Fundamentals of Thermodynamics
Lecture 5. The Pure Substance

5.1. Pure Substance

A substance that has a fixed chemical composition throughout is called a pure substance such as water, air, and nitrogen.

A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous.

A mixture of two or more phases of pure substance is still a pure substance as long as the chemical composition of all phases is the same. A mixture of ice and liquid water, for example, is a pure substance because both phases have the same chemical composition.

5.2. Phase-Change Process of Pure Substance

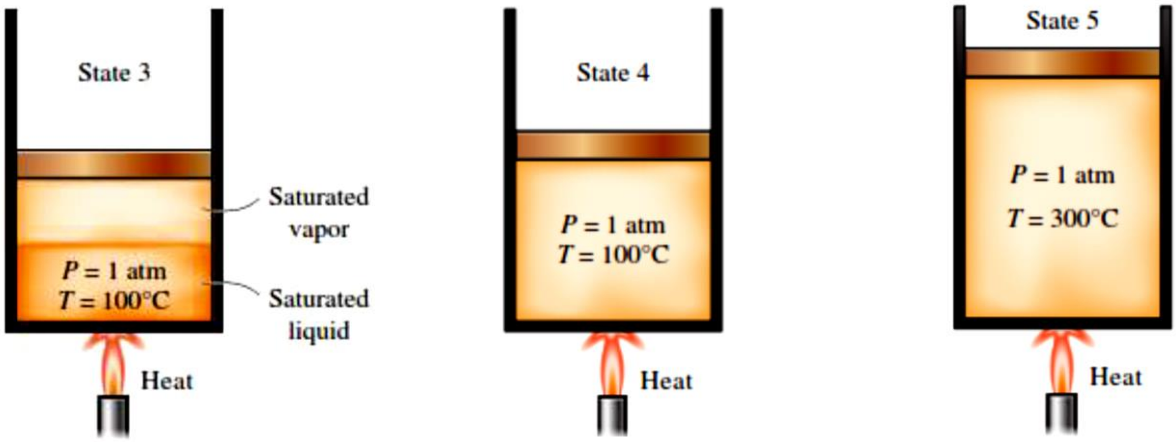
A pure substance may exist in different phases. There are three principal phases *solid*, *liquid*, and *gas*.
Consider a piston-cylinder device containing liquid water at 20 ^oC and 1atm pressure (state 1- fig.15). Under these conditions water exits in the liquid phase, and it is called a **compressed 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 ^oC. As a temperature rises, the liquid water will expand slightly, and so its specific volume will increase. The pressure in the cylinder remains constant at 1atm during the process. Water is still a compressed liquid at this state since it has not started to vaporize.
As more heat is transferred, the temperature will keep rising until it reach 100 ^oC (state 2 Fig.1). At this point water is still a liquid, but any heat addition will cause some of liquid to vaporize. This is a phase change process from liquid to vapor is about to take place. A liquid which is about to vaporize is called a saturated liquid. Therefore, state 2 is a **saturated liquid** state.
The temperature will remain constant during the entire phase change process if the pressure is held constant. During a vaporization (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.1) the cylinder contains equal amount of liquid and vapor. As we continue adding heat, the vaporization process will continue until the last drop of liquid is vaporize (state 4 Fig.1). the vapor which 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 often referred to as **saturated liquid-vapor mixture**.

Once the phase-change process is completed, we are back to a single phase region again (this time vapor), and further transfer of heat will result in an increase in both the temperature and the specific volume (state 5 Fig.1). At state 5, the temperature of the vapor is, let us say 300oC; 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 which is not about to condense (not a saturated vapor) is called a superheated vapor.

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

At 1 atm pressure and 100 °C, water exists a liquid is ready to vaporize



As more heat is transferred, part of saturated liquid vaporizes (saturated liquid-vapor mixture)

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

As more heat is transfer, the temperature of the vapor starts to rise (superheated vapor)

Figure 1. phase-change processes of pure substances

The constant-pressure phase-change process discussed above is illustrated on a T-v diagram in (Fig. 2).

