

### 3.3 INDEPENDENT PROPERTIES OF A PURE SUBSTANCE

One important reason for introducing the concept of a pure substance is that the state of a simple compressible pure substance (that is, a pure substance in the absence of motion, gravity, and surface, magnetic, or electrical effects) is defined by two **independent properties**. For example, if the specific volume and temperature of superheated steam are specified, the state of the steam is determined.

To understand the significance of the term *independent property*, consider the saturated-liquid and saturated-vapor states of a pure substance. These two states have the same pressure and the same temperature, but they are definitely not the same state. In a saturation state, therefore, pressure and temperature are not independent properties. Two independent properties, such as pressure and specific volume or pressure and quality, are required to specify a saturation state of a pure substance.

The reason for mentioning previously that a mixture of gases, such as air, has the same characteristics as a pure substance as long as only one phase is present concerns precisely this point. The state of air, which is a mixture of gases of definite composition, is determined by specifying two properties as long as it remains in the gaseous phase. Air then can be treated as a pure substance.

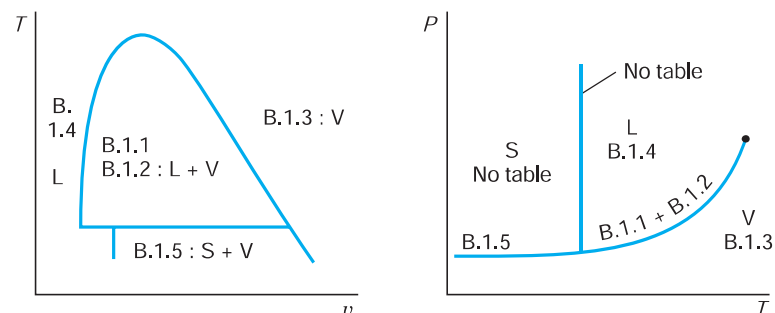
### 3.4 TABLES OF THERMODYNAMIC PROPERTIES

Tables of thermodynamic properties of many substances are available, and in general, all these tables have the same form. In this section we will refer to the steam tables. The steam tables are selected both because they are a vehicle for presenting thermodynamic tables and because steam is used extensively in power plants and industrial processes. Once the steam tables are understood, other thermodynamic tables can be readily used.



Several different versions of steam tables have been published over the years. The set included in Table B.1 in Appendix B is a summary based on a complicated fit to the behavior of water. It is very similar to the *Steam Tables* by Keenan, Keyes, Hill, and Moore, published in 1969 and 1978. We will concentrate here on the three properties already discussed in Chapter 2 and in Section 3.2, namely,  $T$ ,  $P$ , and  $v$ , and note that the other properties listed in the set of Tables B.1— $u$ ,  $h$ , and  $s$ —will be introduced later.

The steam tables in Appendix B consist of five separate tables, as indicated in Fig. 3.8. The region of superheated vapor in Fig. 3.5 is given in Table B.1.3, and that of compressed



**FIGURE 3.8** Listing of the steam tables.

liquid is given in Table B.1.4. The compressed-solid region shown in Fig. 3.5 is not presented in Appendix B. The saturated-liquid and saturated-vapor region, as seen in Fig. 3.3 (and as the vaporization line in Fig. 3.5), is listed according to the values of  $T$  in Table B.1.1 and according to the values of  $P$  ( $T$  and  $P$  are not independent in the two-phase regions) in Table B.1.2. Similarly, the saturated-solid and saturated-vapor region is listed according to  $T$  in Table B.1.5, but the saturated-solid and saturated-liquid region, the third phase boundary line shown in Fig. 3.5, is not listed in Appendix B.

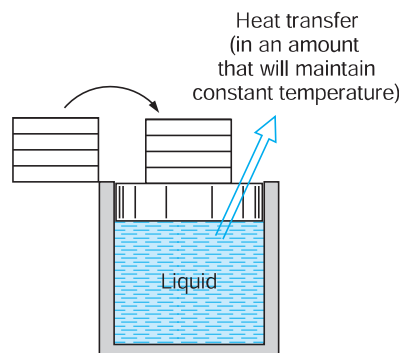
In Table B.1.1, the first column after the temperature gives the corresponding saturation pressure in kilopascals. The next three columns give the specific volume in cubic meters per kilogram. The first of these columns gives the specific volume of the saturated liquid,  $v_f$ ; the third column gives the specific volume of the saturated vapor,  $v_g$ ; and the second column gives the difference between the two,  $v_{fg}$ , as defined in Section 3.2. Table B.1.2 lists the same information as Table B.1.1, but the data are listed according to pressure, as mentioned earlier.

