

CHAPTER 3

PROPERTIES OF COMMON SUBSTANCE

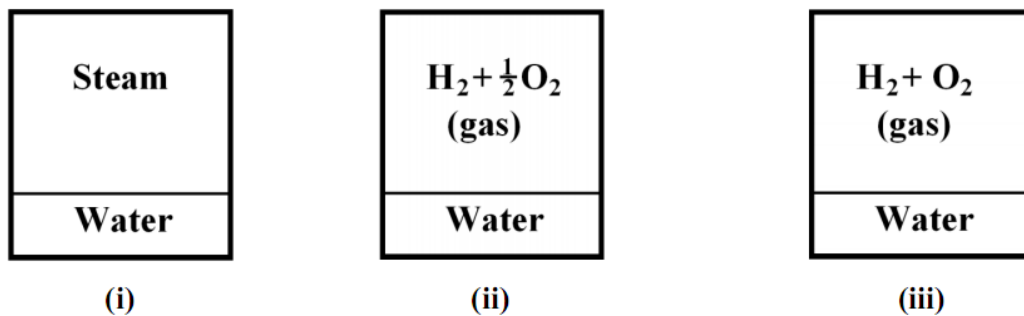
3.1 Pure Substance and State Postulate

Pure implies substances composed of a single chemical species. Hence a pure substance is a system which is

- (a) homogeneous in chemical composition,
- (b) homogeneous in chemical aggregation, and
- (c) invariable in chemical composition.

Homogeneous in chemical composition means that the composition of each part of the system is the same as the compositions of every other part. Composition means relative proportion of the chemical elements into which the sample can be analyzed. It does not matter how these elements are combine.

In Figure 3.1 for example, system (i), comprising steam and water, is homogeneous in composition, since chemical analysis would reveal that hydrogen and oxygen atoms are present in the ratio 2:1 whether the sample be taken from the steam or from the water. The same is true for system (ii), containing uncombined hydrogen and oxygen gas in the atomic ratio 2:1 in the upper part, and water in the lower part. System (iii) however is not homogeneous in composition; for the hydrogen and oxygen are present in the ratio 1:1 in the upper part, but in the ratio 2:1 (as water) in the lower part.



Satisfies condition (a) Satisfies condition (a) Does not satisfies condition (a)
 Satisfies condition (b) Does not satisfies condition (b)

Figure 3.1: Illustrating the definition of a pure substance

Homogeneous in chemical composition means that the chemical elements must be combined chemically in the same way in all parts of the system. Consideration of Figure 3.1 shows that system (i) satisfies this condition also; for steam and water consists of identical molecules. System (ii) on the other hand is not homogeneous in chemical aggregation since, in the upper part of the system, the hydrogen and oxygen are not combined chemically (individual atoms of H and O are not uniquely associated), whereas in the lower part of the system the hydrogen and oxygen are combined in the form of water.

Invariable chemical aggregation means that the state of the chemical combination of the system does not change with time. Thus a mixture of hydrogen and oxygen, which changed into steam during the time that the system was under consideration, would not be a pure substance.

The important characteristic of a pure substance is that it is invariable in chemical composition even though there may be a change of phase. Thus, a system consisting of a mixture of various phases of water viz. water and ice, water and steam is a pure substance. Similarly, a system consisting of oxygen as a vapor; a liquid or a combination of these is also a pure substance. Air, however, though a mixture of several gases is considered as a pure substance only as long as it is all gas or all liquid. A mixture of dry gaseous air and liquid air is not a pure substance, because chemical composition of liquid phase is different from that of vapor phase.

State Postulates

The number of properties required to fix the state of a system is given by the state postulate and is defined as the general rule that is developed as a guide in determining the number of independent properties required to fix the state of a system.

For a pure simple compressible substance, repeated observations and experiments show that two independent properties are necessary and sufficient to establish the stable equilibrium state of a system. The word simple and compressible imply that the only work mode considered is the PdV work form. A system is called a simple compressible system in the absence of electrical, magnetic, gravitational, motion, and surface tension effects.

The observed behavior of a pure simple compressible substance is summarized in the state postulates:

The values of any two independent thermodynamic properties are sufficient to establish the stable thermodynamic state of a pure simple compressible substance.