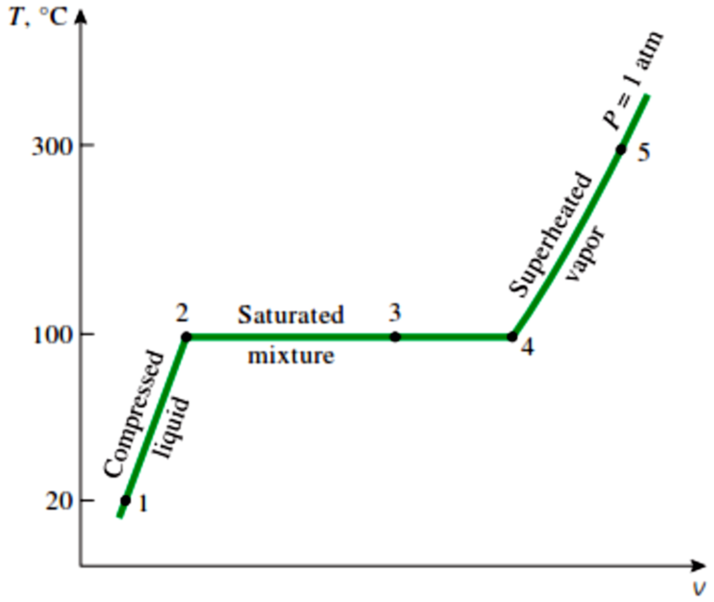


Figure 2. T-v Diagram for the heating process of water at constant pressure

5.3. Saturation Temperature and Saturation Pressure

It probably came as no surprise to you that the water started ‘boiling’ 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”. If the pressure inside the cylinder were raised to 500 kPa by adding weights on top of the piston, the water would start, boiling at 151.9 °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 the given pressure, the temperature at which a pure substance starts boiling is called, the **saturation temperature T_{sat}**. Likewise, at a given temperature, the pressure at which a pure substance starts boiling is called the **saturation pressure P_{sat}**.

During a phase-change process, pressure and temperature are obviously dependent properties, and there is a definite relation between them that is $T_{sat} = f(P_{sat})$. A plot of T_{sat} Vs. P_{sat}, such as the one given for water in Fig. 3 is called liquid-vapor saturation. A curve of this kind is characteristic of all pure substance.

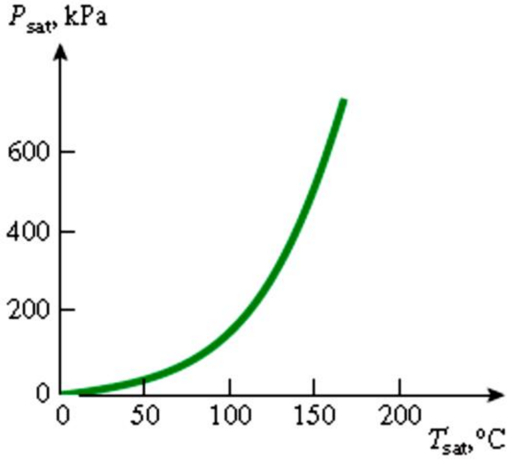


Figure 3. The liquid – vapor saturation curve of a pure substance

5.4. Property Diagram for Phase- Change Process

5.4.1. 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. 2. Now we repeat this process at different pressures to develop the T-v diagram for water. At 1MPa, water will have a somewhat smaller specific volume than it did at 1 atm pressure. As heat is transferred to the water at this pressure, the processes will follow a path which looks very much like the process path at 1 atm pressure, as shown in Fig. 4, but there are some noticeable differences. First, water will start boiling at a much higher temperature (179.9 ^oC) at this pressure. Second, the specific volume of saturated liquid is larger, and the specific volume of 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 increases further, this saturation line will continue to get shorter, as shown in Fig. 4, and it will become a point when the pressure reaches 22.09 MPa for the case of water. This point is called the **critical point**, and it may be defined as the point at which the saturated liquid and saturated vapor states are identical. The temperature, pressure and 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}.

