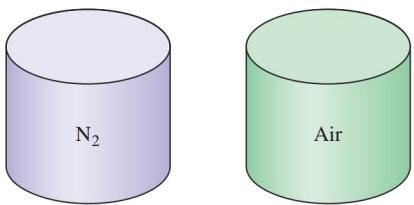
We start this chapter with the introduction of the concept of a *pure substance* and a discussion of the physics of phase-change processes.

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.

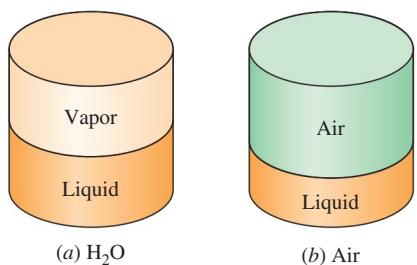
OBJECTIVES

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.

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.

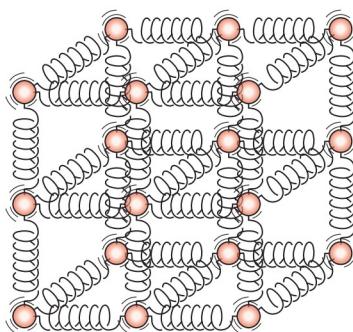
3.2 • PHASES OF A PURE SUBSTANCE

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.

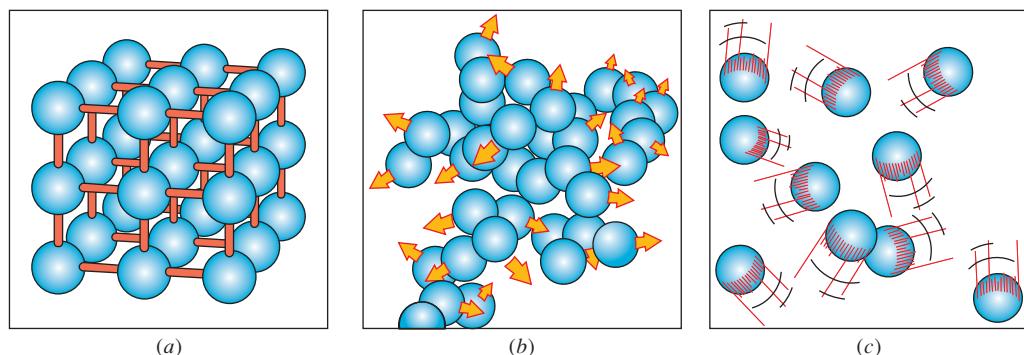
When studying phases or phase changes in thermodynamics, one does not need to be concerned with the molecular structure and behavior of different phases. However, it is very helpful to have some understanding of the molecular phenomena involved in each phase, and a brief discussion of phase transformations 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. Note that the attractive forces between molecules turn to repulsive forces as the distance between the molecules approaches zero, thus preventing the molecules from

**FIGURE 3-3**

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

**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.

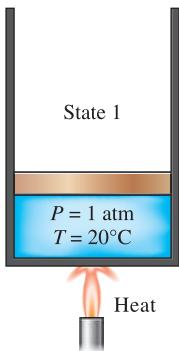
piling up on top of each other. Even though the molecules in a solid cannot move relative to each other, they continually oscillate about their equilibrium positions. The velocity of the molecules during these oscillations depends on the temperature. At sufficiently high temperatures, the velocity (and 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). 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.

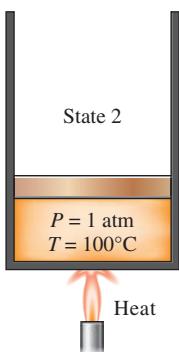
In the **gas** phase, the molecules are far apart from each other, and a molecular order is nonexistent. Gas molecules move about at random, continually colliding with each other and the walls of the container they are in. Particularly at low densities, the intermolecular forces are very small, and collisions 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

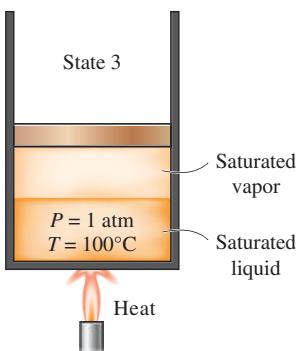
There are many practical situations where two phases of a pure substance coexist in equilibrium. Water exists as a mixture of liquid and vapor in the boiler and the condenser of a steam power plant. The refrigerant turns from liquid to vapor in the freezer of a refrigerator. Even though many home owners consider the freezing of water in underground pipes as the most important phase-change process, attention in this section is focused on the

**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*).

**FIGURE 3–7**

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

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.

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. 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.

One 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). 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. 3–10.

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 .

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 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 practically

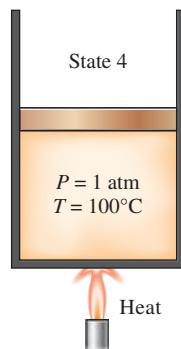


FIGURE 3–8

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

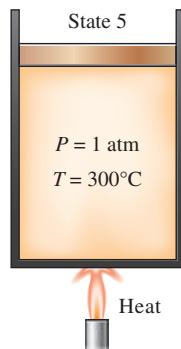


FIGURE 3–9

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

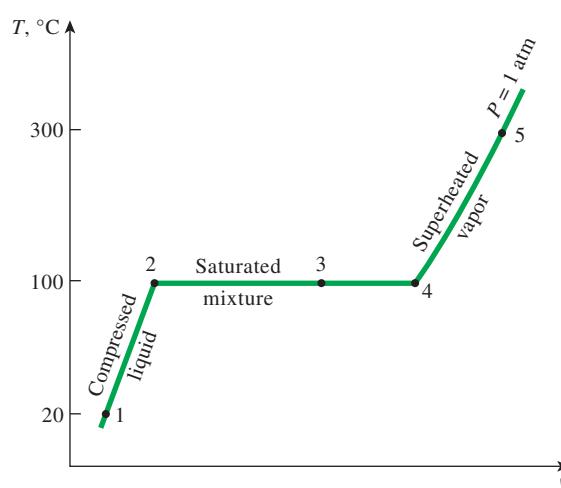


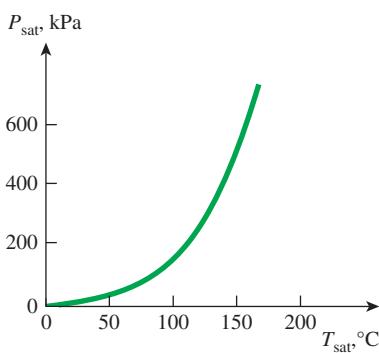
FIGURE 3–10

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

TABLE 3–1

Saturation (or vapor) pressure of water at various temperatures

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

**FIGURE 3–11**

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

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_{sat} versus P_{sat} , such as the one given for water in Fig. 3–11, is called a **liquid–vapor saturation curve**. 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 1°C.

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. 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°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-3a). 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). 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.

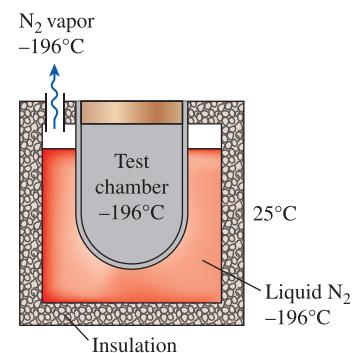
A practical way of cooling leafy vegetables is **vacuum cooling**, which is based on *reducing the pressure* of the sealed cooling chamber to the saturation pressure at the desired low temperature, and evaporating some water from the products to be cooled. The heat of vaporization during evaporation 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).

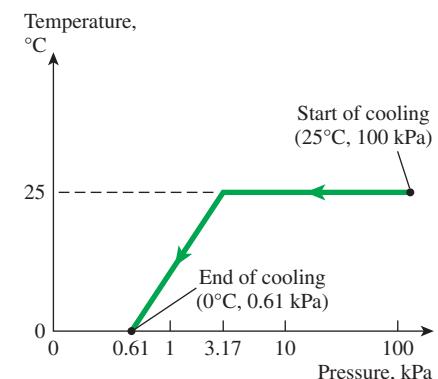
TABLE 3-2

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

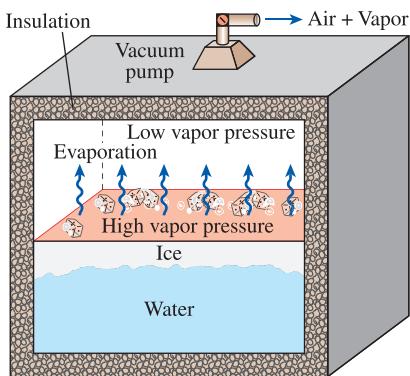
Elevation, m	Atmospheric pressure, kPa	Boiling temperature, $^{\circ}\text{C}$
0	101.33	100.0
1,000	89.55	96.5
2,000	79.50	93.3
5,000	54.05	83.3
10,000	26.50	66.3
20,000	5.53	34.7

**FIGURE 3-12**

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

**FIGURE 3-13**

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

**FIGURE 3–14**

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

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. 3–14).

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.

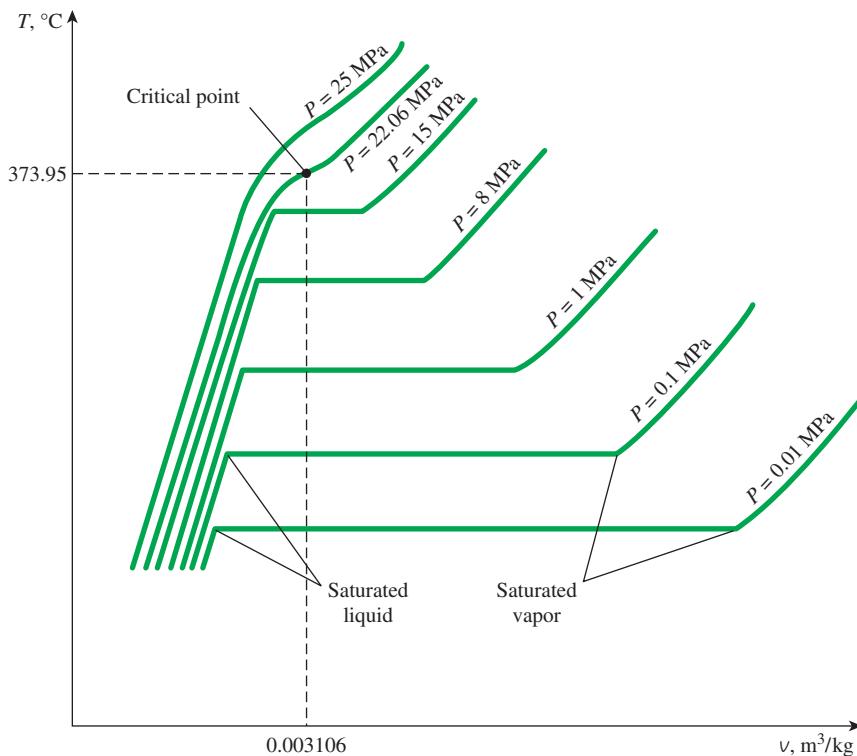
1 The T - v Diagram

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.

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*

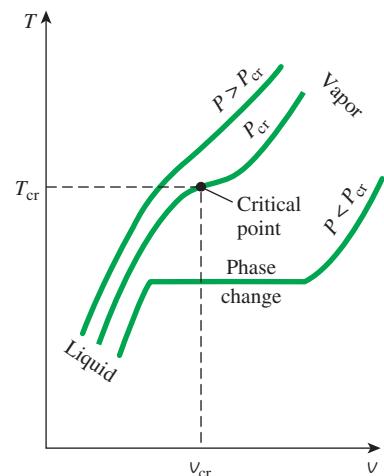
**FIGURE 3–15**

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

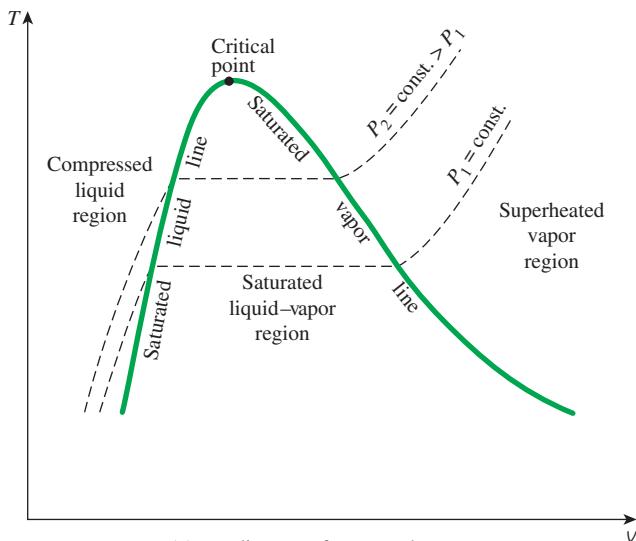
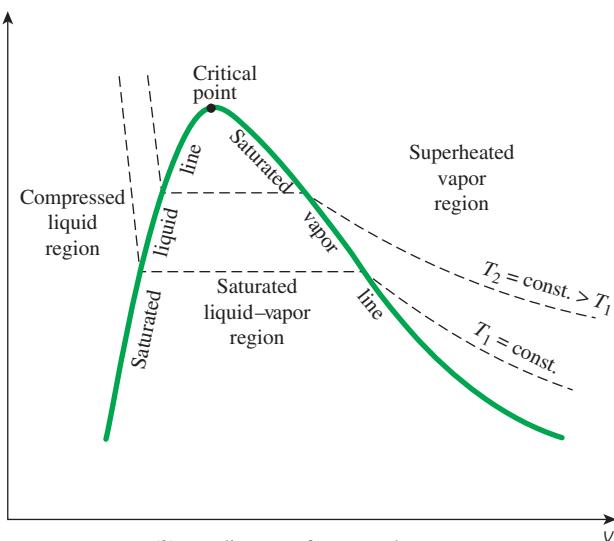
pressure P_{cr} , and critical specific volume v_{cr} . The critical-point properties of water are $P_{\text{cr}} = 22.06 \text{ MPa}$, $T_{\text{cr}} = 373.95^\circ\text{C}$, and $v_{\text{cr}} = 0.003106 \text{ m}^3/\text{kg}$. For helium, they are 0.23 MPa, -267.85°C , and $0.01444 \text{ m}^3/\text{kg}$. 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). 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. 3–17a. 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**.