If T and v are known for a pure compressible substance, then P and u have unique known values. Mathematically this is given as

$$P=P(T,v) \text{ and } u=u(T,v)$$

3.2 Ideal Gas

A perfect gas or an ideal gas is defined as a gas having no forces of molecular attraction. A gas which follows the gas laws at all ranges of pressures and temperatures can be considered as an ideal gas but no such gas exists in nature. However, real gases tend to follow these laws at low pressures or high temperatures or at both. This is because the molecules are far apart at reduced pressures and elevated temperatures and the force of attraction between them tends to be small. At low pressures, the gases behave nearly as ideal gases. The range of this low pressure is different for different gases.

3.2.1 Boyle's Law

This law was enunciated by Robert Boyle in 1661 on the basis of his experimental results. Boyle's law may be stated as follows:

If the temperature remains constant, the volume of a given mass of gas is inversely proportional to the pressure.

$$V \propto \left(\frac{1}{P}\right)_T$$

3.2.2 Charles' Law

This law, also known as Gay-Lussac's law, was enunciated in 1787. It may be stated in parts:

(a) If the pressure is held constant, the volume of a given mass of gas varies directly as the absolute temperature.

$$V \propto (T)_P$$

(b) If the volume is held constant, the pressure of a given mass of gas varies directly as the absolute temperature.

$$P \propto (T)_V$$

A relation between all the three variables P, V and T may be obtained by combining Boyle's law and Charles' law. Referring to Figure 3.2, consider unit mass of a gas in state 1 and let it undergo an arbitrary change to state 2. From state 1, draw a constant pressure line, and from state 2 draw a constant temperature line. The two lines intersect at point A.

Now applying Charles' law for the process 1-A

$$\frac{V_1}{V_A} = \frac{T_1}{T_A}$$

$$V_A = \frac{T_A}{T_1} V_1 = \frac{T_2}{T_1} V_1 \quad (i)$$

Applying Boyle's law for the process A-2

$$\frac{V_2}{V_A} = \frac{P_A}{P_2}$$

$$V_A = \frac{P_2}{P_A} V_1 = \frac{P_2}{P_1} V_1 \quad (ii)$$

Combining equation (i) and (ii)

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \frac{PV}{T} = R$$

where R is a constant for a given gas. The constant is called the characteristic gas constant and has the units of J/kg.K or m-kgf/kg.K.

For a system consisting of a mass of kg of gas,

$$PV = mRT$$

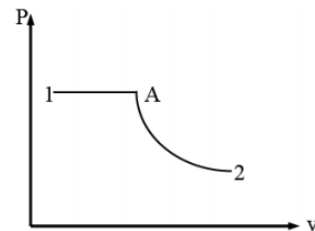


Figure 3.2: Relation between P, v, and T

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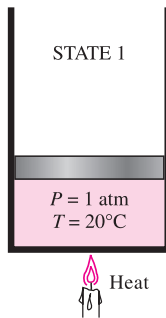


FIGURE 3-6

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

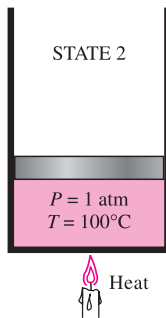


FIGURE 3-7

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

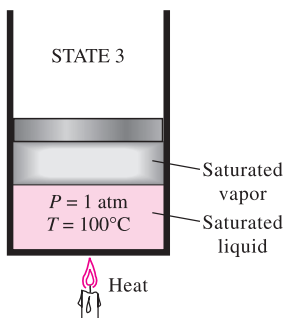


FIGURE 3-8

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

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

Compressed Liquid and Saturated Liquid

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

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

Saturated Vapor and Superheated Vapor

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

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

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

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

If the entire process described here is reversed by cooling the water while maintaining the pressure at the same value, the water will go back to state 1, retracing the same path, and in so doing, the amount of heat released will exactly match the amount of heat added during the heating process.