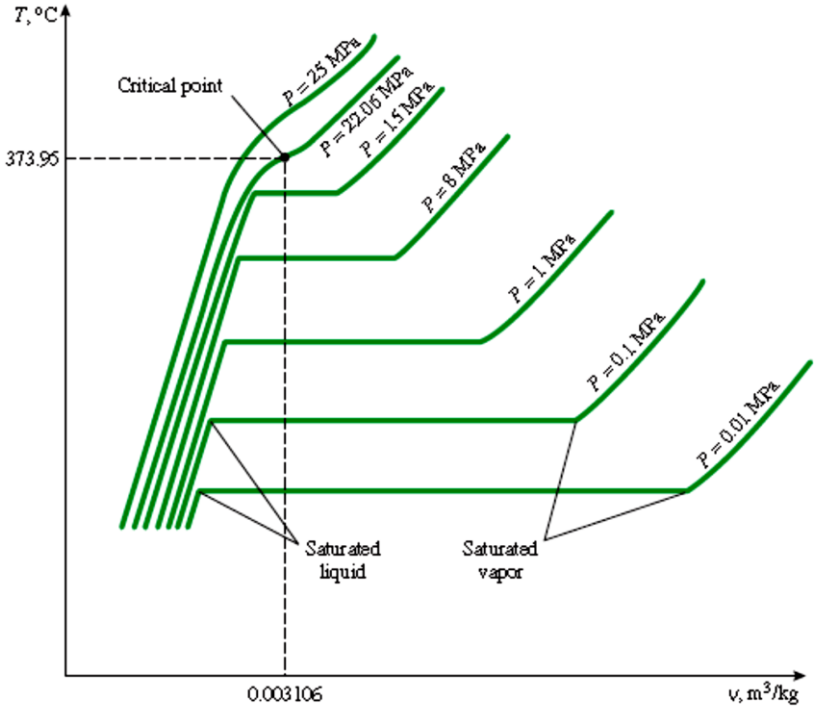


Figure 4. T-υ diagram of constant- pressure phase change process of a pure substance at various pressure.

At pressures above the critical pressure, there will not be a distinct phase-change process, (See Fig. 5). Instead, the specific volume of the substance will continually increase, and at all times there will be only one phase present.
Eventually, it will resemble a vapor, but we can never tell when the change has occurred. Above the critical state there is no line that separate 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.

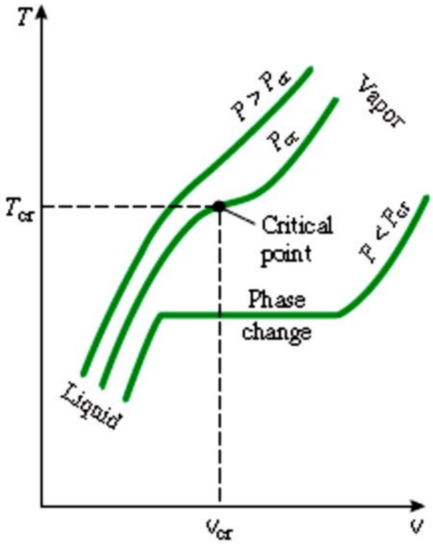


Figure 5. At supercritical pressure ($P > P_{cr}$) there is no distinct phase-change process

The saturated liquid states in Fig. 4 can be connected by a line which is called the **saturated liquid line**, and saturated vapor states in the same figure can be connected by another line which is called the **saturated vapor line**.

These two lines meet each other at the critical point forming a dome as shown in Fig. 6. All the compressed liquid states are located in the region to the left of the saturated liquid line, and it is called the **compressed liquid region**. All the superheated vapor states are located to the right of the saturated vapor line which is called **superheated vapor region**. In these two regions, the substance exits in a single phase, a liquid or a vapor. All the states that involve both phases in equilibrium are located under the dome which is called the **saturated liquid-vapor mixture region** or the **wet region**.

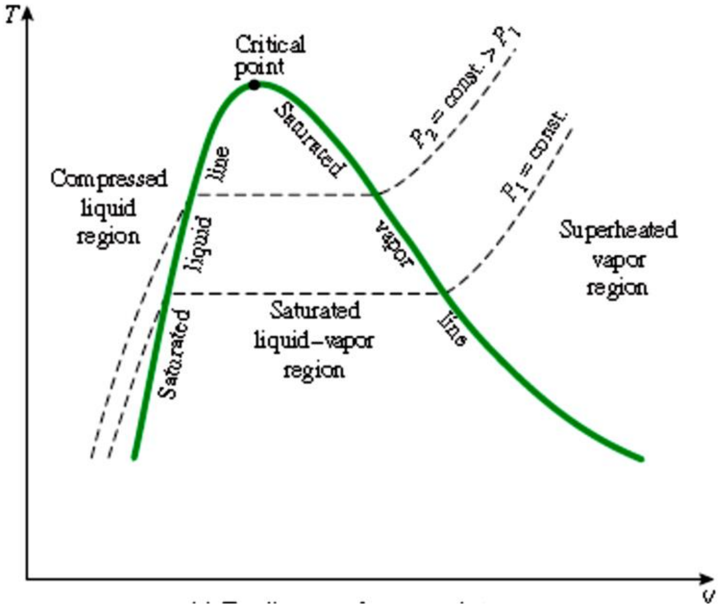


Figure 6. Typical T-v diagram for phase-change region at constant pressure

5.4.2. The P-v Diagram

The general shape of the $P - \upsilon$ diagram of a pure substance is very much like the $T - \upsilon$ diagram, but T=constant lines on this diagram have a down trend as shown in Fig. 7.