**FIGURE 3–16**

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

(a) T - v diagram of a pure substance(b) P - v diagram of a pure substance**FIGURE 3–17**

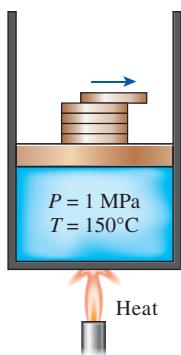
Property diagrams of a pure substance.

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 $T = \text{constant}$ lines on this diagram have a downward trend, as shown in Fig. 3–17b.

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). 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 $T_{\text{sat}} = f(P_{\text{sat}})$], 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. 3–17b.

**FIGURE 3–18**

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

Extending the Diagrams to Include the Solid Phase

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

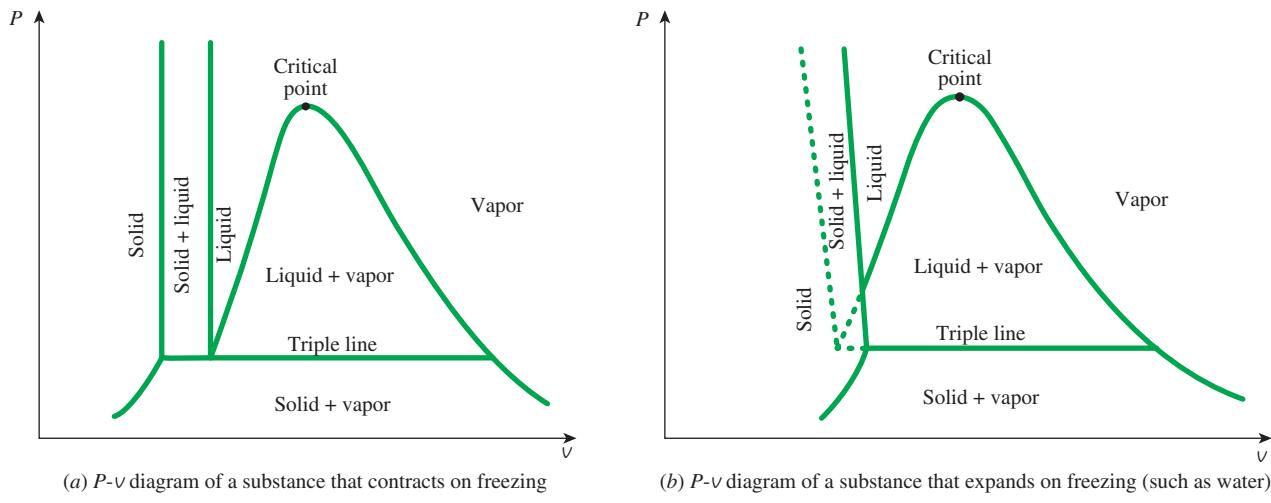


FIGURE 3-19

 P - v diagrams of different substances.

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. 3-19a and 3-19b. 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.

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). 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. For example, water cannot exist in liquid form



FIGURE 3-20

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	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).

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. 3-21). 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 vapor phase at atmospheric conditions.

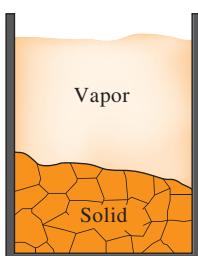


FIGURE 3-21

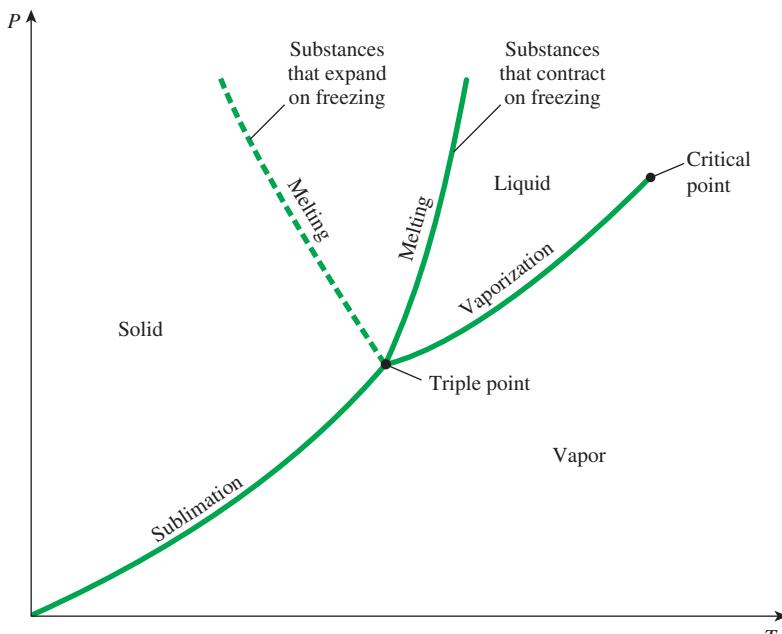
At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).

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

FIGURE 3-22

P-T diagram of pure substances.



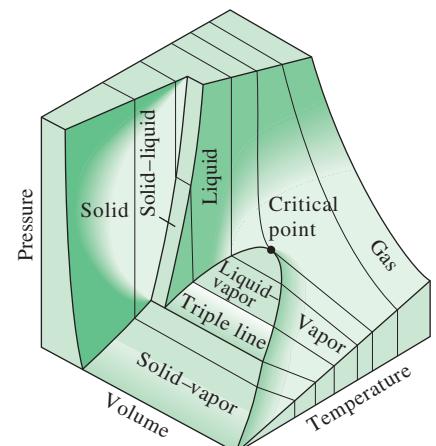
regions, the vaporization line separates the liquid and vapor regions, and the melting (or fusion) line separates the solid and liquid regions. These three lines meet at the triple point, where all three phases coexist in equilibrium. The vaporization line ends at the critical point because no distinction 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.

The *P-v-T* Surface

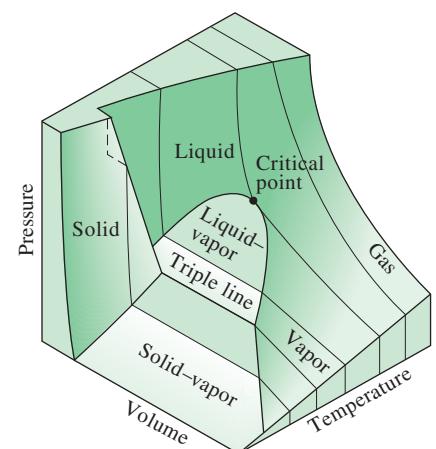
The state of a simple compressible substance is fixed by any two independent, intensive properties. Once the two appropriate properties are fixed, all the other properties become dependent properties. Remembering that any equation with two independent variables in the form $z = z(x, y)$ represents a 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.

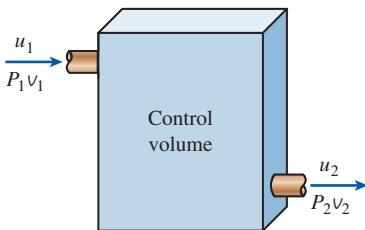
All the two-dimensional diagrams we have discussed so far are merely projections of this three-dimensional surface onto the appropriate planes. A *P-v* diagram is just a projection of the *P-v-T* surface on the *P-v* plane, and a *T-v* diagram is nothing more than the bird's-eye view of this surface.

**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).

**FIGURE 3-25**

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

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*.

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. 3-25), 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 :

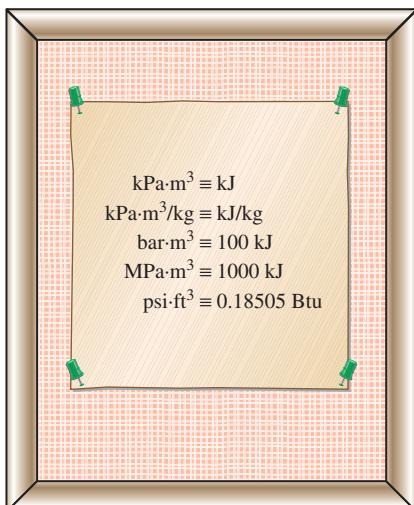
$$h = u + Pv \quad (\text{kJ/kg}) \quad (3-1)$$

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. 3-26). 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

**FIGURE 3-26**

The product *pressure* \times *volume* has energy units.

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

The quantity v_{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.

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

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

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

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

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

Specific temperature Corresponding saturation pressure Specific volume of saturated liquid Specific volume of saturated vapor

FIGURE 3-27

A partial list of Table A-4.

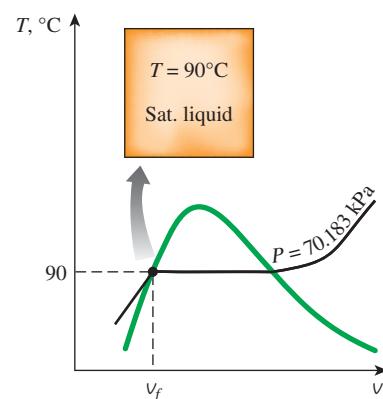


FIGURE 3-28

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

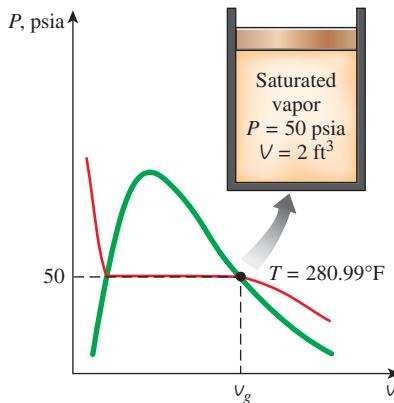


FIGURE 3-29

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^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 - v 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:

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

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

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

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. 3-30. 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,

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

(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

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

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.

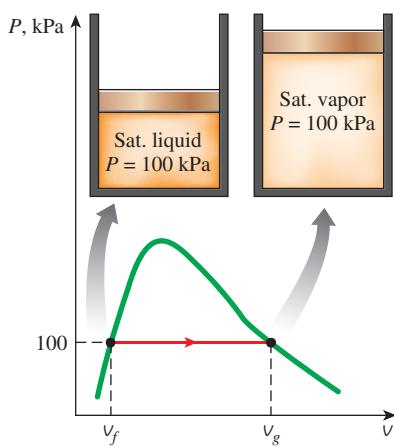


FIGURE 3-30

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:

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

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 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:

$$V = V_f + V_g$$

$$V = mV \longrightarrow m_t V_{\text{avg}} = m_f V_f + m_g V_g$$

$$m_f = m_t - m_g \longrightarrow m_t V_{\text{avg}} = (m_t - m_g)V_f + m_g V_g$$

Dividing by m_t yields

$$V_{\text{avg}} = (1 - x)V_f + xV_g$$

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

$$V_{\text{avg}} = V_f + xV_{fg} \quad (\text{m}^3/\text{kg}) \quad (3-4)$$

where $V_{fg} = V_g - V_f$. Solving for quality, we obtain

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

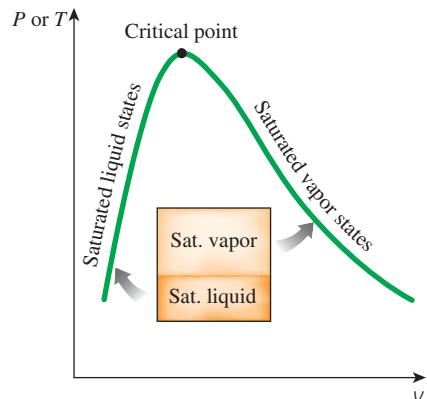


FIGURE 3–31

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

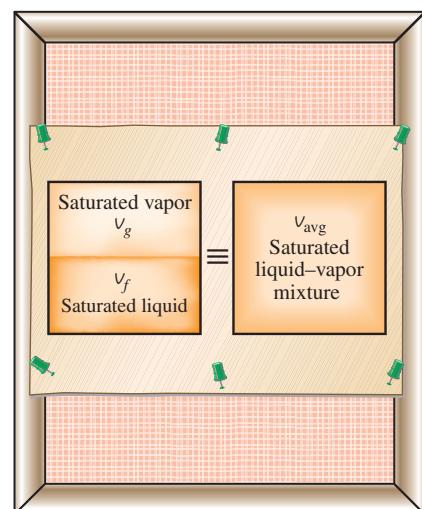
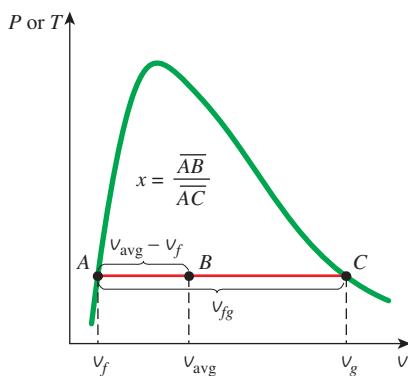
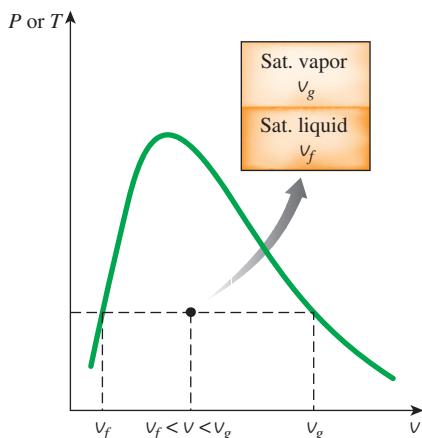


FIGURE 3–32

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

**FIGURE 3-33**

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

**FIGURE 3-34**

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

Based on this equation, quality can be related to the horizontal distances on a P - v or T - v 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:

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

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

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

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

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. 3-34). 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).