In our daily life, water implies liquid water and steam implies water vapor. In thermodynamics, however, both water and steam usually mean only one thing: 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

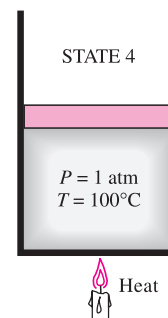


FIGURE 3–9

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

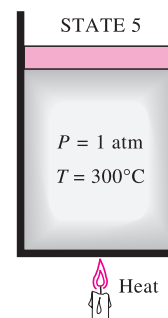


FIGURE 3–10

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

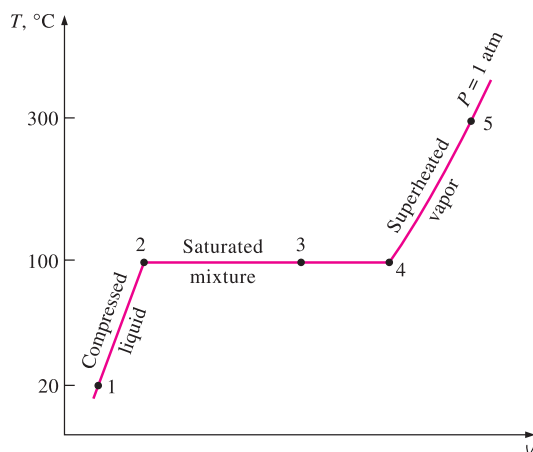


FIGURE 3–11

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

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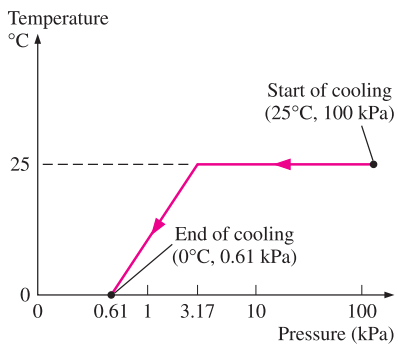


FIGURE 3-14

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

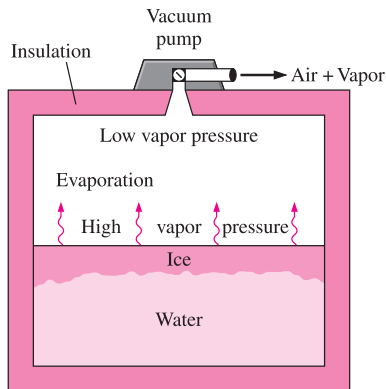


FIGURE 3-15

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



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

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

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

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

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

3-4 ■ PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

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

1 The T - v Diagram

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

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

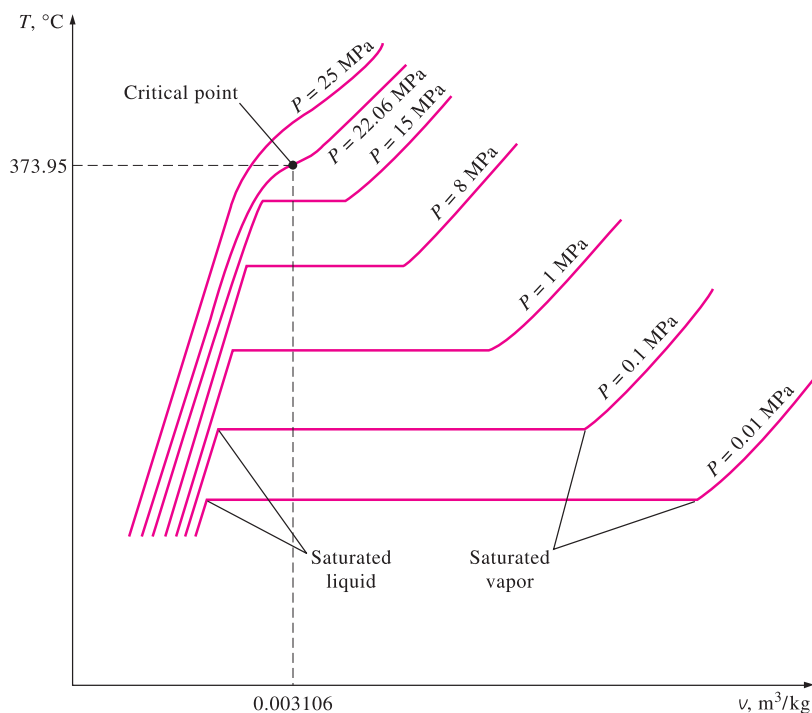


FIGURE 3-16

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

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

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

The temperature, pressure, and specific volume of a substance at the critical point are called, respectively, the *critical temperature* T_{cr} , *critical pressure* P_{cr} , and *critical specific volume* v_{cr} . The critical-point properties of water are $P_{\text{cr}} = 22.06 \text{ MPa}$, $T_{\text{cr}} = 373.95^{\circ}\text{C}$, 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. 3-17). Instead, the specific volume of the substance continually increases, and at all times there is only one phase present. Eventually, it resembles a vapor, but we can never tell when the change