As an example, let us calculate the specific volume of saturated steam at 200°C having a quality of 70%. Using Eq. 3.1 gives

$$\begin{aligned} v &= 0.3(0.001\ 156) + 0.7(0.127\ 36) \\ &= 0.0895\ \text{m}^3/\text{kg} \end{aligned}$$

Table B.1.3 gives the properties of superheated vapor. In the superheated region, pressure and temperature are independent properties; therefore, for each pressure a large number of temperatures are given, and for each temperature four thermodynamic properties are listed, the first one being specific volume. Thus, the specific volume of steam at a pressure of 0.5 MPa and 200°C is 0.4249 m<sup>3</sup>/kg.

Table B.1.4 gives the properties of the compressed liquid. To demonstrate the use of this table, consider a piston and a cylinder (as shown in Fig. 3.9) that contains 1 kg of saturated-liquid water at 100°C. Its properties are given in Table B.1.1, and we note that the pressure is 0.1013 MPa and the specific volume is 0.001 044 m<sup>3</sup>/kg. Suppose the pressure is increased to 10 MPa while the temperature is held constant at 100°C by the necessary transfer of heat,  $Q$ . Since water is slightly compressible, we would expect a slight decrease in specific volume during this process. Table B.1.4 gives this specific volume as 0.001 039 m<sup>3</sup>/kg. This is only a slight decrease, and only a small error would be made if one assumed that the volume of a compressed liquid is equal to the specific volume of the saturated liquid at the same temperature. In many situations this is the most convenient procedure, particularly when compressed-liquid data are not available. It is very important to note, however, that the specific volume of saturated liquid at the given pressure, 10 MPa, does



**FIGURE 3.9**  
Illustration of the  
compressed-liquid state.

not give a good approximation. This value, from Table B.1.2, at a temperature of  $311.1^\circ\text{C}$ , is  $0.001\,452\text{ m}^3/\text{kg}$ , which is in error by almost 40%.

Table B.1.5 of the steam tables gives the properties of saturated solid and saturated vapor that are in equilibrium. The first column gives the temperature, and the second column gives the corresponding saturation pressure. As would be expected, all these pressures are less than the triple-point pressure. The next two columns give the specific volume of the saturated solid and saturated vapor.

Appendix B also includes thermodynamic tables for several other substances; refrigerant fluids R-134a and R-410a, ammonia and carbon dioxide, and the cryogenic fluids nitrogen and methane. In each case, only two tables are given: saturated liquid-vapor listed by temperature (equivalent to Table B.1.1 for water) and superheated vapor (equivalent to Table B.1.3).

Let us now consider a number of examples to illustrate the use of thermodynamic tables for water and for the other substances listed in Appendix B.

**EXAMPLE 3.1** Determine the phase for each of the following water states using the tables in Appendix B and indicate the relative position in the  $P$ - $v$ ,  $T$ - $v$ , and  $P$ - $T$  diagrams.

- $120^\circ\text{C}$ , 500 kPa
- $120^\circ\text{C}$ ,  $0.5\text{ m}^3/\text{kg}$