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:

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

(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:

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

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

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

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

and

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

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.

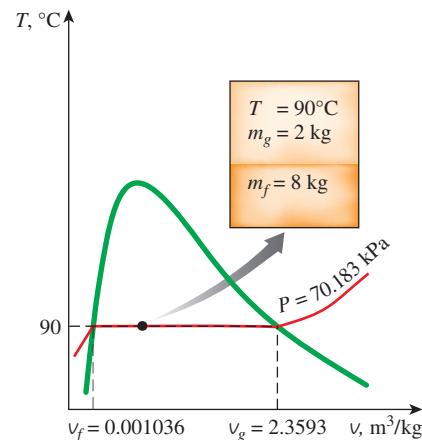


FIGURE 3-35

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

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

$$\begin{aligned} v_f &= 0.0007435 \text{ m}^3/\text{kg} \\ v_g &= 0.12355 \text{ m}^3/\text{kg} \end{aligned} \quad (\text{Table A-12})$$

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:

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

(b) Quality can be determined from

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

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

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

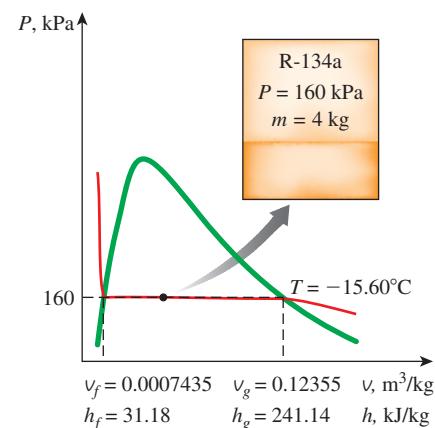


FIGURE 3-36

Schematic and P - v diagram for Example 3-5.

(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

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

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

$T, ^\circ\text{C}$	v m ³ /kg	u kJ/kg	h 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
⋮	⋮	⋮	⋮
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 3–37

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. 3–37.

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

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

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. 3-38, 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

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

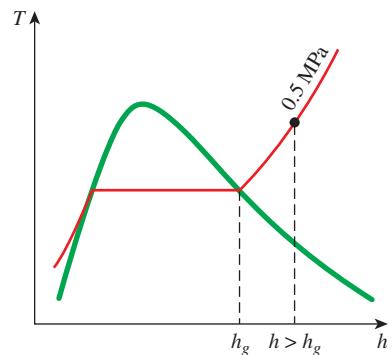


FIGURE 3-38

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.

In the absence of compressed liquid data, a general approximation is to treat compressed liquid as saturated liquid at the given temperature (Fig. 3-39). This is because the compressed liquid properties depend on temperature much more strongly than they do on pressure. Thus,

$$y \approx y_f @ T \quad (3-8)$$

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

$$h \approx h_f @ T + v_f @ T (P - P_{\text{sat} @ T}) \quad (3-9)$$

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, 2006).

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)

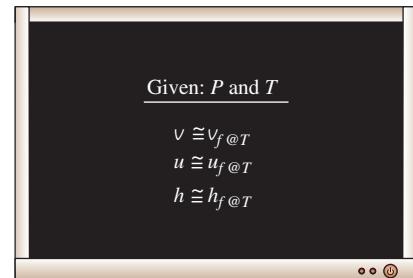


FIGURE 3-39

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

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.

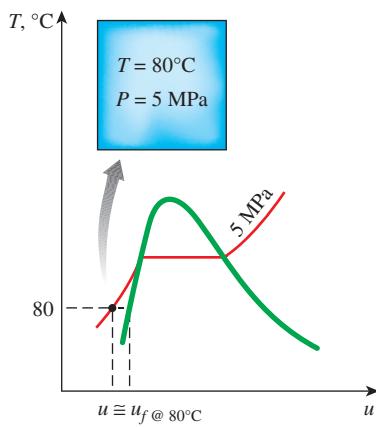


FIGURE 3-40

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 $5 \text{ MPa} > P_{\text{sat}}$, we obviously have compressed liquid, as shown in Fig. 3-40.

(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

$$u \approx u_f @ 80^\circ\text{C} = 334.97 \text{ kJ/kg}$$

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°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°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	$u, \text{kJ/kg}$	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:

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

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

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

(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°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°C . Therefore, we have saturated liquid-vapor mixture. Then the pressure must be the saturation pressure at the given temperature:

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

The quality is determined from

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

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

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

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_{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*

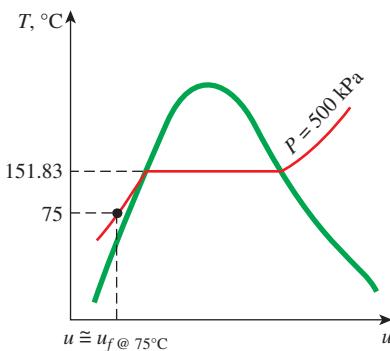


FIGURE 3-41

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

In our case, the given T value is 75°C , which is less than the T_{sat} value at the specified pressure. Therefore, we have compressed liquid (Fig. 3-41), 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):

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

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:

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

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

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. 3–42) and is determined from

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

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

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

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, $M = 28 \text{ kg/kmol} = 28 \text{ lbm/lbmol}$.

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

FIGURE 3–42

Different substances have different gas constants.

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:

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

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

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

where \bar{v} 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. 3-43).

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 $PV = RT$. 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.

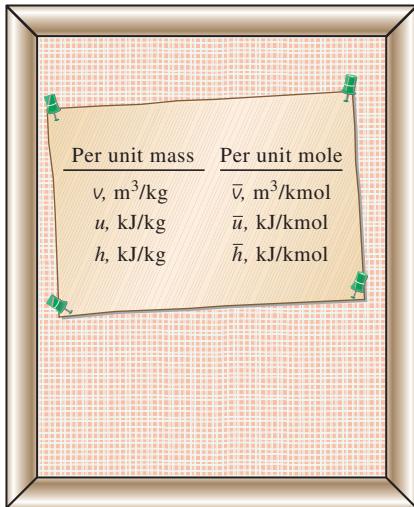


FIGURE 3-43

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

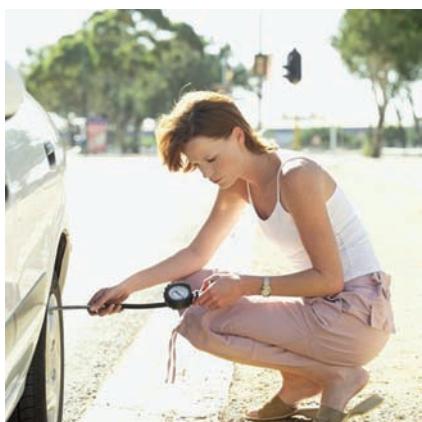


FIGURE 3-44

©Stockbyte/Getty Images RF

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. 3-44). 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 temperatures after the trip is determined to be

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

Therefore, the absolute temperature of air in the tire will increase by 6.9% 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 temperature rise of air in tire. 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. 3–45. It is clear from this figure that at pressures below 10 kPa, water

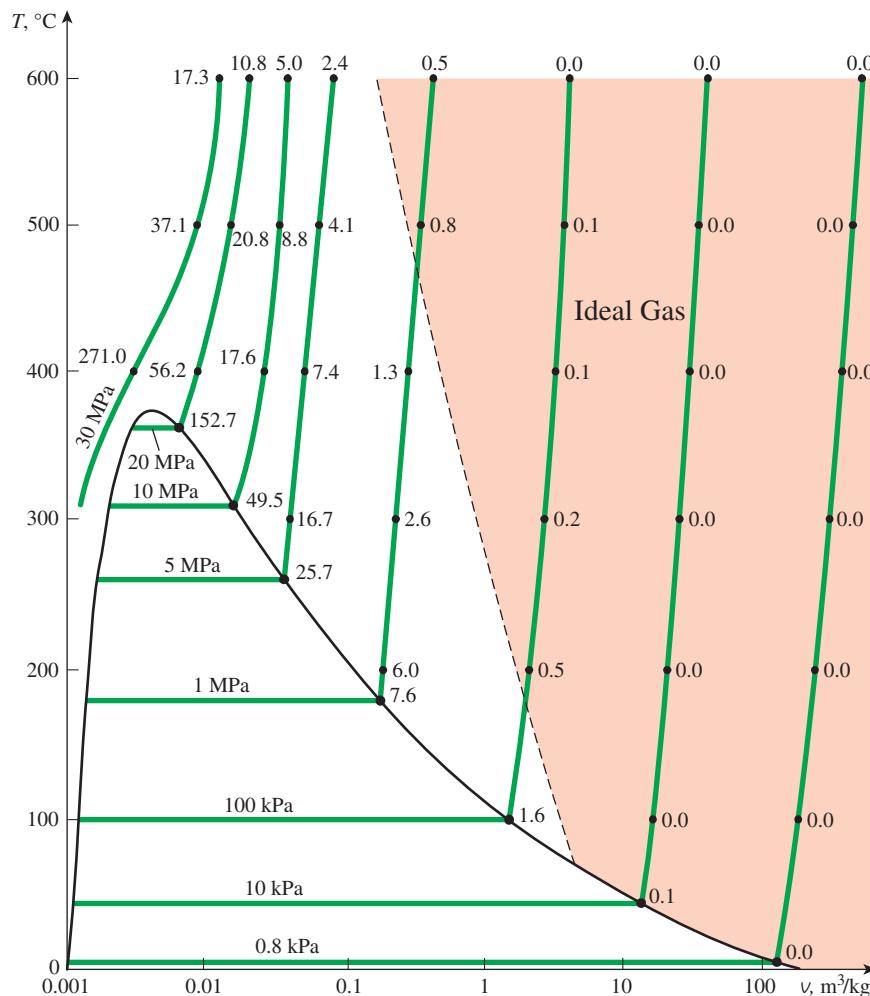


FIGURE 3–45
Percentage of error
($\left| \frac{V_{\text{table}} - V_{\text{ideal}}}{V_{\text{table}}} \right| \times 100$)
involved in assuming steam to be an
ideal gas, and the region where steam
can be treated as an ideal gas with less
than 1 percent error.

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. 3-45, 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

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

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. 3-46). The farther away Z is from unity, the more the gas deviates from ideal-gas behavior.

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°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°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

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

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**.

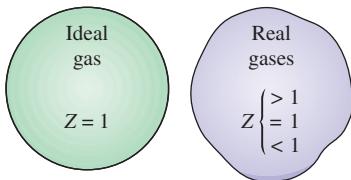
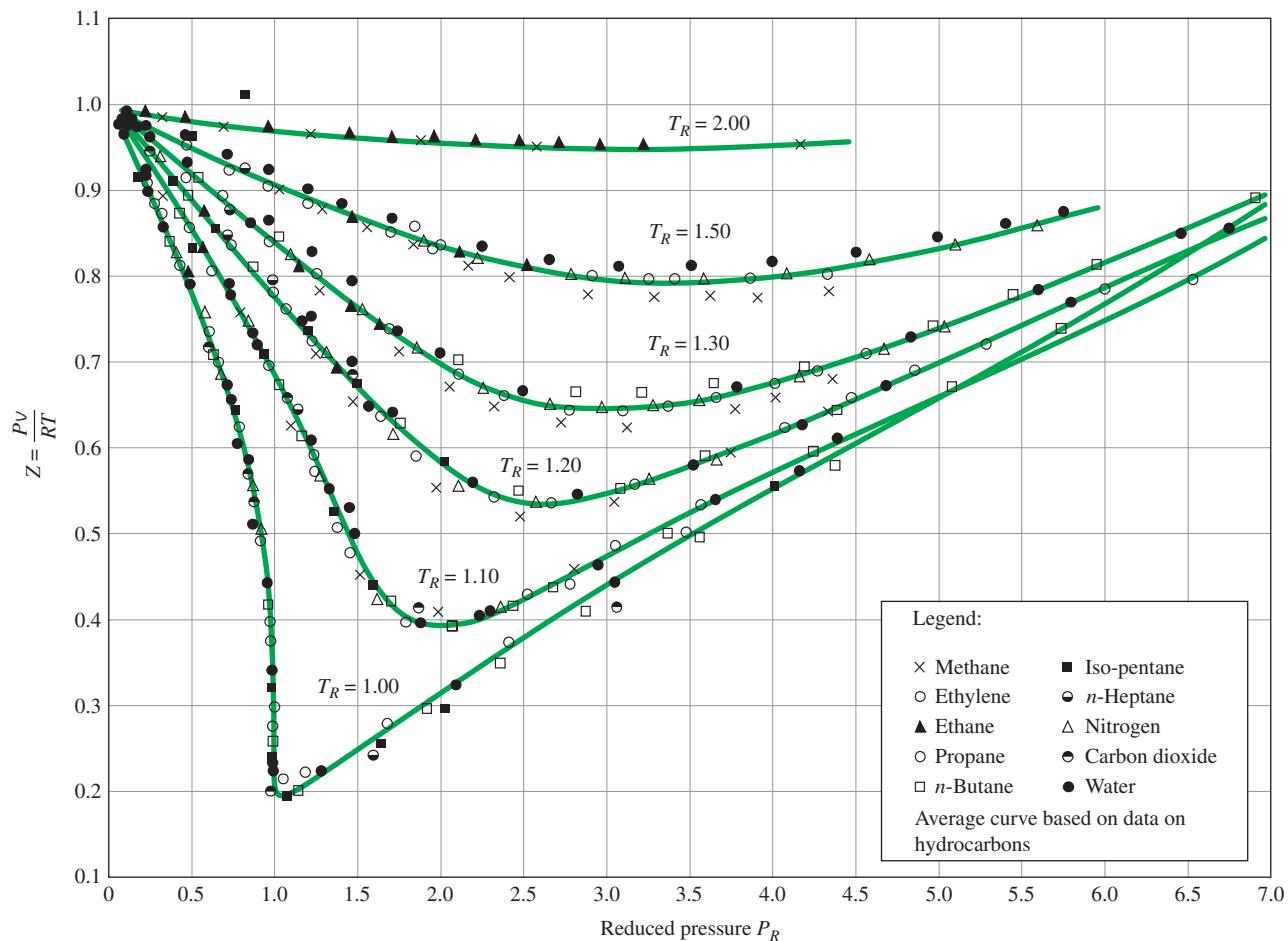


FIGURE 3-46

The compressibility factor is unity for ideal gases.

