Lecture Thirteen

PROPERTIES OF PURE SUBSTANCES

OBJECTIVES

The objectives of this lecture 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.

1.1 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.

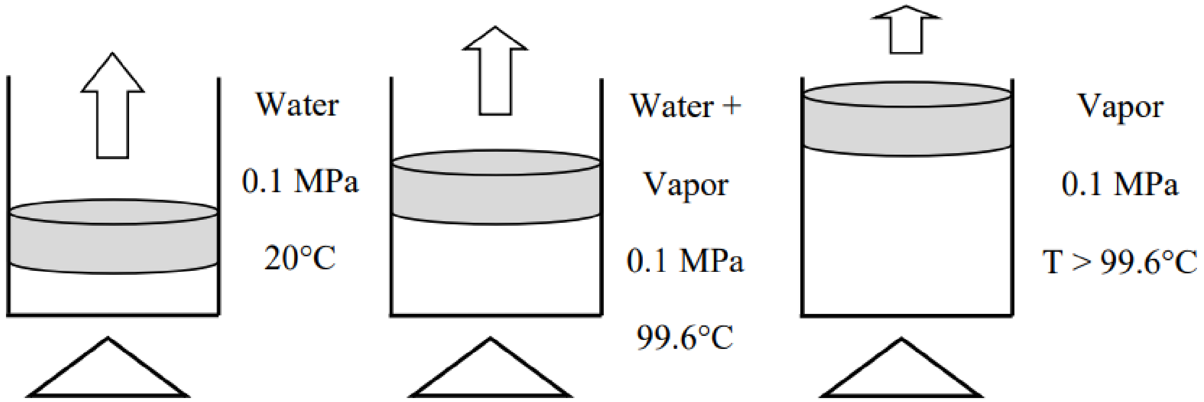
1.2 PHASES OF A PURE SUBSTANCE

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.

1.3 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.

Consider as a system of (1 kg) of water contained in the piston-cylinder arrangement shown in figure below. Suppose that the piston maintains 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. 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.



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.

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 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).

If a substance exists as liquid at the saturation temperature and pressure

$\textbf{liquid} \ @\ P_{sat} + T_{sat} \Rightarrow \textbf{saturated liquid}$

$If\ T < T_{sat}$, for the given P $\Rightarrow$ **subcooled liquid**

$If\ P > P_{sat}$, for the given T $\Rightarrow$ **compressed liquid**

When a substance exists as part liquid and part vapor at saturation temperature, its quality is **defined** as the ratio of the mass of vapor to the total mass. 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 part liquid and part vapor at the saturation temperature

$$state\ is\ mixture\ (saturated\ vapor + \ liquid) \Rightarrow \ dryness\ fraction\ (x)$$

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 a superheated vapor. The pressure and temperature of superheated vapor are independent properties, since the temperature

Email (esam.muhe@uomus.edu.iq)

may increase while the pressure remains constant. This constant-pressure phase-change process is illustrated on a T-V diagram in Figure (1.1). Actually, the substances we call gases are highly superheated vapors.