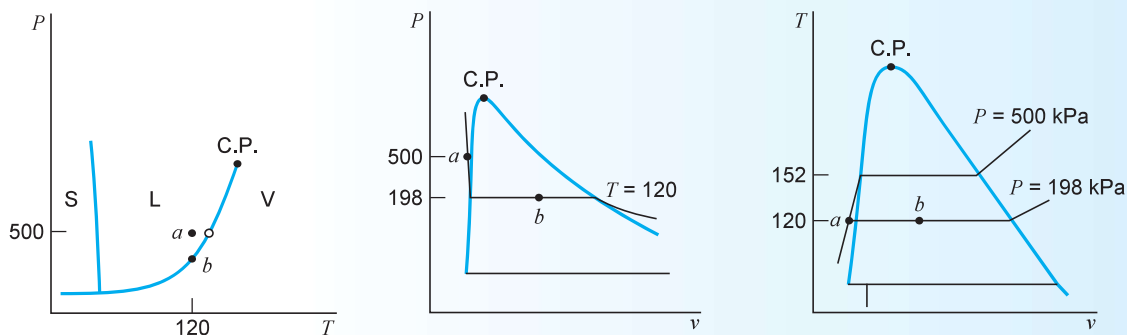
**Solution**

**a.** Enter Table B.1.1 with  $120^\circ\text{C}$ . The saturation pressure is 198.5 kPa, so we have a compressed liquid, point  $a$  in Fig. 3.10. That is above the saturation line for  $120^\circ\text{C}$ . We could also have entered Table B.1.2 with 500 kPa and found the saturation temperature as  $151.86^\circ\text{C}$ , so we would say that it is a subcooled liquid. That is to the left of the saturation line for 500 kPa, as seen in the  $P$ - $T$  diagram.

**b.** Enter Table B.1.1 with  $120^\circ\text{C}$  and notice that

$$v_f = 0.00106 < v < v_g = 0.89186\text{ m}^3/\text{kg}$$

so the state is a two-phase mixture of liquid and vapor, point  $b$  in Fig. 3.10. The state is to the left of the saturated vapor state and to the right of the saturated liquid state, both seen in the  $T$ - $v$  diagram.



**FIGURE 3.10** Diagram for Example 3.1.

**EXAMPLE 3.2** Determine the phase for each of the following states using the tables in Appendix B and indicate the relative position in the  $P$ - $v$ ,  $T$ - $v$ , and  $P$ - $T$  diagrams, as in Figs. 3.11 and 3.12.

- a. Ammonia 30°C, 1000 kPa
- b. R-134a 200 kPa, 0.125 m<sup>3</sup>/kg

**Solution**

- a. Enter Table B.2.1 with 30°C. The saturation pressure is 1167 kPa. As we have a lower  $P$ , it is a superheated vapor state. We could also have entered with 1000 kPa and found a saturation temperature of slightly less than 25°C, so we have a state that is superheated about 5°C.

- b. Enter Table B.5.2 (or B.5.1) with 200 kPa and notice that

$$v > v_g = 0.1000 \text{ m}^3/\text{kg}$$

so from the  $P$ - $v$  diagram the state is superheated vapor. We can find the state in Table B.5.2 between 40 and 50°C.

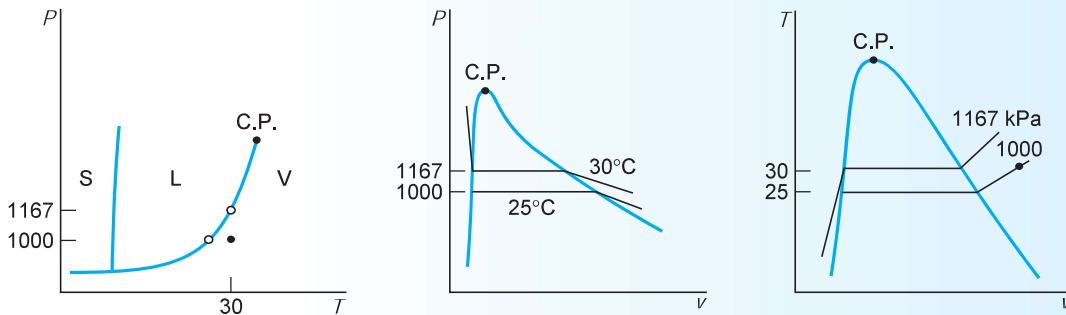


FIGURE 3.11 Diagram for Example 3.2a.

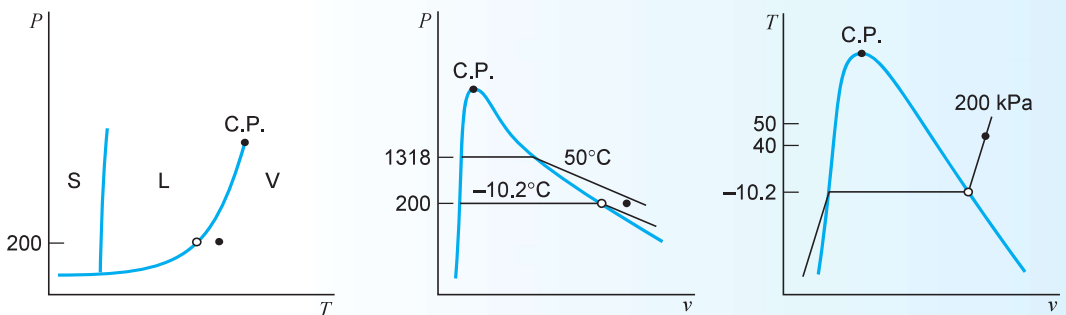


FIGURE 3.12 Diagram for Example 3.2b.

