Properties of a Pure Substance

In the previous chapter we considered three familiar properties of a substance: specific volume, pressure, and temperature. We now turn our attention to pure substances and consider some of the phases in which a pure substance may exist, the number of independent properties a pure substance may have, and methods of presenting thermodynamic properties.

Properties and the behavior of substances are very important for our studies of devices and thermodynamic systems. The steam power plant in Fig. 1.1 and the nuclear propulsion system in Fig. 1.3 have very similar processes, using water as the working substance. Water vapor (steam) is made by boiling at high pressure in the steam generator followed by expansion in the turbine to a lower pressure, cooling in the condenser, and a return to the boiler by a pump that raises the pressure. We must know the properties of water to properly size equipment such as the burners or heat exchangers, turbine, and pump for the desired transfer of energy and the flow of water. As the water is transformed from liquid to vapor, we need to know the temperature for the given pressure, and we must know the density or specific volume so that the piping can be properly dimensioned for the flow. If the pipes are too small, the expansion creates excessive velocities, leading to pressure losses and increased friction, and thus demanding a larger pump and reducing the turbine's work output.

Another example is a refrigerator, shown in Fig. 1.6, where we need a substance that will boil from liquid to vapor at a low temperature, say $-20°C$. This absorbs energy from the cold space, keeping it cold. Inside the black grille in the back or at the bottom, the now hot substance is cooled by air flowing around the grille, so it condenses from vapor to liquid at a temperature slightly higher than room temperature. When such a system is designed, we need to know the pressures at which these processes take place and the amount of energy, covered in Chapter 5, that is involved. We also need to know how much volume the substance occupies, that is, the specific volume, so that the piping diameters can be selected as mentioned for the steam power plant. The substance is selected so that the pressure is reasonable during these processes; it should not be too high, due to leakage and safety concerns, and not too low, as air might leak into the system.

A final example of a system where we need to know the properties of the substance is the gas turbine and a variation thereof, namely, the jet engine shown in Fig. 1.11. In these systems, the working substance is a gas (very similar to air) and no phase change takes place. A combustion process burns fuel and air, freeing a large amount of energy, which heats the gas so that it expands. We need to know how hot the gas gets and how large the expansion is so that we can analyze the expansion process in the turbine and the exit nozzle of the jet engine. In this device, large velocities are needed inside the turbine section and for the exit of the jet engine. This high-velocity flow pushes on the blades in the turbine to create shaft work or pushes on the jet engine (called *thrust*) to move the aircraft forward.

These are just a few examples of complete thermodynamic systems where a substance goes through several processes involving changes of its thermodynamic state and therefore its properties. As your studies progress, many other examples will be used to illustrate the general subjects.

3.1 | THE PURE SUBSTANCE

A pure substance is one that has a homogeneous and invariable chemical composition. It may exist in more than one phase, but the chemical composition is the same in all phases. Thus, liquid water, a mixture of liquid water and water vapor (steam), and a mixture of ice and liquid water are all pure substances; every phase has the same chemical composition. In contrast, a mixture of liquid air and gaseous air is not a pure substance because the composition of the liquid phase is different from that of the vapor phase.

Sometimes a mixture of gases, such as air, is considered a pure substance as long as there is no change of phase. Strictly speaking, this is not true. As we will see later, we should say that a mixture of gases such as air exhibits some of the characteristics of a pure substance as long as there is no change of phase.

In this book the emphasis will be on simple compressible substances. This term designates substances whose surface effects, magnetic effects, and electrical effects are insignificant when dealing with the substances. But changes in volume, such as those associated with the expansion of a gas in a cylinder, are very important. Reference will be made, however, to other substances for which surface, magnetic, and electrical effects are important. We will refer to a system consisting of a simple compressible substance as a *simple compressible system*.