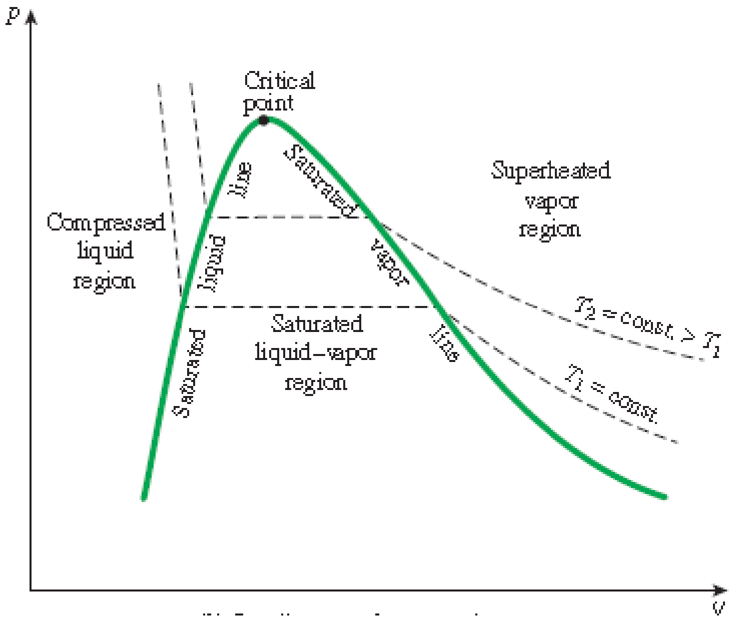


Figure 7. Typical P-v diagram for phase-change region at constant temperature

5.4.3. Extended diagrams to include the solid phase

These two diagrams can easily be extended to include the solid phase as well as the solid-liquid and the solid vapor saturation regions, as in Figs. 8 and 9.

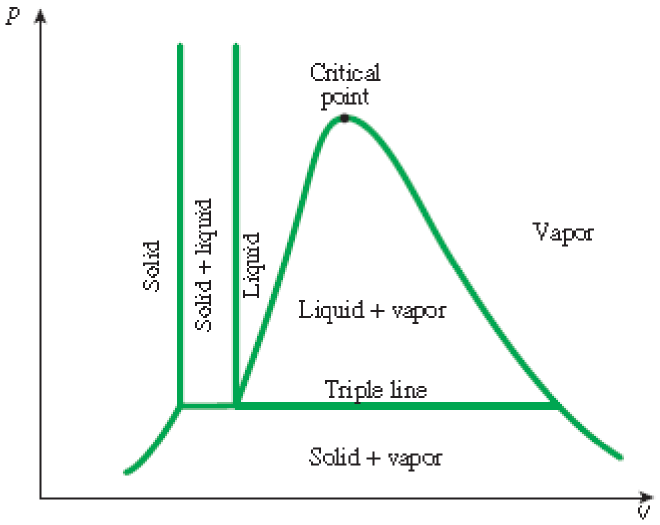


Figure 8. P-υ diagram of substance on freezing

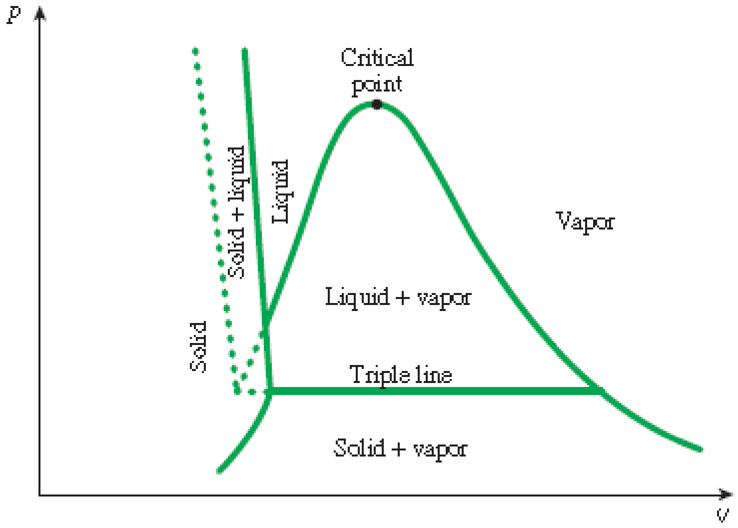


Figure 9. P-υ diagram of substance that expands on freezing (such as water)

We are all familiar with two phase being in equilibrium, but under some conditions all three phases of a pure substance coexist in equilibrium. On P-υ and T- υ diagrams, these triple-phase states from line called **triple line**. The same pressure and temperature but different specific volume. The triple line appears as a point on the P-T diagrams, and, therefore, is often called the **triple point**, Fig. 24.