**EXAMPLE 3.3** Determine the temperature and quality (if defined) for water at a pressure of 300 kPa and at each of these specific volumes:

- a.  $0.5 \text{ m}^3/\text{kg}$
- b.  $1.0 \text{ m}^3/\text{kg}$

**Solution**

For each state, it is necessary to determine what phase or phases are present in order to know which table is the appropriate one to find the desired state information. That is, we must compare the given information with the appropriate phase boundary values. Consider a  $T$ - $v$  diagram (or a  $P$ - $v$  diagram) such as the one in Fig. 3.8. For the constant-pressure line of 300 kPa shown in Fig. 3.13, the values for  $v_f$  and  $v_g$  shown there are found from the saturation table, Table B.1.2.

- a. By comparison with the values in Fig. 3.13, the state at which  $v$  is  $0.5 \text{ m}^3/\text{kg}$  is seen to be in the liquid–vapor two-phase region, at which  $T = 133.6^\circ\text{C}$ , and the quality  $x$  is found from Eq. 3.2 as

$$0.5 = 0.001\,073 + x\,0.604\,75, \quad x = 0.825$$

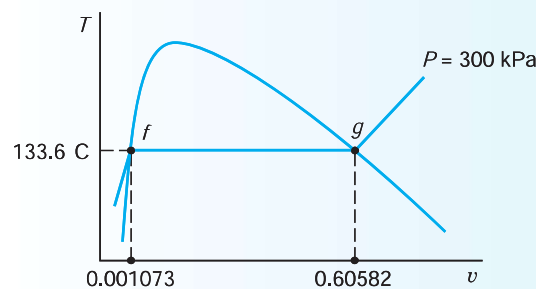
Note that if we did not have Table B.1.2 (as would be the case with the other substances listed in Appendix B), we could have interpolated in Table B.1.1 between the  $130^\circ\text{C}$  and  $135^\circ\text{C}$  entries to get the  $v_f$  and  $v_g$  values for 300 kPa.

- b. By comparison with the values in Fig. 3.13, the state at which  $v$  is  $1.0 \text{ m}^3/\text{kg}$  is seen to be in the superheated vapor region, in which quality is undefined and the temperature for which is found from Table B.1.3. In this case,  $T$  is found by linear interpolation between the 300 kPa specific-volume values at  $300^\circ\text{C}$  and  $400^\circ\text{C}$ , as shown in Fig. 3.14. This is an approximation for  $T$ , since the actual relation along the 300 kPa constant-pressure line is not exactly linear.

From the figure we have

$$\text{slope} = \frac{T - 300}{1.0 - 0.8753} = \frac{400 - 300}{1.0315 - 0.8753}$$

Solving this gives  $T = 379.8^\circ\text{C}$ .



**FIGURE 3.13** A  $T$ - $v$  diagram for water at 300 kPa.

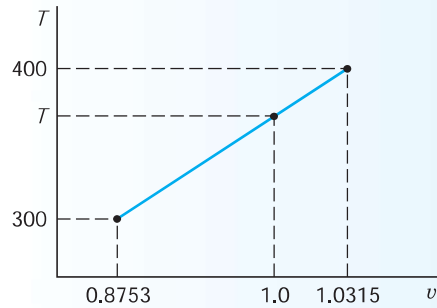


FIGURE 3.14  $T$  and  $v$  values for superheated vapor water at 300 kPa.

**EXAMPLE 3.4** A closed vessel contains  $0.1 \text{ m}^3$  of saturated liquid and  $0.9 \text{ m}^3$  of saturated vapor R-134a in equilibrium at  $30^\circ\text{C}$ . Determine the percent vapor on a mass basis.

**Solution**

Values of the saturation properties for R-134a are found from Table B.5.1. The mass–volume relations then give

$$V_{\text{liq}} = m_{\text{liq}} v_f, \quad m_{\text{liq}} = \frac{0.1}{0.000843} = 118.6 \text{ kg}$$

$$V_{\text{vap}} = m_{\text{vap}} v_g, \quad m_{\text{vap}} = \frac{0.9}{0.02671} = 33.7 \text{ kg}$$

$$m = 152.3 \text{ kg}$$

$$x = \frac{m_{\text{vap}}}{m} = \frac{33.7}{152.3} = 0.221$$

That is, the vessel contains 90% vapor by volume but only 22.1% vapor by mass.