## 3.2 | VAPOR–LIQUID–SOLID-PHASE EQUILIBRIUM IN A PURE SUBSTANCE

Consider as a system 1 kg of water contained in the piston/cylinder arrangement shown in Fig. 3.1*a*. Suppose that the piston and weight maintain a pressure of 0.1 MPa in the cylinder and that the initial temperature is 20°C. As heat is transferred to the water, the temperature increases appreciably, the specific volume increases slightly, and the pressure remains constant. When the temperature reaches 99.6°C, additional heat transfer results in a change of phase, as indicated in Fig. 3.1*b*. That is, some of the liquid becomes vapor, and during this process both the temperature and pressure remain constant, but the specific volume increases considerably. When the last drop of liquid has vaporized, further transfer of heat results in an increase in both the temperature and specific volume of the vapor, as shown in Fig. 3.1*c*.

The term saturation temperature designates the temperature at which vaporization takes place at a given pressure. This pressure is called the saturation pressure for the given temperature. Thus, for water at 99.6°C the saturation pressure is 0.1 MPa, and for water at 0.1 MPa the saturation temperature is 99.6°C. For a pure substance there is a definite relation between saturation pressure and saturation temperature. A typical curve, called the *vapor-pressure curve*, is shown in Fig. 3.2.

If a substance exists as liquid at the saturation temperature and pressure, it is called a saturated liquid. If the temperature of the liquid is lower than the saturation temperature for

FIGURE 3.1
Constant-pressure change from liquid to vapor phase for a pure substance.
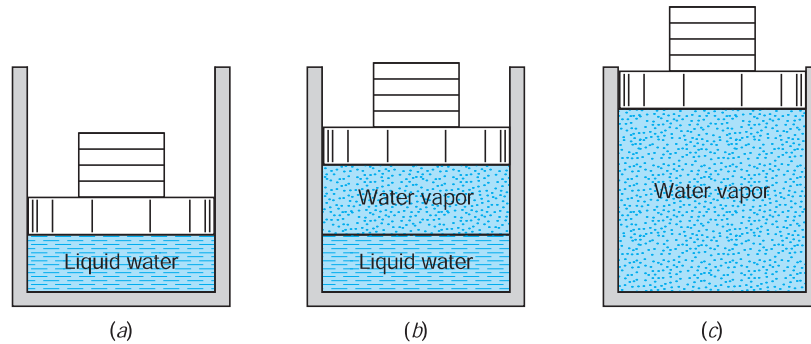
the existing pressure, it is called either a subcooled liquid (implying that the temperature is lower than the saturation temperature for the given pressure) or a compressed liquid (implying that the pressure is greater than the saturation pressure for the given temperature). Either term may be used, but the latter term will be used in this book.

When a substance exists as part liquid and part vapor at the saturation temperature, its quality is defined as the ratio of the mass of vapor to the total mass. Thus, in Fig. 3.1*b*, if the mass of the vapor is 0.2 kg and the mass of the liquid is 0.8 kg, the quality is 0.2 or 20%. The quality may be considered an intensive property and has the symbol *x*. Quality has meaning only when the substance is in a saturated state, that is, at saturation pressure and temperature.

If a substance exists as vapor at the saturation temperature, it is called saturated vapor. (Sometimes the term *dry saturated vapor* is used to emphasize that the quality is 100%.) When the vapor is at a temperature greater than the saturation temperature, it is said to exist as superheated vapor. The pressure and temperature of superheated vapor are independent properties, since the temperature may increase while the pressure remains constant. Actually, the substances we call gases are highly superheated vapors.

Consider Fig. 3.1 again. Let us plot on the temperature–volume diagram of Fig. 3.3 the constant-pressure line that represents the states through which the water passes as it is heated from the initial state of 0.1 MPa and 20°C. Let state *A* represent the initial state, *B* the saturated-liquid state (99.6°C), and line *AB* the process in which the liquid is heated from the initial temperature to the saturation temperature. Point *C* is the saturated-vapor state, and line *BC* is the constant-temperature process in which the change of phase from liquid to vapor occurs. Line *CD* represents the process in which the steam is superheated at constant pressure. Temperature and volume both increase during this process.