If a substance exists as vapor at the saturation temperature

vapor $@\, T_{sat} \Rightarrow$ **saturated vapor**

$If\ T > T_{sat}$, for the given $P\ \Rightarrow$ **superheated vapor**

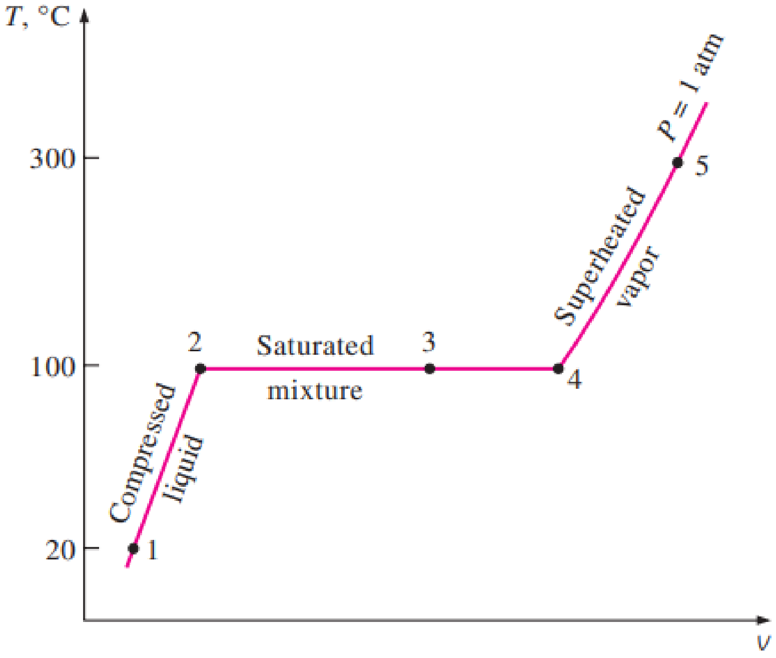


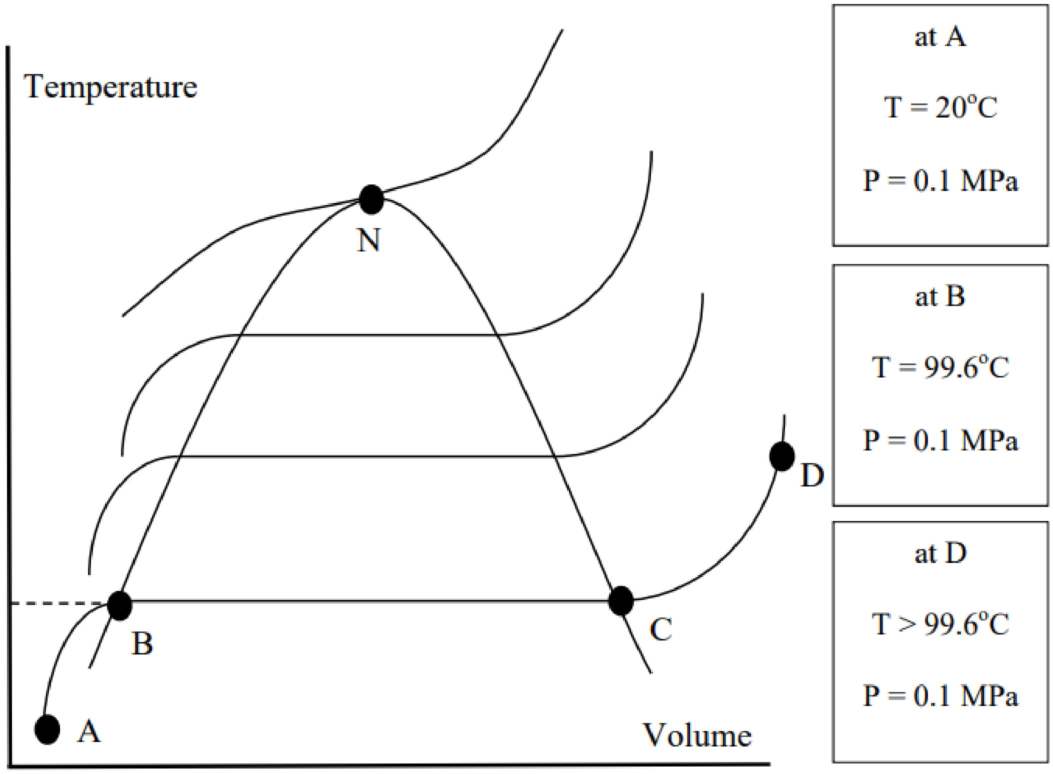
Figure (1.1) T-V diagram for the heating process of water at constant pressure.

1.4 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.

1.4.1 THE (T-V) DIAGRAM

Let us consider a temperature-volume (T-V) diagram for a heating process at constant pressure for a pure substance.



- Point A represents the initial state, point B is the saturation temperature at 0.1 MPa (99.6°C). Line AB represents a heating process with no change of phase.

- Point C is the saturated vapor state. Line BC is the constant temperature and pressure (change of phase; evaporation).

- Line CD represents the process during which the steam becomes superheated. During this process the temperature and specific volume increase and the pressure remains constant.

- Line ABCD represents a constant pressure line on the (T-V) diagram, i.e. heating process of constant pressure with change of phase.

Similar lines may be drawn for heating processes at other pressure values. At a pressure of (22.06 MPa), we find that there is no constant temperature vaporization process. Instead point (N) is a point of inflection with zero slop. This point is called the **critical point** which is the point where the **saturated vapor** and **liquid can coexist**. At the critical point the temperature, pressure and specific volume are called **critical temperature**, **critical pressure** and **critical specific volume**. The line joining the saturated liquid temperatures is called the saturated liquid line, and the line joining the saturated vapor temperatures is called the saturated vapor line as illustrated in Figure (1.2).