**EXAMPLE 3.4E** A closed vessel contains  $0.1 \text{ ft}^3$  of saturated liquid and  $0.9 \text{ ft}^3$  of saturated vapor R-134a in equilibrium at  $90 \text{ F}$ . Determine the percent vapor on a mass basis.

**Solution**

Values of the saturation properties for R-134a are found from Table F.10. The mass–volume relations then give

$$V_{\text{liq}} = m_{\text{liq}} v_f, \quad m_{\text{liq}} = \frac{0.1}{0.0136} = 7.353 \text{ lbm}$$

$$V_{\text{vap}} = m_{\text{vap}} v_g, \quad m_{\text{vap}} = \frac{0.9}{0.4009} = 2.245 \text{ lbm}$$

$$m = 9.598 \text{ lbm}$$

$$x = \frac{m_{\text{vap}}}{m} = \frac{2.245}{9.598} = 0.234$$

That is, the vessel contains 90% vapor by volume but only 23.4% vapor by mass.

**EXAMPLE 3.5** A rigid vessel contains saturated ammonia vapor at 20°C. Heat is transferred to the system until the temperature reaches 40°C. What is the final pressure?

**Solution**

Since the volume does not change during this process, the specific volume also remains constant. From the ammonia tables, Table B.2.1, we have

$$v_1 = v_2 = 0.14922 \text{ m}^3/\text{kg}$$

Since  $v_g$  at 40°C is less than 0.14922 m<sup>3</sup>/kg, it is evident that in the final state the ammonia is superheated vapor. By interpolating between the 800- and 1000-kPa columns of Table B.2.2, we find that

$$P_2 = 945 \text{ kPa}$$

**EXAMPLE 3.5E** A rigid vessel contains saturated ammonia vapor at 70 F. Heat is transferred to the system until the temperature reaches 120 F. What is the final pressure?

**Solution**

Since the volume does not change during this process, the specific volume also remains constant. From the ammonia table, Table F.8,

$$v_1 = v_2 = 2.311 \text{ ft}^3/\text{lbm}$$

Since  $v_g$  at 120 F is less than 2.311 ft<sup>3</sup>/lbm, it is evident that in the final state the ammonia is superheated vapor. By interpolating between the 125- and 150-lbf/in.<sup>2</sup> columns of Table F.8, we find that

$$P_2 = 145 \text{ lbf/in.}^2$$

**EXAMPLE 3.6** Determine the missing property of  $P$ - $v$ - $T$  and  $x$  if applicable for the following states.

- a. Nitrogen:  $-53.2^\circ\text{C}$ , 600 kPa
- b. Nitrogen: 100 K, 0.008 m<sup>3</sup>/kg

**Solution**

For nitrogen the properties are listed in Table B.6 with temperature in Kelvin.

- a. Enter in Table B.6.1 with  $T = 273.2 - 53.2 = 220 \text{ K}$ , which is higher than the critical  $T$  in the last entry. Then proceed to the superheated vapor tables. We would also have realized this by looking at the critical properties in Table A.2. From Table B.6.2 in the subsection for 600 kPa ( $T_{\text{sat}} = 96.37 \text{ K}$ )

$$v = 0.10788 \text{ m}^3/\text{kg}$$

shown as point  $a$  in Fig. 3.15.

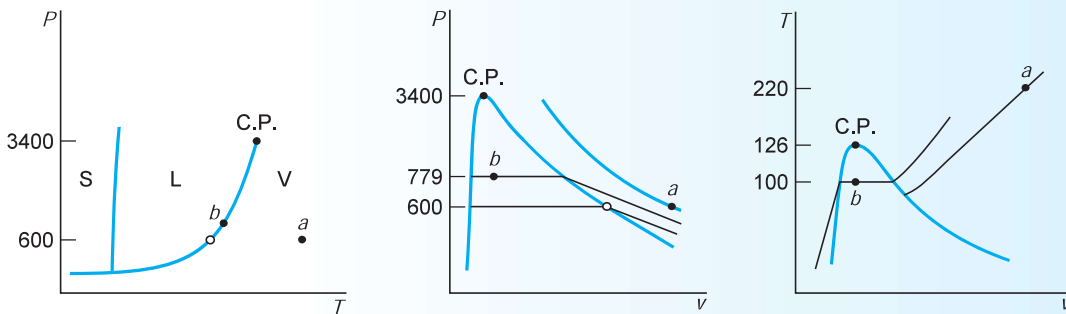


FIGURE 3.15 Diagram for Example 3.6.