Now let the process take place at a constant pressure of 1 MPa, starting from an initial temperature of 20°C. Point *E* represents the initial state, in which the specific volume

FIGURE 3.2
Vapor-pressure curve of a pure substance.
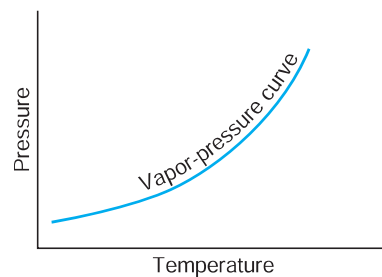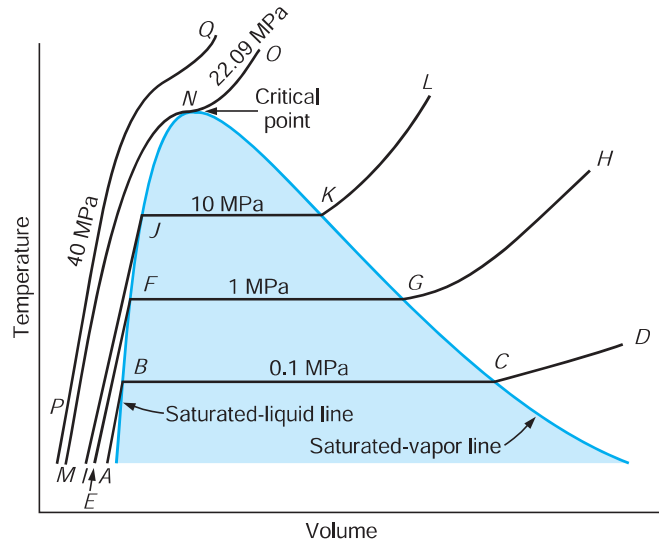
FIGURE 3.3
Temperature–volume diagram for water showing liquid and vapor phases (not to scale).

is slightly less than that at 0.1 MPa and 20°C. Vaporization begins at point F, where the temperature is 179.9°C. Point G is the saturated-vapor state, and line GH is the constant-pressure process in which the steam in superheated.

In a similar manner, a constant pressure of 10 MPa is represented by line $IJKL$, for which the saturation temperature is 311.1°C.

At a pressure of 22.09 MPa, represented by line MNO, we find, however, that there is no constant-temperature vaporization process. Instead, point N is a point of inflection with a zero slope. This point is called the critical point. At the critical point the saturated-liquid and saturated-vapor states are identical. The temperature, pressure, and specific volume at the critical point are called the *critical temperature*, *critical pressure*, and *critical volume*. The critical-point data for some substances are given in Table 3.1. More extensive data are given in Table A.2 in Appendix A.

A constant-pressure process at a pressure greater than the critical pressure is represented by line PQ. If water at 40 MPa and 20°C is heated in a constant-pressure process in a cylinder, as shown in Fig. 3.1, two phases will never be present and the state shown in Fig. 3.1*b* will never exist. Instead, there will be a continuous change in density, and at all times only one phase will be present. The question then is, when do we have a liquid and when do we have a vapor? The answer is that this is not a valid question at supercritical pressures. We simply call the substance a *fluid*. However, rather arbitrarily, at temperatures below the

TABLE 3.1
Some Critical-Point Data

	Critical Temperature, °C	Critical Pressure, MPa	Critical Volume, m³/kg
Water	374.14	22.09	0.003 155
Carbon dioxide	31.05	7.39	0.002 143
Oxygen	−118.35	5.08	0.002 438
Hydrogen	−239.85	1.30	0.032 192

critical temperature we usually refer to it as a *compressed liquid* and at temperatures above the critical temperature as a *superheated vapor*. It should be emphasized, however, that at pressures above the critical pressure a liquid phase and a vapor phase of a pure substance never exist in equilibrium.

In Fig. 3.3, line *NJFB* represents the saturated-liquid line and line *NKGC* represents the saturated-vapor line.