**FIGURE 3-47**

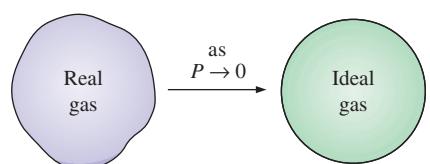
Comparison of Z factors for various gases.

Source: Gour-Jen Su, "Modified Law of Corresponding States," *Ind. Eng. Chem. (international ed.)* 38 (1946), p. 803.

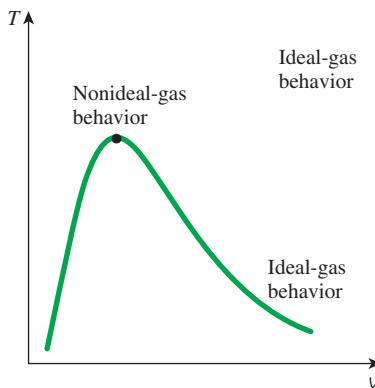
In Fig. 3-47, the experimentally determined Z values are plotted against P_R and T_R for several gases. The gases seem to obey the principle of corresponding states reasonably well. By curve-fitting all the data, we obtain the **generalized compressibility chart** that can be used for all gases (Fig. 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. 3-48).
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. 3-49).

**FIGURE 3-48**

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

**FIGURE 3-49**

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

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 m³/kg and determine the error involved in each case.

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

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 $(0.026325 - 0.021796)/0.021796 = 0.208$, or 20.8 percent in this case.

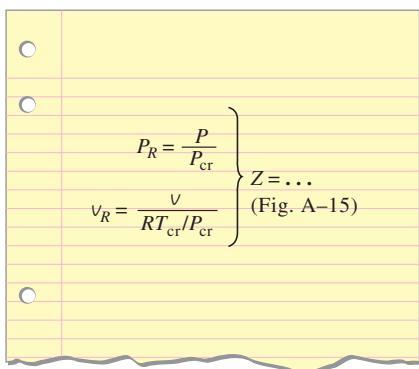
(b) To determine the correction factor Z from the compressibility chart, we first need to calculate the reduced pressure and temperature:

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

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.

**FIGURE 3-50**

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

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_{cr} and P_{cr} instead of v_{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. 3-50).

EXAMPLE 3-12 Using Generalized Charts to Determine Pressure

- Determine the pressure of water vapor at 600°F and 0.51431 ft³/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. 3-51. 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

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

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

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

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:

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

Thus,

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

Discussion Using the compressibility chart reduced the error from 22.8 to 5.6 percent, which is acceptable for most engineering purposes (Fig. 3-52). 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.

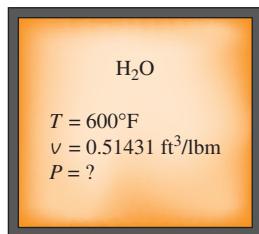


FIGURE 3-51

Schematic for Example 3-12.

	P, psia
Exact	1000
Z chart	1056
Ideal gas	1228
(from Example 3-12)	

FIGURE 3-52

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

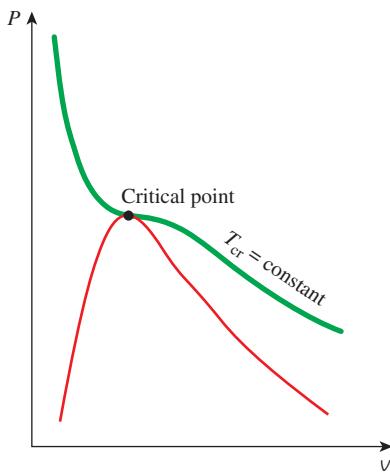


FIGURE 3-53

Several equations of state have been proposed throughout history.

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. 3-53), but we shall discuss only three: the *van der Waals* equation

**FIGURE 3-54**

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

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

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

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. 3-54). 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

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

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 .

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

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

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 m^3/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	4.34×10^4
Argon, Ar	130.7802	0.02328	0.03931	0.0	5.99×10^4
Carbon dioxide, CO_2	507.2836	0.07132	0.10476	0.07235	6.60×10^5
Helium, He	2.1886	0.05984	0.01400	0.0	40
Hydrogen, H_2	20.0117	-0.00506	0.02096	-0.04359	504
Nitrogen, N_2	136.2315	0.02617	0.05046	-0.00691	4.20×10^4
Oxygen, O_2	151.0857	0.02562	0.04624	0.004208	4.80×10^4

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 m^3/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	α	γ
n-Butane, C_4H_{10}	190.68	1021.6	0.039998	0.12436	3.205×10^7	1.006×10^8	1.101×10^{-3}	0.0340
Carbon dioxide, CO_2	13.86	277.30	0.007210	0.04991	1.511×10^6	1.404×10^7	8.470×10^{-5}	0.00539
Carbon monoxide, CO	3.71	135.87	0.002632	0.05454	1.054×10^5	8.673×10^5	1.350×10^{-4}	0.0060
Methane, CH_4	5.00	187.91	0.003380	0.04260	2.578×10^5	2.286×10^6	1.244×10^{-4}	0.0060
Nitrogen, N_2	2.54	106.73	0.002328	0.04074	7.379×10^4	8.164×10^5	1.272×10^{-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.

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 $0.8\rho_{\text{cr}}$, where ρ_{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

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

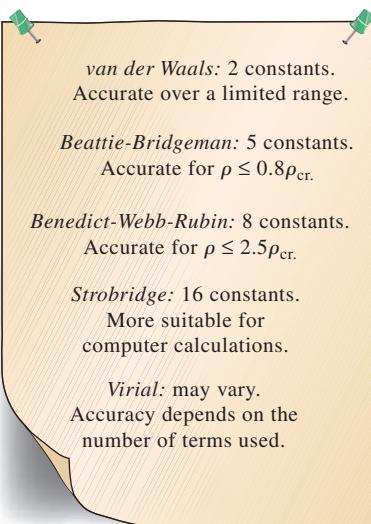
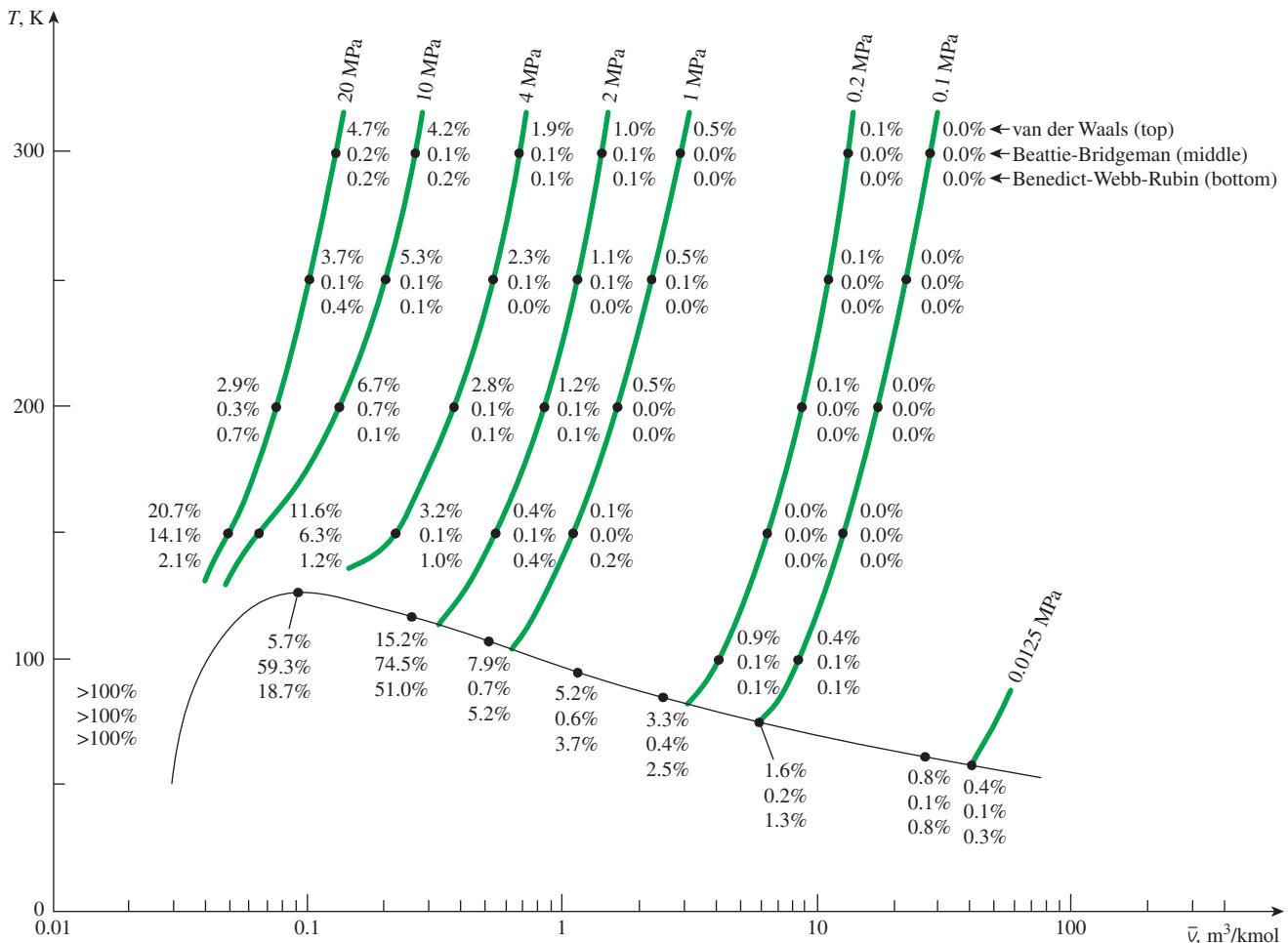
The values of the constants appearing in this equation are given in Table 3–4. This equation can handle substances at densities up to about $2.5\rho_{\text{cr}}$. In 1962, Strobridge further extended this equation by raising the number of constants to 16 (Fig. 3–55).

FIGURE 3–55
Complex equations of state represent the P - v - T behavior of gases more accurately over a wider range.

**FIGURE 3-56**

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

Virial Equation of State

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

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

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, Beattie-Bridgeman, and Benedict-Webb-Rubin equations of state is illustrated in Fig. 3–56. 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 $T = 175$ 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

$$\begin{aligned} a &= 0.175 \text{ m}^6\cdot\text{kPa}/\text{kg}^2 \\ b &= 0.00138 \text{ m}^3/\text{kg} \end{aligned}$$

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

$$\begin{aligned} A &= 102.29 \\ B &= 0.05378 \\ c &= 4.2 \times 10^4 \end{aligned}$$

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

$$\begin{aligned} a &= 2.54 & A_0 &= 106.73 \\ b &= 0.002328 & B_0 &= 0.04074 \\ c &= 7.379 \times 10^4 & C_0 &= 8.164 \times 10^5 \\ \alpha &= 1.272 \times 10^{-4} & \gamma &= 0.0053 \end{aligned}$$

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.

TOPIC OF SPECIAL INTEREST*

Vapor Pressure and Phase Equilibrium

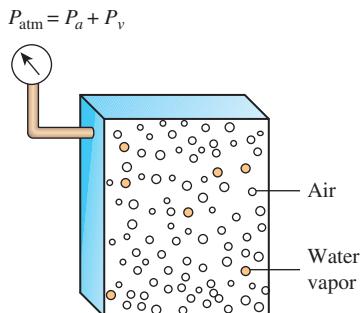


FIGURE 3-57

Atmospheric pressure is the sum of the dry air pressure P_a and the vapor pressure P_v .