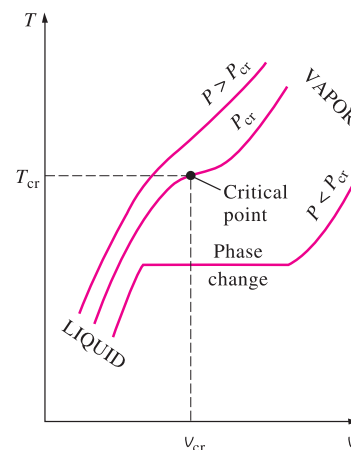


FIGURE 3-17

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

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

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

2 The P - v Diagram

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

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

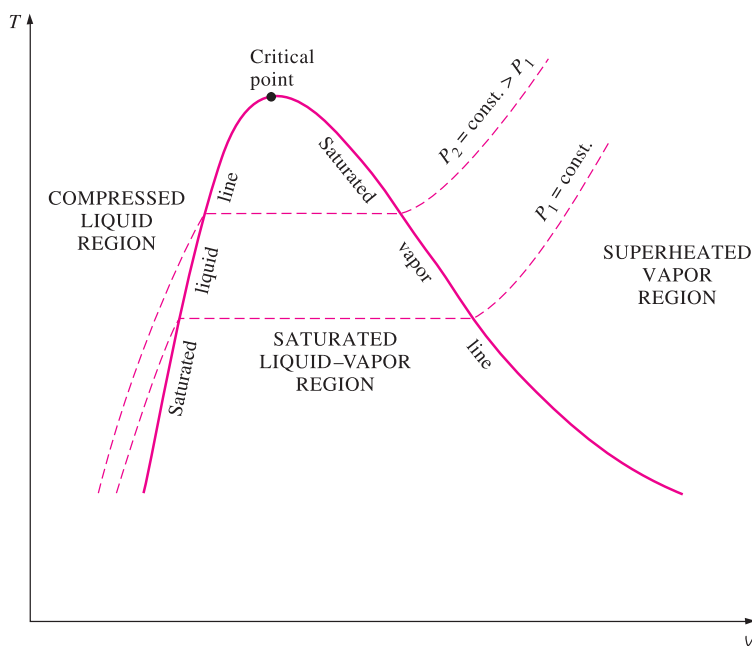


FIGURE 3–18

T - v diagram of a pure substance.

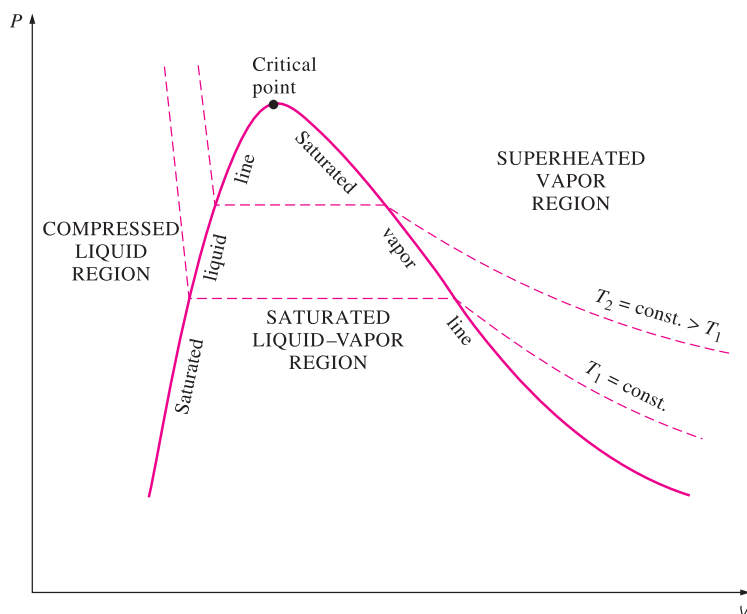


FIGURE 3-19

P - v diagram of a pure substance.