By convention, the subscript *f* is used to designate a property of a saturated liquid and the subscript *g* a property of a saturated vapor (the subscript *g* being used to denote saturation temperature and pressure). Thus, a saturation condition involving part liquid and part vapor, such as that shown in Fig. 3.1*b*, can be shown on *T–v* coordinates, as in Fig. 3.4. All of the liquid present is at state *f* with specific volume v_f and all of the vapor present is at state *g* with v_g. The total volume is the sum of the liquid volume and the vapor volume, or

$$V = V_{\text{liq}} + V_{\text{vap}} = m_{\text{liq}} v_f + m_{\text{vap}} v_g$$

The average specific volume of the system *v* is then

$$v = \frac{V}{m} = \frac{m_{\text{liq}}}{m} v_f + \frac{m_{\text{vap}}}{m} v_g = (1 - x) v_f + x v_g \tag{3.1}$$

in terms of the definition of quality $x = m_{\text{vap}}/m$.

Using the definition

$$v_{fg} = v_g - v_f$$

Eq. 3.1 can also be written as

$$v = v_f + x v_{fg} \tag{3.2}$$

Now the quality *x* can be viewed as the fraction $(v - v_f)/v_{fg}$ of the distance between saturated liquid and saturated vapor, as indicated in Fig. 3.4.

Let us now consider another experiment with the piston/cylinder arrangement. Suppose that the cylinder contains 1 kg of ice at $-20°$C, 100 kPa. When heat is transferred to the ice, the pressure remains constant, the specific volume increases slightly, and the temperature increases until it reaches $0°$C, at which point the ice melts and the temperature remains constant. In this state the ice is called a *saturated solid*. For most substances the specific volume increases during this melting process, but for water the specific volume of the liquid is less than the specific volume of the solid. When all the ice has melted, further heat transfer causes an increase in the temperature of the liquid.

If the initial pressure of the ice at $-20°$C is 0.260 kPa, heat transfer to the ice results in an increase in temperature to $-10°$C. At this point, however, the ice passes directly from
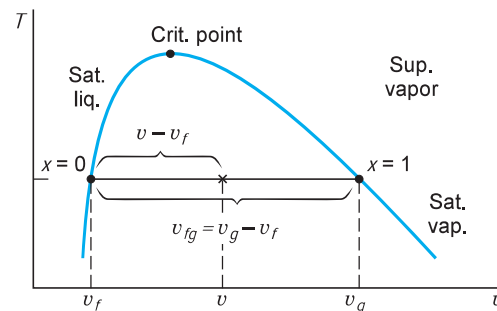
FIGURE 3.4 *T–v* diagram for the two-phase liquid–vapor region showing the quality–specific volume relation.

TABLE 3.2
Some Solid–Liquid–Vapor Triple-Point Data

	Temperature, °C	Pressure, kPa
Hydrogen (normal)	−259	7.194
Oxygen	−219	0.15
Nitrogen	−210	12.53
Carbon dioxide	−56.4	520.8
Mercury	−39	0.000 000 13
Water	0.01	0.6113
Zinc	419	5.066
Silver	961	0.01
Copper	1083	0.000 079

the solid phase to the vapor phase in the process known as sublimation. Further heat transfer results in superheating of the vapor.

Finally, consider an initial pressure of the ice of 0.6113 kPa and a temperature of −20°C. Through heat transfer, let the temperature increase until it reaches 0.01°C. At this point, however, further heat transfer may cause some of the ice to become vapor and some to become liquid, for at this point it is possible to have the three phases in equilibrium. This point is called the triple point, defined as the state in which all three phases may be present in equilibrium. The pressure and temperature at the triple point for a number of substances are given in Table 3.2.