The pressure in a gas container is due to the individual molecules striking the wall of the container and exerting a force on it. This force is proportional to the average velocity of the molecules and the number of molecules per unit volume of the container (i.e., molar density). Therefore, the pressure exerted by a gas is a strong function of the density and the temperature of the gas. For a gas mixture, the pressure measured by a sensor such as a transducer is the sum of the pressures exerted by the individual gas species, called the *partial pressure*. It can be shown (see Chap. 13) that the partial pressure of a gas in a mixture is proportional to the number of moles (or the mole fraction) of that gas.

Atmospheric air can be viewed as a mixture of dry air (air with zero moisture content) and water vapor (also referred to as moisture), and the atmospheric pressure is the sum of the pressure of dry air P_a and the pressure of water vapor, called the **vapor pressure** P_v (Fig. 3-57). That is,

$$P_{\text{atm}} = P_a + P_v \quad (3-28)$$

(Note that in some applications, the phrase “vapor pressure” is used to indicate saturation pressure.) The vapor pressure constitutes a small fraction (usually under 3 percent) of the atmospheric pressure since air is mostly nitrogen and oxygen, and the water molecules constitute a small fraction (usually under 3 percent) of the total molecules in the air. However, the amount of water vapor in the air has a major impact on thermal comfort and many processes such as drying.

*This section can be skipped without a loss in continuity.

Air can hold a certain amount of moisture only, and the ratio of the actual amount of moisture in the air at a given temperature to the maximum amount air can hold at that temperature is called the **relative humidity** ϕ . The relative humidity ranges from 0 for dry air to 100 percent for **saturated air** (air that cannot hold any more moisture). The vapor pressure of saturated air at a given temperature is equal to the saturation pressure of water at that temperature. For example, the vapor pressure of saturated air at 25°C is 3.17 kPa.

The amount of moisture in the air is completely specified by the temperature and the relative humidity, and the vapor pressure is related to relative humidity ϕ by

$$P_v = \phi P_{\text{sat} @ T} \quad (3-29)$$

where $P_{\text{sat} @ T}$ is the saturation pressure of water at the specified temperature. For example, the vapor pressure of air at 25°C and 60 percent relative humidity is

$$P_v = \phi P_{\text{sat} @ 25^\circ\text{C}} = 0.6 \times (3.17 \text{ kPa}) = 1.90 \text{ kPa}$$

The desirable range of relative humidity for thermal comfort is 40 to 60 percent.

Note that the amount of moisture air can hold is proportional to the saturation pressure, which increases with temperature. Therefore, air can hold more moisture at higher temperatures. Dropping the temperature of moist air reduces its moisture capacity and may result in the condensation of some of the moisture in the air as suspended water droplets (fog) or as a liquid film on cold surfaces (dew). So it is no surprise that fog and dew are common occurrences at humid locations especially in the early morning hours when the temperatures are the lowest. Both fog and dew disappear (evaporate) as the air temperature rises shortly after sunrise. You also may have noticed that electronic devices such as camcorders come with warnings against bringing them into moist indoors when the devices are cold to avoid moisture condensation on the sensitive electronics of the devices.

It is a common observation that whenever there is an imbalance of a commodity in a medium, nature tends to redistribute it until a “balance” or “equality” is established. This tendency is often referred to as the *driving force*, which is the mechanism behind many naturally occurring transport phenomena such as heat transfer, fluid flow, electric current, and mass transfer. If we define the amount of a commodity per unit volume as the *concentration* of that commodity, we can say that the flow of a commodity is always in the direction of decreasing concentration, that is, from the region of high concentration to the region of low concentration (Fig. 3–58). The commodity simply creeps away during redistribution, and thus the flow is a *diffusion process*.

We know from experience that a wet T-shirt hanging in an open area eventually dries, a small amount of water left in a glass evaporates, and the aftershave in an open bottle quickly disappears. These and many other similar examples suggest that there is a driving force between the two phases of a substance that forces the mass to transform from one phase to another. The magnitude of this force depends on the relative concentrations of the two phases. A wet T-shirt dries much faster in dry air than it would in humid air. In fact, it does not dry at all if the relative humidity of the environment is 100 percent and thus the air is saturated. In this case, there is no transformation from the liquid phase to the vapor phase, and the two phases are in

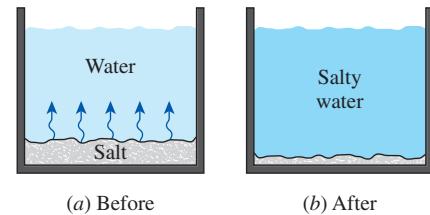
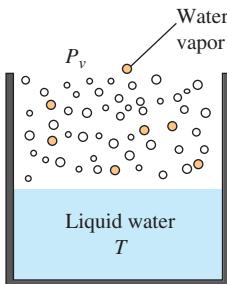


FIGURE 3–58

Whenever there is a concentration difference of a physical quantity in a medium, nature tends to equalize things by forcing a flow from the high to the low concentration region.

**FIGURE 3–59**

When open to the atmosphere, water is in phase equilibrium with the vapor in the air if the vapor pressure is equal to the saturation pressure of water.

phase equilibrium. For liquid water that is open to the atmosphere, the criterion for phase equilibrium can be expressed as follows: *The vapor pressure in the air must be equal to the saturation pressure of water at the water temperature.* That is (Fig. 3–59),

$$\text{Phase equilibrium criterion for water exposed to air: } P_v = P_{\text{sat} @ T} \quad (3-30)$$

Therefore, if the vapor pressure in the air is less than the saturation pressure of water at the water temperature, some liquid will evaporate. The larger the difference between the vapor and saturation pressures, the higher the rate of evaporation. The evaporation has a cooling effect on water, and thus reduces its temperature. This, in turn, reduces the saturation pressure of water and thus the rate of evaporation until some kind of quasi-steady operation is reached. This explains why water is usually at a considerably lower temperature than the surrounding air, especially in dry climates. It also suggests that the rate of evaporation of water can be increased by increasing the water temperature and thus the saturation pressure of water.

Note that the air at the water surface is always saturated because of the direct contact with water, and thus the vapor pressure. Therefore, the vapor pressure at the lake surface is the saturation pressure of water at the temperature of the water at the surface. If the air is not saturated, then the vapor pressure decreases to the value in the air at some distance from the water surface, and the difference between these two vapor pressures is the driving force for the evaporation of water.

The natural tendency of water to evaporate in order to achieve phase equilibrium with the water vapor in the surrounding air forms the basis for the operation of the **evaporative coolers** (also called the *swamp coolers*). In such coolers, hot and dry outdoor air is forced to flow through a wet cloth before entering a building. Some of the water evaporates by absorbing heat from the air, and thus cooling it. Evaporative coolers are commonly used in dry climates and provide effective cooling. They are much cheaper to run than air conditioners since they are inexpensive to buy, and the fan of an evaporative cooler consumes much less power than the compressor of an air conditioner.

Boiling and evaporation are often used interchangeably to indicate *phase change from liquid to vapor*. Although they refer to the same physical process, they differ in some aspects. **Evaporation** occurs at the *liquid-vapor interface* when the vapor pressure is less than the saturation pressure of the liquid at a given temperature. Water in a lake at 20°C, for example, evaporates to air at 20°C and 60 percent relative humidity since the saturation pressure of water at 20°C is 2.34 kPa, and the vapor pressure of air at 20°C and 60 percent relative humidity is 1.4 kPa. Other examples of evaporation are the drying of clothes, fruits, and vegetables; the evaporation of sweat to cool the human body; and the rejection of waste heat in wet cooling towers. Note that evaporation involves no bubble formation or bubble motion (Fig. 3–60).

Boiling, on the other hand, occurs at the *solid-liquid interface* when a liquid is brought into contact with a surface maintained at a temperature T_s sufficiently above the saturation temperature T_{sat} of the liquid. At 1 atm, for example, liquid water in contact with a solid surface at 110°C boils since

the saturation temperature of water at 1 atm is 100°C. The boiling process is characterized by the rapid motion of *vapor bubbles* that form at the solid–liquid interface, detach from the surface when they reach a certain size, and attempt to rise to the free surface of the liquid. When cooking, we do not say water is boiling unless we see the bubbles rising to the top.



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FIGURE 3–60

A liquid-to-vapor phase change process is called *evaporation* if it occurs at a liquid–vapor interface, and *boiling* if it occurs at a solid–liquid interface.

EXAMPLE 3–14 Temperature Drop of a Lake Due to Evaporation

- On a summer day, the air temperature over a lake is measured to be 25°C.
- Determine water temperature of the lake when phase equilibrium conditions are established between the water in the lake and the vapor in the air for relative humidities of 10, 80, and 100 percent for the air (Fig. 3–61).

SOLUTION Air at a specified temperature is blowing over a lake. The equilibrium temperatures of water for three different cases are to be determined.

Analysis The saturation pressure of water at 25°C, from Table 3–1, is 3.17 kPa. Then the vapor pressures at relative humidities of 10, 80, and 100 percent are determined from Eq. 3–29 to be

$$\begin{aligned}\text{Relative humidity} = 10\%: \quad P_{v1} &= \phi_1 P_{\text{sat} @ 25^\circ\text{C}} = 0.1 \times (3.17 \text{ kPa}) \\ &= 0.317 \text{ kPa}\end{aligned}$$

$$\begin{aligned}\text{Relative humidity} = 80\%: \quad P_{v2} &= \phi_2 P_{\text{sat} @ 25^\circ\text{C}} = 0.8 \times (3.17 \text{ kPa}) \\ &= 2.536 \text{ kPa}\end{aligned}$$

$$\begin{aligned}\text{Relative humidity} = 100\% \quad P_{v3} &= \phi_3 P_{\text{sat} @ 25^\circ\text{C}} = 1.0 \times (3.17 \text{ kPa}) \\ &= 3.17 \text{ kPa}\end{aligned}$$

The saturation temperatures corresponding to these pressures are determined from Table 3–1 (or Table A–5) by interpolation to be

$$T_1 = -8.0^\circ\text{C} \quad T_2 = 21.2^\circ\text{C} \quad \text{and} \quad T_3 = 25^\circ\text{C}$$

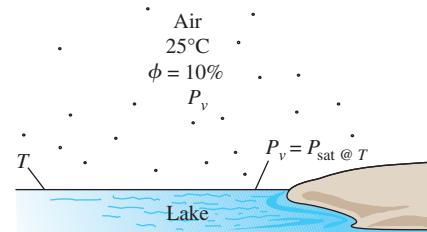


FIGURE 3–61
Schematic for Example 3–14.

Therefore, water will freeze in the first case even though the surrounding air is hot. In the last case the water temperature will be the same as the surrounding air temperature.

Discussion You are probably skeptical about the lake freezing when the air is at 25°C, and you are right. The water temperature drops to –8°C in the limiting case of no heat transfer to the water surface. In practice the water temperature drops below the air temperature, but it does not drop to –8°C because (1) it is very unlikely for the air over the lake to be so dry (a relative humidity of just 10 percent) and (2) as the water temperature near the surface drops, heat transfer from the air and the lower parts of the water body will tend to make up for this heat loss and prevent the water temperature from dropping too much. The water temperature stabilizes when the heat gain from the surrounding air and the water body equals the heat loss by evaporation, that is, when a *dynamic balance* is established between heat and mass transfer instead of phase equilibrium. If you try this experiment using a shallow layer of water in a well-insulated pan, you can actually freeze the water if the air is very dry and relatively cool.

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*,

$$y \equiv y_f @ T$$

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_{cr} and T_{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

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

where

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

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

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.

REFERENCES AND SUGGESTED READINGS

- ASHRAE *Handbook of Fundamentals*. SI version. Atlanta, GA: American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc., 1993.
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- A. Bejan. *Advanced Engineering Thermodynamics*. 3rd ed. New York: Wiley, 2006.
- M. Kostic. *Analysis of Enthalpy Approximation for Compressed Liquid Water*. ASME J. Heat Transfer, Vol. 128, pp. 421–426, 2006.

PROBLEMS*

Pure Substances, Phase-Change Processes, Property Diagrams

3–1C Is iced water a pure substance? Why?

3–2C What is the difference between saturated vapor and superheated vapor?

* Problems designated by a “C” are concept questions, and students are encouraged to answer them all. Problems designated by an “E” are in English units, and the SI users can ignore them. Problems with the  icon are solved using EES, and complete solutions together with parametric studies are included on the text website. Problems with the  icon are comprehensive in nature, and are intended to be solved with an equation solver such as EES.

3–3C Is there any difference between the intensive properties of saturated vapor at a given temperature and the vapor of a saturated mixture at the same temperature?

3–4C Why are the temperature and pressure dependent properties in the saturated mixture region?

3–5C Is it true that water boils at higher temperature at higher pressure? Explain

3–6C What is the difference between the critical point and the triple point?

3–7C Is it possible to have water vapor at -10°C ?

3–8C A househusband is cooking beef stew for his family in a pan that is (a) uncovered, (b) covered with a light lid, and (c) covered with a heavy lid. For which case will the cooking time be the shortest? Why?

Property Tables

3-9C In what kind of pot will a given volume of water boil at a higher temperature: a tall and narrow one or a short and wide one? Explain.

3-10C It is well known that warm air in a cooler environment rises. Now consider a warm mixture of air and gasoline on top of an open gasoline can. Do you think this gas mixture will rise in a cooler environment?

3-11C Does the amount of heat absorbed as 1 kg of saturated liquid water boils at 100°C have to be equal to the amount of heat released as 1 kg of saturated water vapor condenses at 100°C?

3-12C Does the reference point selected for the properties of a substance have any effect on thermodynamic analysis? Why?

3-13C What is the physical significance of h_{fg} ? Can it be obtained from a knowledge of h_f and h_g ? How?

3-14C Does h_{fg} change with pressure? How?