b. Enter in Table B.6.1 with  $T = 100$  K, and we see that

$$v_f = 0.001452 < v < v_g = 0.0312 \text{ m}^3/\text{kg}$$

so we have a two-phase state with a pressure as the saturation pressure, shown as  $b$  in Fig. 3.15:

$$P_{\text{sat}} = 779.2 \text{ kPa}$$

and the quality from Eq. 3.2 becomes

$$x = (v - v_f)/v_{fg} = (0.008 - 0.001452)/0.02975 = 0.2201$$

**EXAMPLE 3.7** Determine the pressure for water at  $200^\circ\text{C}$  with  $v = 0.4 \text{ m}^3/\text{kg}$ .

**Solution**

Start in Table B.1.1 with  $200^\circ\text{C}$  and note that  $v > v_g = 0.12736 \text{ m}^3/\text{kg}$ , so we have superheated vapor. Proceed to Table B.1.3 at any subsection with  $200^\circ\text{C}$ ; suppose we start at 200 kPa. There  $v = 1.08034$ , which is too large, so the pressure must be higher. For 500 kPa,  $v = 0.42492$ , and for 600 kPa,  $v = 0.35202$ , so it is bracketed. This is shown in Fig. 3.16.

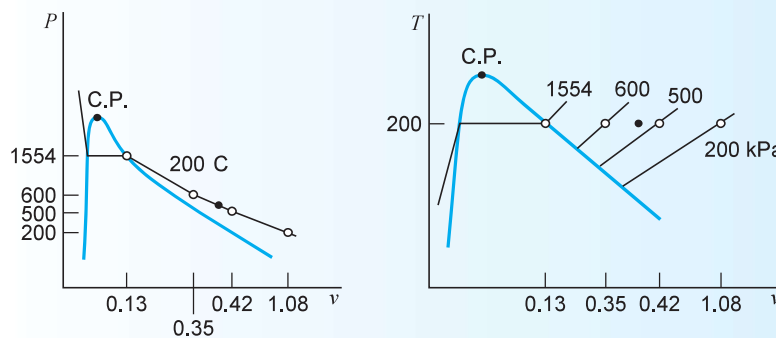
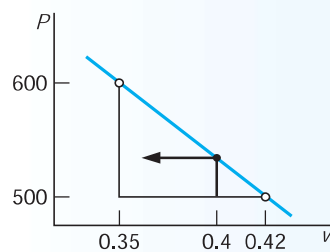


FIGURE 3.16 Diagram for Example 3.7.



**FIGURE 3.17** Linear interpolation for Example 3.7.



The real constant- $T$  curve is slightly curved and not linear, but for manual interpolation we assume a linear variation.

A linear interpolation, Fig. 3.17, between the two pressures is done to get  $P$  at the desired  $v$ .

$$P = 500 + (600 - 500) \frac{0.4 - 0.42492}{0.35202 - 0.42492} = 534.2 \text{ kPa}$$