This whole matter is best summarized by Fig. 3.5, which shows how the solid, liquid, and vapor phases may exist together in equilibrium. Along the sublimation line the solid
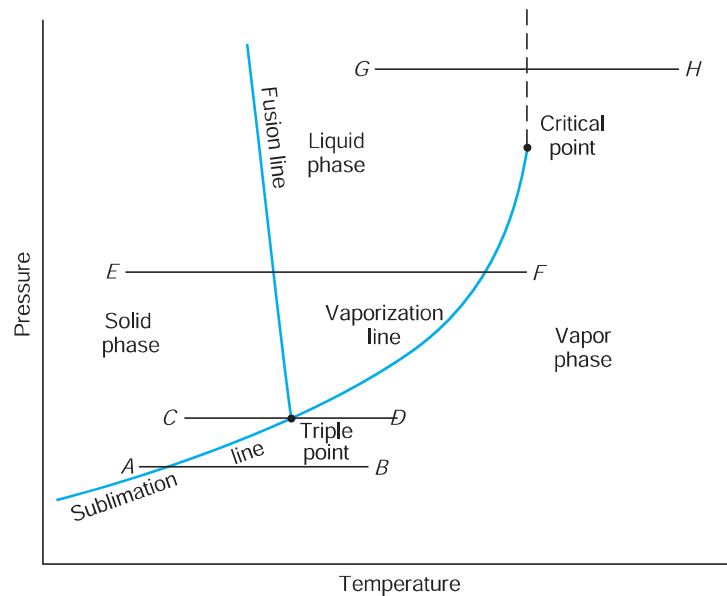

FIGURE 3.5 *P–T* diagram for a substance such as water.

and vapor phases are in equilibrium, along the fusion line the solid and liquid phases are in equilibrium, and along the vaporization line the liquid and vapor phases are in equilibrium. The only point at which all three phases may exist in equilibrium is the triple point. The vaporization line ends at the critical point because there is no distinct change from the liquid phase to the vapor phase above the critical point.

Consider a solid in state *A*, as shown in Fig. 3.5. When the temperature increases but the pressure (which is less than the triple-point pressure) is constant, the substance passes directly from the solid to the vapor phase. Along the constant-pressure line *EF*, the substance passes from the solid to the liquid phase at one temperature and then from the liquid to the vapor phase at a higher temperature. The constant-pressure line *CD* passes through the triple point, and it is only at the triple point that the three phases may exist together in equilibrium. At a pressure above the critical pressure, such as *GH*, there is no sharp distinction between the liquid and vapor phases.

Although we have made these comments with specific reference to water (only because of our familiarity with water), all pure substances exhibit the same general behavior. However, the triple-point temperature and critical temperature vary greatly from one substance to another. For example, the critical temperature of helium, as given in Table A.2, is 5.3 K. Therefore, the absolute temperature of helium at ambient conditions is over 50 times greater than the critical temperature. In contrast, water has a critical temperature of 374.14°C (647.29 K), and at ambient conditions the temperature of water is less than half the critical temperature. Most metals have a much higher critical temperature than water. When we consider the behavior of a substance in a given state, it is often helpful to think of this state in relation to the critical state or triple point. For example, if the pressure is greater than the critical pressure, it is impossible to have a liquid phase and a vapor phase in equilibrium. Or, to consider another example, the states at which vacuum melting a given metal is possible can be ascertained by a consideration of the properties at the triple point. Iron at a pressure just above 5 Pa (the triple-point pressure) would melt at a temperature of about 1535°C (the triple-point temperature).