3-15C Is it true that it takes more energy to vaporize 1 kg of saturated liquid water at 100°C than it would at 120°C?

3-16C What is quality? Does it have any meaning in the superheated vapor region?

3-17C Which process requires more energy: completely vaporizing 1 kg of saturated liquid water at 1 atm pressure or completely vaporizing 1 kg of saturated liquid water at 8 atm pressure?

3-18C In the absence of compressed liquid tables, how is the specific volume of a compressed liquid at a given P and T determined?

3-19C In 1775, Dr. William Cullen made ice in Scotland by evacuating the air in a water tank. Explain how that device works, and discuss how the process can be made more efficient.

3-20 Complete this table for H₂O:

$T, ^\circ\text{C}$	P, kPa	$u, \text{kJ/kg}$	Phase description
220	400	1450	Saturated vapor
190	2500		
	4000	3040	

3-21 Complete this table for H₂O:

$T, ^\circ\text{C}$	P, kPa	$v, \text{m}^3/\text{kg}$	Phase description
50		7.72	
	400		Saturated vapor
250	500		
110	350		

3-22  Reconsider Prob. 3-21. Using EES (or other) software, determine the missing properties of water. Repeat the solution for refrigerant-134a, refrigerant-22, and ammonia.

3-23 Complete this table for H₂O:

$T, ^\circ\text{C}$	P, kPa	$v, \text{m}^3/\text{kg}$	Phase description
140		0.05	
	550		Saturated liquid
125	750		
500		0.140	

3-24E Complete this table for H₂O:

$T, ^\circ\text{F}$	P, psia	$u, \text{Btu/lbm}$	Phase description
300		782	
	40		Saturated liquid
500	120		
400	400		

3-25E  Reconsider Prob. 3-24E. Using EES (or other) software, determine the missing properties of water. Repeat the solution for refrigerant-134a, refrigerant-22, and ammonia.

3-26 Complete this table for refrigerant-134a:

$T, ^\circ\text{C}$	P, kPa	$v, \text{m}^3/\text{kg}$	Phase description
-4	320		
10		0.0065	
	850		Saturated vapor
90	600		

3-27E Complete this table for refrigerant-134a:

$T, ^\circ\text{F}$	P, psia	$h, \text{Btu/lbm}$	x	Phase description
	80	78		
15			0.6	
10	70	180	129.46	
110			1.0	

3-28 A 1.8-m³ rigid tank contains steam at 220°C. One-third of the volume is in the liquid phase and the rest is in the vapor form. Determine (a) the pressure of the steam, (b) the quality of the saturated mixture, and (c) the density of the mixture.

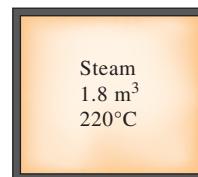


FIGURE P3-28

3–29 A piston–cylinder device contains 0.85 kg of refrigerant-134a at -10°C . The piston that is free to move has a mass of 12 kg and a diameter of 25 cm. The local atmospheric pressure is 88 kPa. Now, heat is transferred to refrigerant-134a until the temperature is 15°C . Determine (a) the final pressure, (b) the change in the volume of the cylinder, and (c) the change in the enthalpy of the refrigerant-134a.

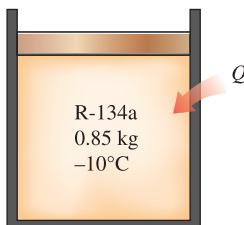


FIGURE P3–29

3–30E R-134a, whose specific volume is $0.6243 \text{ ft}^3/\text{lbm}$, flows through a tube at 80 psia. What is the temperature in the tube?

3–31 10-kg of R-134a fill a 1.348-m^3 rigid container at an initial temperature of -40°C . The container is then heated until the pressure is 200 kPa. Determine the final temperature and the initial pressure. *Answers: 66.3°C , 51.25 kPa*

3–32 A 9-m^3 container is filled with 300 kg of R-134a at 10°C . What is the specific enthalpy of the R-134a in the container?

3–33 Refrigerant-134a at 200 kPa and 25°C flows through a refrigeration line. Determine its specific volume.

3–34 The average atmospheric pressure in Denver (elevation = 1610 m) is 83.4 kPa. Determine the temperature at which water in an uncovered pan boils in Denver. *Answer: 94.6°C*

3–35E The temperature in a pressure cooker during cooking at sea level is measured to be 250°F . Determine the absolute pressure inside the cooker in psia and in atm. Would you modify your answer if the place were at a higher elevation?



FIGURE P3–35E

3–36E A spring-loaded piston-cylinder device is initially filled with 0.13 lbm of an R-134a liquid-vapor mixture

whose temperature is -30°F and whose quality is 80 percent. The spring constant in the spring force relation $F = kx$ is 37 lbf/in, and the piston diameter is 12 in. The R-134a undergoes a process that increases its volume by 50 percent. Calculate the final temperature and enthalpy of the R-134a. *Answers: 105°F , 125 Btu/lbm*

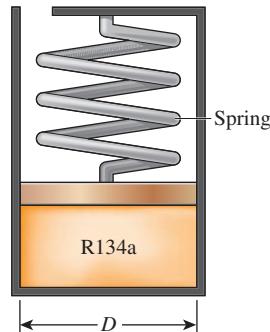


FIGURE P3–36E

3–37E One pound-mass of water fills a 2.4264-ft^3 weighted piston-cylinder device at a temperature of 600°F . The piston–cylinder device is now cooled until its temperature is 200°F . Determine the final pressure of water, in psia, and the volume, in ft^3 . *Answers: 250 psia, 0.01663 ft^3*

3–38 Three kilograms of water in a container have a pressure of 100 kPa and temperature of 150°C . What is the volume of this container?

3–39 Water is to be boiled at sea level in a 30-cm-diameter stainless steel pan placed on top of a 3-kW electric burner. If 60 percent of the heat generated by the burner is transferred to the water during boiling, determine the rate of evaporation of water.

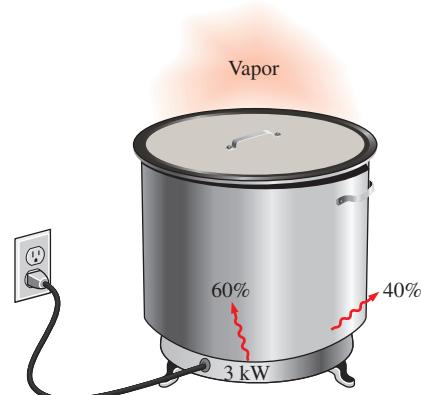


FIGURE P3–39

3–40 Repeat Prob. 3–39 for a location at an elevation of 1500 m where the atmospheric pressure is 84.5 kPa and thus the boiling temperature of water is 95°C .

3–41 10-kg of R-134a at 300 kPa fills a rigid container whose volume is 14 L. Determine the temperature and total enthalpy in the container. The container is now heated until the pressure is 600 kPa. Determine the temperature and total enthalpy when the heating is completed.

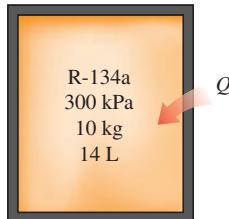


FIGURE P3–41

3–42 100-kg of R-134a at 200 kPa are contained in a piston-cylinder device whose volume is 12.322 m^3 . The piston is now moved until the volume is one-half its original size. This is done such that the pressure of the R-134a does not change. Determine the final temperature and the change in the total internal energy of the R-134a.

3–43 Water initially at 200 kPa and 300°C is contained in a piston-cylinder device fitted with stops. The water is allowed to cool at constant pressure until it exists as a saturated vapor and the piston rests on the stops. Then the water continues to cool until the pressure is 100 kPa. On the $T-v$ diagrams sketch, with respect to the saturation lines, the process curves passing through both the initial, intermediate, and final states of the water. Label the T , P and v values for end states on the process curves. Find the overall change in internal energy between the initial and final states per unit mass of water.

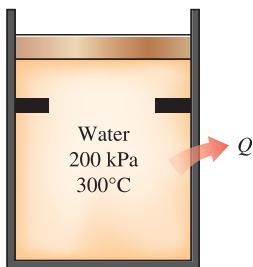


FIGURE P3–43

3–44 Saturated steam coming off the turbine of a steam power plant at 40°C condenses on the outside of a 3-cm-outer-diameter, 35-m-long tube at a rate of 130 kg/h. Determine the rate of heat transfer from the steam to the cooling water flowing through the pipe.

3–45 Water in a 5-cm-deep pan is observed to boil at 98°C . At what temperature will the water in a 40-cm-deep pan boil? Assume both pans are full of water.

3–46 A cooking pan whose inner diameter is 20 cm is filled with water and covered with a 4-kg lid. If the local atmospheric pressure is 101 kPa, determine the temperature at which the water starts boiling when it is heated. *Answer: 100.2°C*

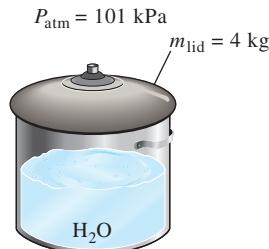


FIGURE P3–46

3–47 Reconsider Prob. 3–46. Using EES (or other) software, investigate the effect of the mass of the lid on the boiling temperature of water in the pan. Let the mass vary from 1 kg to 10 kg. Plot the boiling temperature against the mass of the lid, and discuss the results.

3–48 Water is being heated in a vertical piston–cylinder device. The piston has a mass of 40 kg and a cross-sectional area of 150 cm^2 . If the local atmospheric pressure is 100 kPa, determine the temperature at which the water starts boiling.

3–49 Water is boiled in a pan covered with a poorly fitting lid at a specified location. Heat is supplied to the pan by a 2-kW resistance heater. The amount of water in the pan is observed to decrease by 1.19 kg in 30 minutes. If it is estimated that 75 percent of electricity consumed by the heater is transferred to the water as heat, determine the local atmospheric pressure in that location. *Answer: 85.4 kPa*

3–50 A rigid tank with a volume of 1.8 m^3 contains 15 kg of saturated liquid–vapor mixture of water at 90°C . Now the water is slowly heated. Determine the temperature at which the liquid in the tank is completely vaporized. Also, show the process on a $T-v$ diagram with respect to saturation lines. *Answer: 202.9°C*

3–51 A piston–cylinder device contains 0.005 m^3 of liquid water and 0.9 m^3 of water vapor in equilibrium at 600 kPa. Heat is transferred at constant pressure until the temperature reaches 200°C .

- What is the initial temperature of the water?
- Determine the total mass of the water.
- Calculate the final volume.
- Show the process on a $P-v$ diagram with respect to saturation lines.

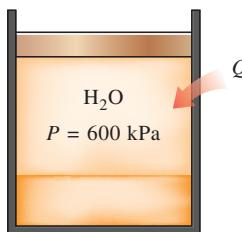


FIGURE P3–51

- 3–52** Reconsider Prob. 3–51. Using EES (or other) software, investigate the effect of pressure on the total mass of water in the tank. Let the pressure vary from 0.1 MPa to 1 MPa. Plot the total mass of water against pressure, and discuss the results. Also, show the process in Prob. 3–51 on a *P*-*v* diagram using the property plot feature of EES.

3–53E A 5-ft³ rigid tank contains 5 lbm of water at 20 psia. Determine (a) the temperature, (b) the total enthalpy, and (c) the mass of each phase of water.

3–54E A 5-ft³ rigid tank contains a saturated mixture of refrigerant-34a at 50 psia. If the saturated liquid occupies 20 percent of the volume, determine the quality and the total mass of the refrigerant in the tank.

3–55E Superheated water vapor at 180 psia and 500°F is allowed to cool at constant volume until the temperature drops to 250°F. At the final state, determine (a) the pressure, (b) the quality, and (c) the enthalpy. Also, show the process on a *T*-*v* diagram with respect to saturation lines.

Answers: (a) 29.84 psia, (b) 0.219, (c) 426.0 Btu/lbm

- 3–56E** Reconsider Prob. 3–55E. Using EES (or other) software, investigate the effect of initial pressure on the quality of water at the final state. Let the pressure vary from 100 psi to 300 psi. Plot the quality against initial pressure, and discuss the results. Also, show the process in Prob. 3–55E on a *T*-*v* diagram using the property plot feature of EES.

3–57 A piston–cylinder device contains 0.6 kg of steam at 200°C and 0.5 MPa. Steam is cooled at constant pressure until one-half of the mass condenses.

- (a) Show the process on a *T*-*v* diagram.
- (b) Find the final temperature.
- (c) Determine the volume change.

3–58 A rigid tank contains water vapor at 250°C and an unknown pressure. When the tank is cooled to 124°C, the vapor starts condensing. Estimate the initial pressure in the tank. *Answer:* 0.30 MPa

3–59 A piston–cylinder device initially contains 1.4-kg saturated liquid water at 200°C. Now heat is transferred to the water until the volume quadruples and the cylinder contains

saturated vapor only. Determine (a) the volume of the tank, (b) the final temperature and pressure, and (c) the internal energy change of the water.

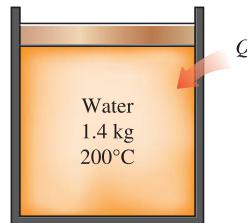


FIGURE P3–59

3–60E How much error would one expect in determining the specific enthalpy by applying the incompressible-liquid approximation to water at 3000 psia and 400°F?

3–61 100 grams of R-134a initially fill a weighted piston–cylinder device at 60 kPa and –20°C. The device is then heated until the temperature is 100°C. Determine the change in the device's volume as a result of the heating.