### In-Text Concept Questions

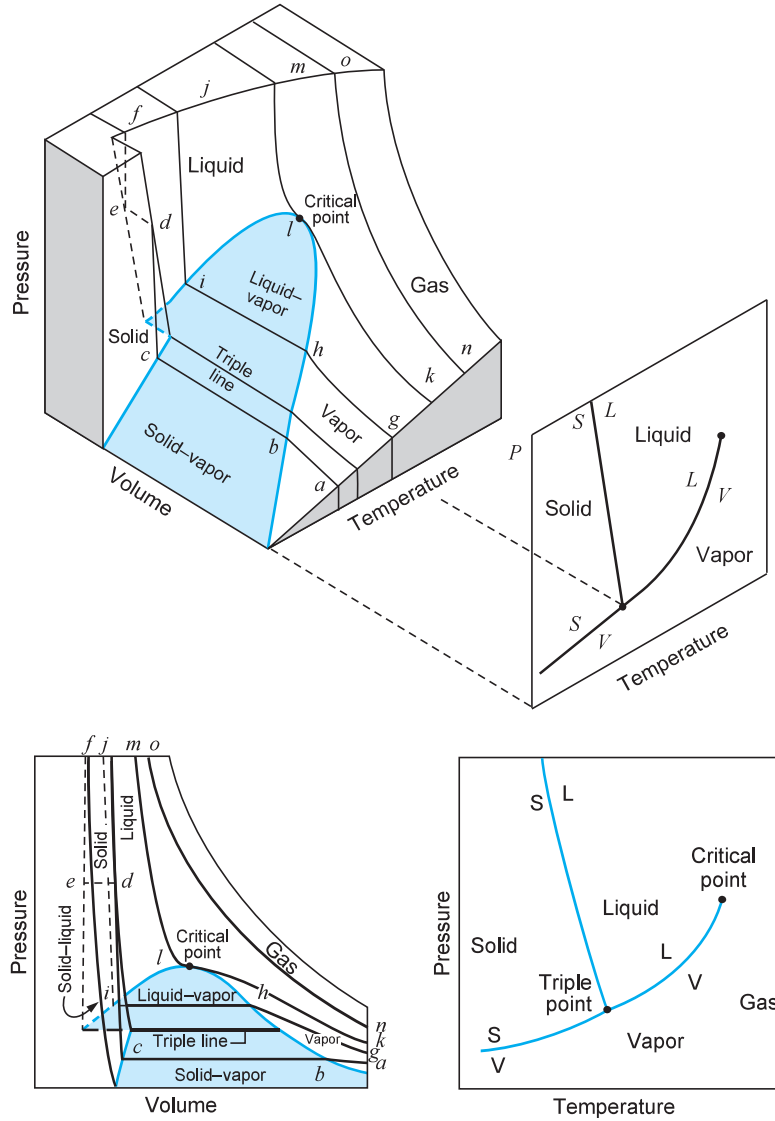
- d. Some tools should be cleaned in liquid water at  $150^\circ\text{C}$ . How high a  $P$  is needed?
- e. Water at 200 kPa has a quality of 50%. Is the volume fraction  $V_g/V_{\text{tot}} < 50\%$  or  $> 50\%$ ?
- f. Why are most of the compressed liquid or solid regions not included in the printed tables?
- g. Why is it not typical to find tables for argon, helium, neon, or air in a B-section table?
- h. What is the percent change in volume as liquid water freezes? Mention some effects the volume change can have in nature and in our households.

## 3.5 THERMODYNAMIC SURFACES

The matter discussed to this point can be well summarized by consideration of a **pressure-specific volume-temperature surface**. Two such surfaces are shown in Figs. 3.18 and 3.19. Figure 3.18 shows a substance such as water, in which the specific volume increases during freezing. Figure 3.19 shows a substance in which the specific volume decreases during freezing.

In these diagrams the pressure, specific volume, and temperature are plotted on mutually perpendicular coordinates, and each possible equilibrium state is thus represented by a point on the surface. This follows directly from the fact that a pure substance has only two independent intensive properties. All points along a quasi-equilibrium process lie on the  $P$ - $v$ - $T$  surface, since such a process always passes through equilibrium states.

The regions of the surface that represent a single phase—the solid, liquid, and vapor phases—are indicated. These surfaces are curved. The two-phase regions—the solid-liquid, solid-vapor, and liquid-vapor regions—are ruled surfaces. By this we understand that they are made up of straight lines parallel to the specific-volume axis. This, of course, follows from the fact that in the two-phase region, lines of constant pressure are also lines of constant temperature, although the specific volume may change. The triple point actually appears as the triple line on the  $P$ - $v$ - $T$  surface, since the pressure and temperature of the triple point are fixed, but the specific volume may vary, depending on the proportion of each phase.



**FIGURE 3.18**  $P$ - $v$ - $T$  surface for a substance that expands on freezing.

It is also of interest to note the pressure–temperature and pressure–volume projections of these surfaces. We have already considered the pressure–temperature diagram for a substance such as water. It is on this diagram that we observe the triple point. Various lines of constant temperature are shown on the pressure–volume diagram, and the corresponding constant-temperature sections are lettered identically on the  $P$ - $v$ - $T$  surface. The critical isotherm has a point of inflection at the critical point.

Notice that for a substance such as water, which expands on freezing, the freezing temperature decreases with an increase in pressure. For a substance that contracts on freezing, the freezing temperature increases as the pressure increases. Thus, as the pressure of vapor is increased along the constant-temperature line  $abcdef$  in Fig. 3.18, a substance that