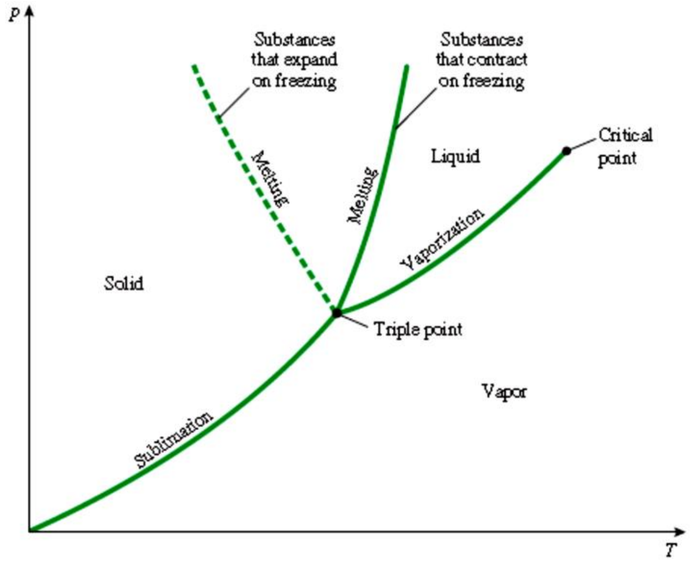


Figure 10. *P-T* diagram for pure substance

5.5. 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 be measured directly and calculated by using the relations that relate them to measurable properties.

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.

5.5.1. Enthalpy-A combination property

A person looking at the tables carefully will notice two new properties:

enthalpy h and entropy s. Entropy is a property associated with the second law of thermodynamic and we will not use it until it is properly defined. It is appropriate to introduce enthalpy at this point. The enthalpy is a combination of U and PV and it is written as:

$$H = U + PV \qquad [kJ]$$

or per unit mass

$$h = u + Pv \qquad [kJ/kg]$$

In some tables encountered in practice, the internal ***u*** is frequently not listed, but it can be determined from

$$u = h - Pv \qquad [kJ/kg]$$

5.5.2. Saturation Liquid and Saturation Vapor

The properties of saturated liquid and saturated vapor of water are listed in two tables. Both give the same information. The only difference is that in one table properties are listed under temperature and in other under pressure.

Therefore, it is more convenient to use temperature table when temperature is given and the other table when pressure is given.

The subscript f is used to denote properties of a saturated liquid, and the subscript g to denote the properties of saturated vapor. Another subscript commonly is fg, which denotes the difference between the saturated liquid values of same property.

For example:

υ_f =specific volume of saturated liquid

υ_g=specific volume of saturated vapor

υ_{fg} =difference between υ_g and υ_f (that is $\upsilon_{fg}= \upsilon_g- \upsilon_f$)

The quantity h_{fg} is called the **enthalpy of vaporization** (or latent heat of vaporization). It represents amount of energy needed to vaporize a unit mass of saturated liquid at given pressure and temperature. It is decreases as the pressure and temperature increases, it becomes zero at the critical point.

Example 5.1

A rigid tank contains 50 kg of saturated liquid water at 85 °C. Determine the pressure in the tank and the volume of the tank?

Solution: The state of the saturated liquid water is shown on a ***T- v*** diagram (see Fig. 11).

Since saturated condition exist in the tank, the pressure must be the saturation pressure at 85 °C.

$P=P_{sat}$ at 85 °C =57.83 kPa (Table A-4)

The specific volume of the saturated liquid at 85 °C.

$\upsilon = \upsilon_f\ at$ 85 °C= 0.001033 m^3/kg (Table A-4)

Then the total volume of the tank

$V = m\,\upsilon$ =(50 kg)(0.001033 m^3/kg) =0.050165 m^3

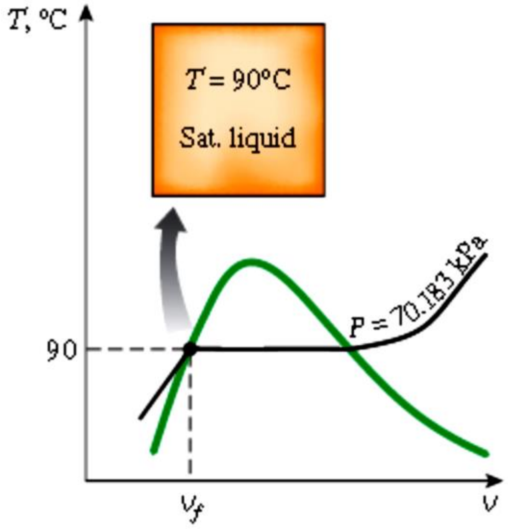


Figure 11. Schematic and T-v diagram for example 5–1