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

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

Extending the Diagrams to Include the Solid Phase

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

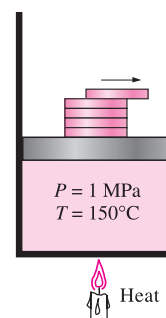


FIGURE 3-20

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

3.4 Property of a Two phase Mixture/Quality

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

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

where, $m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_l + m_g$

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).

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

$$V = V_l + V_g$$

$$mv = m_l v_l + m_g v_g$$

$$v = \frac{m_l}{m} v_l + \frac{m_g}{m} v_g$$

$$v = (1 - x)v_l + xv_g$$

$$v = v_l + x(v_g - v_l)$$

$$v = v_l + xv_{lg}$$

where, v_{lg} is defined as the difference between the specific volumes of the saturated vapor and the saturated liquid i.e. $v_{lg} = (v_g - v_l)$.

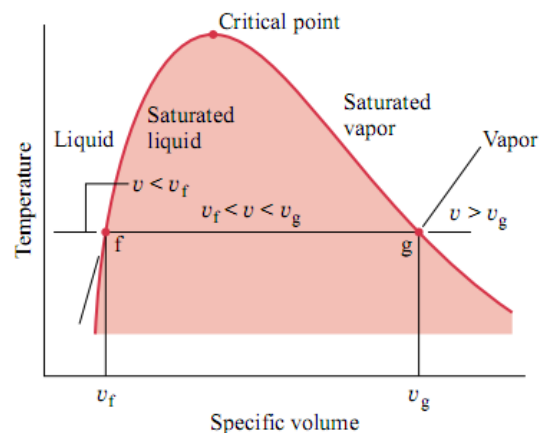
Any intensive property such as h, u, s can be evaluated for a state in the saturated/wet region by relating it with quality (x) i.e. for any intensive property ' z ', we can write,

$$z = z_l + xz_{lg}$$

i.e.

$$u = u_l + xu_{lg}$$

$$h = h_l + xh_{lg}$$



3.5 Other Thermodynamic Properties

3.5.1. Enthalpy: A combine property

In the analysis of certain types of processes, particularly in power generation and refrigeration, 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 denoted by 'h'

$$h = u + Pv \text{ (kJ/kg)}$$

$$H = U + PV \text{ (kJ)}$$

3.5.2 Specific Heat

The specific heat is defined as the energy required to raise the temperature of a unit mass of a substance by one degree. In thermodynamics, we are interested in two kinds of specific heats: specific heat at constant volume c_v and specific heat at constant pressure c_p .

Physically, the specific heat at constant volume c_v can be viewed as the energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant. The energy required to do the same as the pressure is maintained constant is the specific heat at constant pressure c_p . The specific heat at constant pressure c_p is always greater than c_v because at constant pressure the system is allowed to expand and the energy for this expansion work must also be supplied to the system.

In thermodynamics, specific heat at constant volume c_v is defined as the change in the internal energy of a substance per unit change in temperature at constant volume.

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v$$

Likewise, specific heat at constant pressure c_p can be defined as the change in the enthalpy of a substance per unit change in temperature at constant pressure.

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p$$

In other words, c_v is a measure of the variation of internal energy of a substance with temperature, and c_p is a measure of the variation of enthalpy of a substance with temperature. Thus, change in internal energy and enthalpy can be written as:

$$du = c_v(T) dT$$

$$dh = c_p(T) dT$$

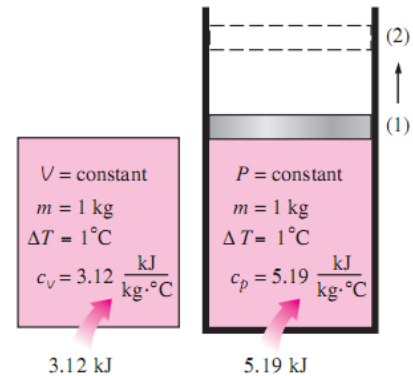


FIGURE 4-19

Constant-volume and constant-pressure specific heats c_v and c_p (values given are for helium gas).