Answer: 0.0168 m³

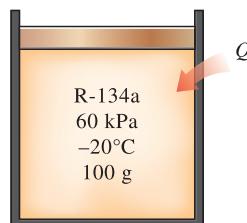


FIGURE P3–61

3–62 A rigid vessel contains 8 kg of refrigerant-134a at 500 kPa and 120°C. Determine the volume of the vessel and the total internal energy. *Answers:* 0.494 m³, 2639 kJ

3–63 A rigid tank initially contains 1.4-kg saturated liquid water at 200°C. At this state, 25 percent of the volume is occupied by water and the rest by air. Now heat is supplied to the water until the tank contains saturated vapor only. Determine (a) the volume of the tank, (b) the final temperature and pressure, and (c) the internal energy change of the water.



FIGURE P3–63

3-64 A piston-cylinder device initially contains 50 L of liquid water at 40°C and 200 kPa. Heat is transferred to the water at constant pressure until the entire liquid is vaporized.

- (a) What is the mass of the water?
- (b) What is the final temperature?
- (c) Determine the total enthalpy change.
- (d) Show the process on a $T-v$ diagram with respect to saturation lines.

Answers: (a) 49.61 kg, (b) 120.21°C, (c) 125,950 kJ

Ideal Gas

3-65C Under what conditions is the ideal-gas assumption suitable for real gases?

3-66C What is the difference between R and R_u ? How are these two related?

3-67C Propane and methane are commonly used for heating in winter, and the leakage of these fuels, even for short periods, poses a fire danger for homes. Which gas leakage do you think poses a greater risk for fire? Explain.

3-68 A 400-L rigid tank contains 5 kg of air at 25°C. Determine the reading on the pressure gage if the atmospheric pressure is 97 kPa.

3-69E A 3-ft³ container is filled with 2-lbm of oxygen at a pressure of 80 psia. What is the temperature of the oxygen?

3-70 A 2-kg mass of helium is maintained at 300 kPa and 27°C in a rigid container. How large is the container, in m³?

3-71 The pressure gage on a 2.5-m³ oxygen tank reads 500 kPa. Determine the amount of oxygen in the tank if the temperature is 28°C and the atmospheric pressure is 97 kPa.

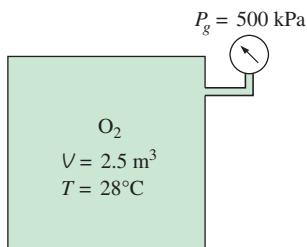


FIGURE P3-71

3-72 A spherical balloon with a diameter of 9 m is filled with helium at 27°C and 200 kPa. Determine the mole number and the mass of the helium in the balloon.

Answers: 30.6 kmol, 123 kg

3-73 Reconsider Prob. 3-72. Using EES (or other) software, investigate the effect of the balloon diameter on the mass of helium contained in the balloon for the pressures of (a) 100 kPa and (b) 200 kPa. Let the diameter vary from 5 m to 15 m. Plot the mass of helium against the diameter for both cases.

3-74E The air in an automobile tire with a volume of 0.53 ft³ is at 90°F and 20 psig. Determine the amount of air that must be added to raise the pressure to the recommended value of 30 psig. Assume the atmospheric pressure to be 14.6 psia and the temperature and the volume to remain constant.

Answer: 0.0260 lbm

3-75 A 1-m³ tank containing air at 10°C and 350 kPa is connected through a valve to another tank containing 3 kg of air at 35°C and 200 kPa. Now the valve is opened, and the entire system is allowed to reach thermal equilibrium with the surroundings, which are at 20°C. Determine the volume of the second tank and the final equilibrium pressure of air. Answers: 1.33 m³, 264 kPa

3-76 A rigid tank whose volume is unknown is divided into two parts by a partition. One side of the tank contains an ideal gas at 927°C. The other side is evacuated and has a volume twice the size of the part containing the gas. The partition is now removed and the gas expands to fill the entire tank. Heat is now applied to the gas until the pressure equals the initial pressure. Determine the final temperature of the gas. Answer: 3327°C

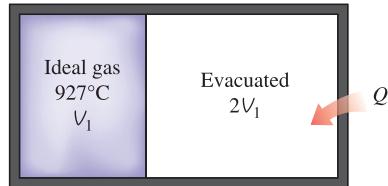


FIGURE P3-76

3-77 Argon in the amount of 1.5 kg fills a 0.04-m³ piston-cylinder device at 550 kPa. The piston is now moved by changing the weights until the volume is twice its original size. During this process, argon's temperature is maintained constant. Determine the final pressure in the device.

3-78E A rigid tank contains 20 lbm of air at 20 psia and 70°F. More air is added to the tank until the pressure and temperature rise to 35 psia and 90°F, respectively. Determine the amount of air added to the tank. Answer: 13.73 lbm

Compressibility Factor

3-79C What is the principle of corresponding states?

3-80C How are the reduced pressure and reduced temperature defined?

3-81E Refrigerant-134a at 400 psia has a specific volume of 0.1384 ft³/lbm. Determine the temperature of the refrigerant based on (a) the ideal-gas equation, (b) the generalized compressibility chart, and (c) the refrigerant tables.

3-82 Determine the specific volume of superheated water vapor at 15 MPa and 350°C, using (a) the ideal-gas equation, (b) the generalized compressibility chart, and (c) the

steam tables. Also determine the error involved in the first two cases. *Answers:* (a) $0.01917 \text{ m}^3/\text{kg}$, 67.0 percent, (b) $0.01246 \text{ m}^3/\text{kg}$, 8.5 percent, (c) $0.01148 \text{ m}^3/\text{kg}$

3-83  Reconsider Prob. 3-82. Solve the problem using the generalized compressibility factor feature of the EES software. Again using EES, compare the specific volume of water for the three cases at 15 MPa over the temperature range of 350 to 600°C in 25°C intervals. Plot the percent error involved in the ideal-gas approximation against temperature, and discuss the results.

3-84 Determine the specific volume of superheated water vapor at 3.5 MPa and 450°C based on (a) the ideal-gas equation, (b) the generalized compressibility chart, and (c) the steam tables. Determine the error involved in the first two cases.

3-85 Somebody claims that oxygen gas at 160 K and 3 MPa can be treated as an ideal gas with an error of less than 10 percent. Is this claim valid?

3-86E Ethane in a rigid vessel is to be heated from 50 psia and 100°F until its temperature is 540°F. What is the final pressure of the ethane as predicted by the compressibility chart?

3-87 Ethylene is heated at constant pressure from 5 MPa and 20°C to 200°C. Using the compressibility chart, determine the change in the ethylene's specific volume as a result of this heating. *Answer:* $0.0172 \text{ m}^3/\text{kg}$

3-88 What is the percentage of error involved in treating carbon dioxide at 7 MPa and 380 K as an ideal gas?

3-89 Saturated water vapor at 350°C is heated at constant pressure until its volume has doubled. Determine the final temperature using the ideal gas equation of state, the compressibility charts, and the steam tables.

3-90 Methane at 10 MPa and 300 K is heated at constant pressure until its volume has increased by 80 percent. Determine the final temperature using the ideal gas equation of state and the compressibility factor. Which of these two results is more accurate?

3-91 Carbon dioxide gas enters a pipe at 3 MPa and 500 K at a rate of 2 kg/s. CO_2 is cooled at constant pressure as it flows in the pipe and the temperature of CO_2 drops to 450 K at the exit. Determine the volume flow rate and the density of carbon dioxide at the inlet and the volume flow rate at the exit of the pipe using (a) the ideal-gas equation and (b) the generalized compressibility chart. Also, determine (c) the error involved in the first case.

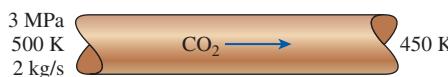


FIGURE P3-91

3-92 A 0.016773-m³ tank contains 1 kg of refrigerant-134a at 110°C. Determine the pressure of the refrigerant, using (a) the ideal-gas equation, (b) the generalized compressibility chart, and (c) the refrigerant tables. *Answers:* (a) 1.861 MPa, (b) 1.583 MPa, (c) 1.6 MPa

Other Equations of State

3-93C What is the physical significance of the two constants that appear in the van der Waals equation of state? On what basis are they determined?

3-94 A 3.27-m³ tank contains 100 kg of nitrogen at 175 K. Determine the pressure in the tank, using (a) the ideal-gas equation, (b) the van der Waals equation, and (c) the Beattie-Bridgeman equation. Compare your results with the actual value of 1505 kPa.

3-95 Methane is heated in a rigid container from 80 kPa and 20°C to 300°C. Determine the final pressure of the methane treating it as (a) an ideal gas and (b) a Benedict-Webb-Rubin gas.

3-96E Refrigerant-134a at 400 psia has a specific volume of 0.1144 ft³/lbm. Determine the temperature of the refrigerant based on (a) the ideal-gas equation, (b) the van der Waals equation, and (c) the refrigerant tables.

3-97  Nitrogen at 150 K has a specific volume of 0.041884 m³/kg. Determine the pressure of the nitrogen, using (a) the ideal-gas equation and (b) the Beattie-Bridgeman equation. Compare your results to the experimental value of 1000 kPa. *Answers:* (a) 1063 kPa, (b) 1000.4 kPa

3-98  Reconsider Prob. 3-97. Using EES (or other) software, compare the pressure results of the ideal-gas and Beattie-Bridgeman equations with nitrogen data supplied by EES. Plot temperature versus specific volume for a pressure of 1000 kPa with respect to the saturated liquid and saturated vapor lines of nitrogen over the range of 110 K < T < 150 K.

3-99 1-kg of carbon dioxide is compressed from 1 MPa and 200°C to 3 MPa in a piston-cylinder device arranged to execute a polytropic process for which $PV^{1.2} = \text{constant}$. Determine the final temperature treating the carbon dioxide as (a) an ideal gas and (b) a van der Waals gas.

3-100 A 1-m³ tank contains 2.841 kg of steam at 0.6 MPa. Determine the temperature of the steam, using (a) the ideal-gas equation, (b) the van der Waals equation, and (c) the steam tables. *Answers:* (a) 457.6 K, (b) 465.9 K, (c) 473 K

3-101  Reconsider Prob. 3-100. Solve the problem using EES (or other) software. Again using the EES, compare the temperature of water for the three cases at constant specific volume over the pressure range of 0.1 MPa to 1 MPa in 0.1 MPa increments. Plot the percent error involved in the ideal-gas approximation against pressure, and discuss the results.

Special Topic: Vapor Pressure and Phase Equilibrium

3-102 During a hot summer day at the beach when the air temperature is 30°C, someone claims the vapor pressure in the air to be 5.2 kPa. Is this claim reasonable?

3-103 Consider a glass of water in a room that is at 20°C and 40 percent relative humidity. If the water temperature is 15°C, determine the vapor pressure (a) at the free surface of the water and (b) at a location in the room far from the glass.

3-104 On a certain day, the temperature and relative humidity of air over a large swimming pool are measured to be 25°C and 60 percent, respectively. Determine the water temperature of the pool when phase equilibrium conditions are established between the water in the pool and the vapor in the air.

3-105 During a hot summer day when the air temperature is 35°C and the relative humidity is 70 percent, you buy a supposedly “cold” canned drink from a store. The store owner claims that the temperature of the drink is below 10°C. Yet the drink does not feel so cold and you are skeptical since you notice no condensation forming outside the can. Can the store owner be telling the truth?

3-106 Consider two rooms that are identical except that one is maintained at 25°C and 40 percent relative humidity while the other is maintained at 20°C and 55 percent relative humidity. Noting that the amount of moisture is proportional to the vapor pressure, determine which room contains more moisture.

3-107E A thermos bottle is half-filled with water and is left open to the atmospheric air at 60°F and 35 percent relative humidity. If heat transfer to the water through the thermos walls and the free surface is negligible, determine the temperature of water when phase equilibrium is established.

Review Problems

3-108E Water in a pressure cooker is observed to boil at 260°F. What is the absolute pressure in the pressure cooker, in psia?

3-109 Carbon-dioxide gas at 3 MPa and 500 K flows steadily in a pipe at a rate of 0.4 kmol/s. Determine (a) the volume and mass flow rates and the density of carbon dioxide at this state. If CO₂ is cooled at constant pressure as it flows in the pipe so that the temperature of CO₂ drops to 450 K at the exit of the pipe, determine (b) the volume flow rate at the exit of the pipe.

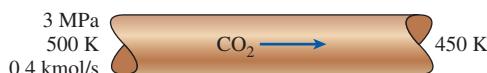


FIGURE P3-109

3-110 A tank contains argon at 600°C and 200 kPa gage. The argon is cooled in a process by heat transfer to the surroundings such that the argon reaches a final equilibrium

state at 300°C. Determine the final gage pressure of the argon. Assume atmospheric pressure is 100 kPa.

3-111 The combustion in a gasoline engine may be approximated by a constant volume heat addition process. There exists the air-fuel mixture in the cylinder before the combustion and the combustion gases after it, and both may be approximated as air, an ideal gas. In a gasoline engine, the cylinder conditions are 1.2 MPa and 450°C before the combustion and 1750°C after it. Determine the pressure at the end of the combustion process. *Answer: 3.36 MPa*

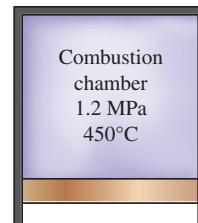


FIGURE P3-111

3-112 One kilogram of R-134a fills a 0.090 m³ rigid container at an initial temperature of -40°C. The container is then heated until the pressure is 280 kPa. Determine the initial pressure and final temperature. *Answers: 51.25 kPa, 50°C*

3-113 A rigid tank with a volume of 0.117 m³ contains 1 kg of refrigerant-134a vapor at 240 kPa. The refrigerant is now allowed to cool. Determine the pressure when the refrigerant first starts condensing. Also, show the process on a P-v diagram with respect to saturation lines.