Figure 3.6 shows the three-phase diagram for carbon dioxide, in which it is seen (see also Table 3.2) that the triple-point pressure is greater than normal atmospheric pressure,
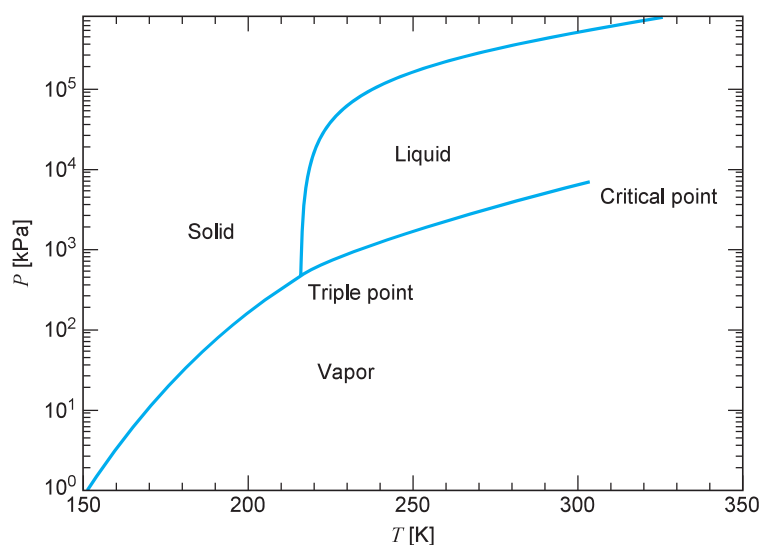
FIGURE 3.6 Carbon dioxide phase diagram.
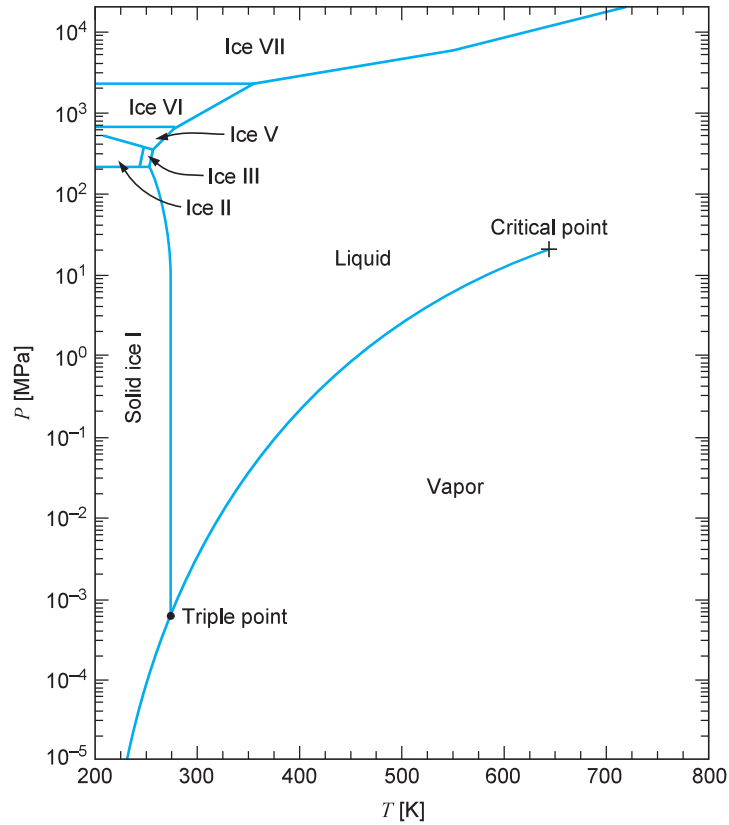
FIGURE 3.7 Water phase diagram.

which is very unusual. Therefore, the commonly observed phase transition under conditions of atmospheric pressure of about 100 kPa is a sublimation from solid directly to vapor, without passing through a liquid phase, which is why solid carbon dioxide is commonly referred to as *dry ice*. We note from Fig. 3.6 that this phase transformation at 100 kPa occurs at a temperature below 200 K.

Finally, it should be pointed out that a pure substance can exist in a number of different solid phases. A transition from one solid phase to another is called an allotropic transformation. Figure 3.7 shows a number of solid phases for water. A pure substance can have a number of triple points, but only one triple point has a solid, liquid, and vapor equilibrium. Other triple points for a pure substance can have two solid phases and a liquid phase, two solid phases and a vapor phase, or three solid phases.

In-Text Concept Questions

a. If the pressure is smaller than P_{sat} at a given T, what is the phase?

b. An external water tap has the valve activated by a long spindle, so the closing mechanism is located well inside the wall. Why?

c. What is the lowest temperature (approximately) at which water can be liquid?