3-114E One pound-mass of water fills a 2.649 ft³ weighted piston-cylinder device at a temperature of 400°F. The piston-cylinder device is now cooled until its temperature is 100°F. Determine the final pressure and volume of the water.

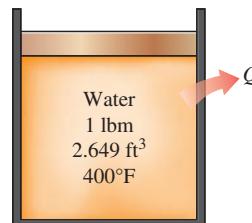


FIGURE P3-114E

3-115 Ethane at 10 MPa and 100°C is heated at constant pressure until its volume has increased by 60 percent. Determine the final temperature using (a) the ideal gas equation of state and (b) the compressibility factor. Which of these two results is the more accurate?

3-116 A 13-m³ tank contains nitrogen at 17°C and 600 kPa. Some nitrogen is allowed to escape until the pressure in

the tank drops to 400 kPa. If the temperature at this point is 15°C, determine the amount of nitrogen that has escaped. *Answer: 29.8 kg*

3–117 A 10-kg mass of superheated refrigerant-134a at 1.2 MPa and 70°C is cooled at constant pressure until it exists as a compressed liquid at 20°C.

(a) Show the process on a T - v diagram with respect to saturation lines.

(b) Determine the change in volume.

(c) Find the change in total internal energy.

Answers: (b) -0.187 m^3 (c) -1984 kJ

3–118 A 4-L rigid tank contains 2 kg of saturated liquid-vapor mixture of water at 50°C. The water is now slowly heated until it exists in a single phase. At the final state, will the water be in the liquid phase or the vapor phase? What would your answer be if the volume of the tank were 400 L instead of 4 L?

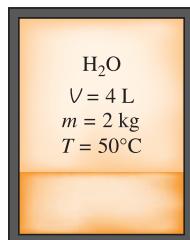


FIGURE P3–118

3–119 The gage pressure of an automobile tire is measured to be 200 kPa before a trip and 220 kPa after the trip at a location where the atmospheric pressure is 90 kPa. Assuming the volume of the tire remains constant at 0.035 m^3 , determine the percent increase in the absolute temperature of the air in the tire.

3–120 A piston-cylinder device initially contains 0.2 kg of steam at 200 kPa and 300°C. Now, the steam is cooled at constant pressure until it is at 150°C. Determine the volume change of the cylinder during this process using the compressibility factor and compare the result to the actual value.

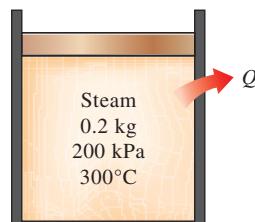


FIGURE P3–120

3–121 Steam at 400°C has a specific volume of $0.02 \text{ m}^3/\text{kg}$. Determine the pressure of the steam based on (a) the ideal-gas equation, (b) the generalized compressibility chart, and

(c) the steam tables. *Answers: (a) 15,529 kPa, (b) 12,574 kPa, (c) 12,515 kPa*

3–122 A tank whose volume is unknown is divided into two parts by a partition. One side of the tank contains 0.03 m^3 of refrigerant-134a that is a saturated liquid at 0.9 MPa, while the other side is evacuated. The partition is now removed, and the refrigerant fills the entire tank. If the final state of the refrigerant is 20°C and 280 kPa, determine the volume of the tank.

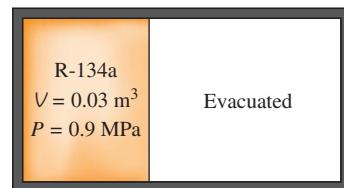


FIGURE P3–122

3–123 Reconsider Prob. 3–122. Using EES (or other) software, investigate the effect of the initial pressure of refrigerant-134a on the volume of the tank. Let the initial pressure vary from 0.5 to 1.5 MPa. Plot the volume of the tank versus the initial pressure, and discuss the results.

3–124 Liquid propane is commonly used as a fuel for heating homes, powering vehicles such as forklifts, and filling portable picnic tanks. Consider a propane tank that initially contains 5 L of liquid propane at the environment temperature of 20°C. If a hole develops in the connecting tube of a propane tank and the propane starts to leak out, determine the temperature of propane when the pressure in the tank drops to 1 atm. Also, determine the total amount of heat transfer from the environment to the tank to vaporize the entire propane in the tank.

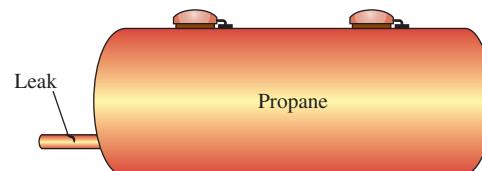


FIGURE P3–124

3–125 Repeat Prob. 3–124 for isobutane.

3–126 A tank contains helium at 37°C and 140 kPa gage. The helium is heated in a process by heat transfer from the surroundings such that the helium reaches a final equilibrium state at 200°C. Determine the final gage pressure of the helium. Assume atmospheric pressure is 100 kPa.

3–127 If sufficient data are provided, complete the blank cells in the following table of properties of water. In the last column describe the condition of water as compressed liquid,

saturated mixture, superheated vapor, or insufficient information; and, if applicable, give the quality.

P , kPa	T , °C	v , m^3/kg	u , kJ/kg	Phase description
	250		2728.9	
300			1560.0	
101.42	100			
3000	180			

3-128 Water initially at 300 kPa and $0.5 \text{ m}^3/\text{kg}$ is contained in a piston-cylinder device fitted with stops so that the water supports the weight of the piston and the force of the atmosphere. The water is heated until it reaches the saturated vapor state and the piston rests against the stops. With the piston against the stops, the water is further heated until the pressure is 600 kPa. On the P - v and T - v diagrams sketch, with respect to the saturation lines, the process curves passing through both the initial and final states of the water. Label the states on the process as 1, 2, and 3. On both the P - v and T - v diagrams, sketch the isotherms passing through the states and show their values, in °C, on the isotherms.

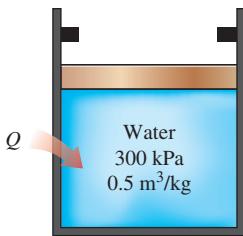


FIGURE P3-128

3-129E 0.5-lbm of argon is compressed from 1000 psia and 300°F to 2000 psia in a piston-cylinder device which executes a polytropic process for which $PV^{1.6} = \text{constant}$. Determine the final temperature treating the argon as (a) an ideal gas and (b) a Beattie-Bridgeman gas.

3-130E Nitrogen is maintained at 400 psia and -100°F . Compare the specific volume of this nitrogen as predicted by (a) the ideal gas equation of state, (b) the Benedict-Webb-Rubin equation of state, and (c) with the compressibility factor.

3-131 Although balloons have been around since 1783 when the first balloon took to the skies in France, a real breakthrough in ballooning occurred in 1960 with the design of the modern hot-air balloon fueled by inexpensive propane and constructed of lightweight nylon fabric. Over the years, ballooning has become a sport and a hobby for many people around the world. Unlike balloons filled with the light helium gas, hot-air balloons are open to the atmosphere. Therefore, the pressure in the balloon is always the same as the local atmospheric pressure, and the balloon is never in danger of exploding.

Hot-air balloons range from about 15 to 25 m in diameter. The air in the balloon cavity is heated by a propane burner located at the top of the passenger cage. The flames from the burner that shoot into the balloon heat the air in the balloon cavity, raising the air temperature at the top of the balloon from 65°C to over 120°C . The air temperature is maintained at the desired levels by periodically firing the propane burner.

The buoyancy force that pushes the balloon upward is proportional to the density of the cooler air outside the balloon and the volume of the balloon, and can be expressed as

$$F_B = \rho_{\text{cool air}} g V_{\text{balloon}}$$

where g is the gravitational acceleration. When air resistance is negligible, the buoyancy force is opposed by (1) the weight of the hot air in the balloon, (2) the weight of the cage, the ropes, and the balloon material, and (3) the weight of the people and other load in the cage. The operator of the balloon can control the height and the vertical motion of the balloon by firing the burner or by letting some hot air in the balloon escape, to be replaced by cooler air. The forward motion of the balloon is provided by the winds.

Consider a 20-m-diameter hot-air balloon that, together with its cage, has a mass of 80 kg when empty. This balloon is hanging still in the air at a location where the atmospheric pressure and temperature are 90 kPa and 15°C , respectively, while carrying three 65-kg people. Determine the average temperature of the air in the balloon. What would your response be if the atmospheric air temperature were 30°C ?



FIGURE P3-131

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3-132  Reconsider Prob. 3-131. Using EES (or other) software, investigate the effect of the environment temperature on the average air temperature in the balloon when the balloon is suspended in the air. Assume the environment temperature varies from -10 to 30°C . Plot the average air temperature in the balloon versus the environment temperature, and discuss the results. Investigate how the number of people carried affects the temperature of the air in the balloon.

3-133 Consider an 18-m-diameter hot-air balloon that, together with its cage, has a mass of 120 kg when empty. The air in the balloon, which is now carrying two 70-kg people, is heated by propane burners at a location where the atmospheric pressure and temperature are 93 kPa and 12°C , respectively. Determine the average temperature of the air in the balloon when the balloon first starts rising. What would your response be if the atmospheric air temperature were 25°C ?

Fundamentals of Engineering (FE) Exam Problems

3-134 A 300-m³ rigid tank is filled with saturated liquid-vapor mixture of water at 200 kPa. If 25 percent of the mass is liquid and 75 percent of the mass is vapor, the total mass in the tank is

- (a) 451 kg (b) 556 kg (c) 300 kg
 (d) 331 kg (e) 195 kg

3-135 Water is boiled at 1 atm pressure in a coffee maker equipped with an immersion-type electric heating element. The coffee maker initially contains 1 kg of water. Once boiling started, it is observed that half of the water in the coffee maker evaporated in 10 minutes. If the heat loss from the coffee maker is negligible, the power rating of the heating element is

- (a) 3.8 kW (b) 2.2 kW (c) 1.9 kW
 (d) 1.6 kW (e) 0.8 kW

3-136 A 1-m³ rigid tank contains 10 kg of water (in any phase or phases) at 160°C . The pressure in the tank is

- (a) 738 kPa (b) 618 kPa (c) 370 kPa
 (d) 2000 kPa (e) 1618 kPa

3-137 Water is boiling at 1 atm pressure in a stainless steel pan on an electric range. It is observed that 2 kg of liquid water evaporates in 30 min. The rate of heat transfer to the water is

- (a) 2.51 kW (b) 2.32 kW (c) 2.97 kW
 (d) 0.47 kW (e) 3.12 kW

3-138 Water is boiled in a pan on a stove at sea level. During 10 min of boiling, it is observed that 200 g of water has evaporated. Then the rate of heat transfer to the water is

- (a) 0.84 kJ/min (b) 45.1 kJ/min (c) 41.8 kJ/min
 (d) 53.5 kJ/min (e) 225.7 kJ/min

3-139 A 3-m³ rigid vessel contains steam at 4 MPa and 500°C . The mass of the steam is

- (a) 3 kg (b) 9 kg (c) 26 kg
 (d) 35 kg (e) 52 kg

3-140 Consider a sealed can that is filled with refrigerant-134a. The contents of the can are at the room temperature of 25°C . Now a leak develops, and the pressure in the can drops to the local atmospheric pressure of 90 kPa. The temperature of the refrigerant in the can is expected to drop to (rounded to the nearest integer)

- (a) 0°C (b) -29°C (c) -16°C
 (d) 5°C (e) 25°C

3-141 A rigid tank contains 2 kg of an ideal gas at 4 atm and 40°C . Now a valve is opened, and half of mass of the gas is allowed to escape. If the final pressure in the tank is 2.2 atm, the final temperature in the tank is

- (a) 71°C (b) 44°C (c) -100°C
 (d) 20°C (e) 172°C

3-142 The pressure of an automobile tire is measured to be 190 kPa (gage) before a trip and 215 kPa (gage) after the trip at a location where the atmospheric pressure is 95 kPa. If the temperature of air in the tire before the trip is 25°C , the air temperature after the trip is

- (a) 51.1°C (b) 64.2°C (c) 27.2°C
 (d) 28.3°C (e) 25.0°C

Design and Essay Problems

3-143 In an article on tire maintenance, it is stated that tires lose air over time, and pressure losses as high as 90 kPa (13 psi) per year are measured. The article recommends checking tire pressure at least once a month to avoid low tire pressure that hurts fuel efficiency and causes uneven thread wear on tires. Taking the beginning tire pressure to be 220 kPa (gage) and the atmospheric pressure to be 100 kPa, determine the fraction of air that can be lost from a tire per year.

3-144 It is well known that water freezes at 0°C at atmospheric pressure. The mixture of liquid water and ice at 0°C is said to be at stable equilibrium since it cannot undergo any changes when it is isolated from its surroundings. However, when water is free of impurities and the inner surfaces of the container are smooth, the temperature of water can be lowered to -2°C or even lower without any formation of ice at atmospheric pressure. But at that state even a small disturbance can initiate the formation of ice abruptly, and the water temperature stabilizes at 0°C following this sudden change. The water at -2°C is said to be in a *metastable state*. Write an essay on metastable states and discuss how they differ from stable equilibrium states.

3-145 A solid normally absorbs heat as it melts, but there is a known exception at temperatures close to absolute zero. Find out which solid it is and give a physical explanation for it.

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