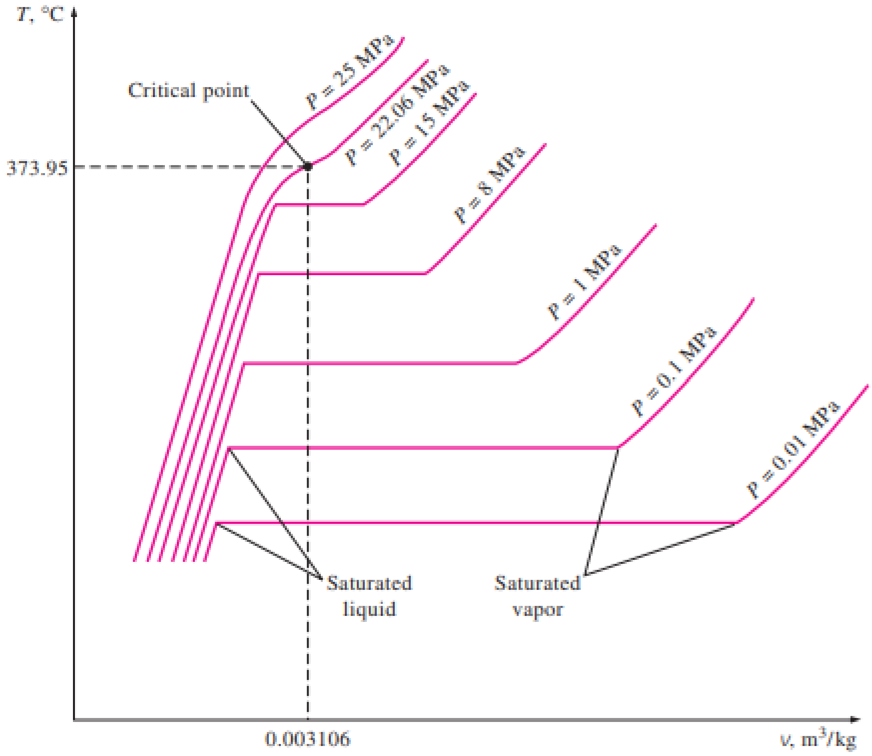
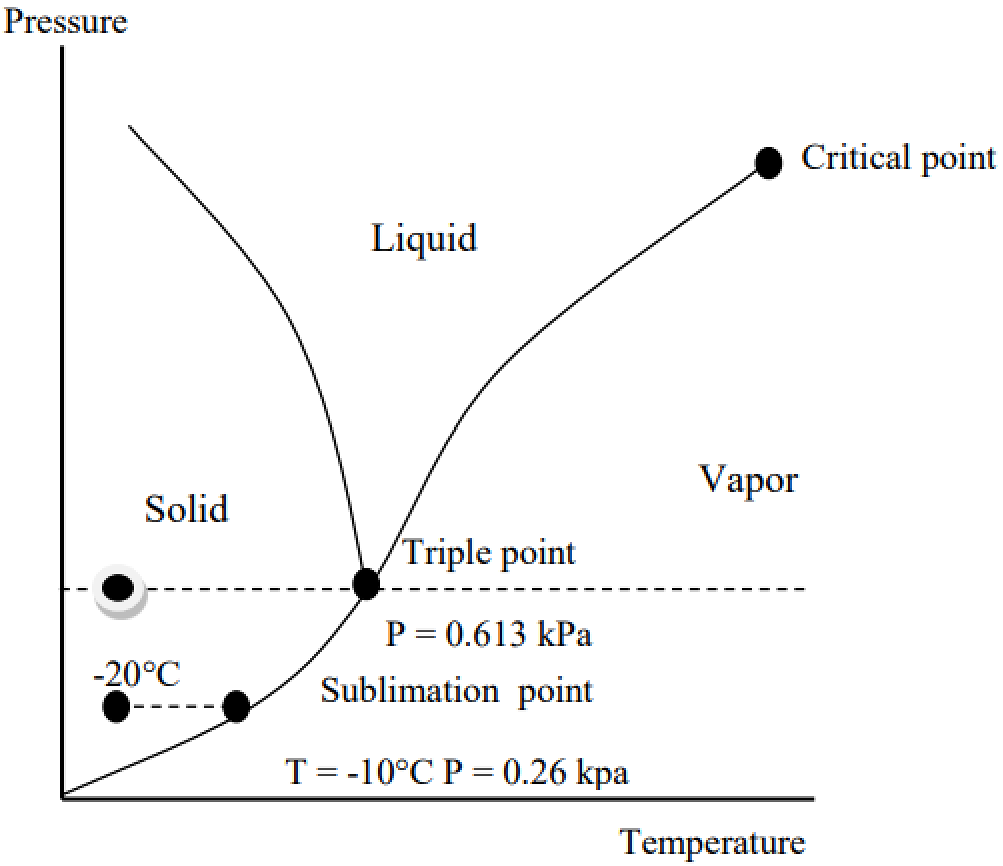


Figure (1.2) T-V diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

1.4.2 THE (P-T) DIAGRAM

Assume that a system consisting of (1 kg) of ice at (-20 °C) and (100 kPa) is contained in a piston-cylinder arrangement as in the previous example. When the system is **heated** the **pressure** remains **constant**. The **specific volume increases** slightly, and it reaches (0 °C). At this point the ice melts while the temperature remains constant and in this state the ice is called **saturated solid**. When all the ice melts, any **further heating** results in an **increase** in the **temperature** of the **liquid**. Let the initial state of the ice be (-20 °C) and (0.26 kPa). The heating would result in increasing the temperature to (-10 °C). At this point the ice would pass directly from solid phase to vapor phase in a process known as **Sublimation**. Any further heating results in superheating the vapor.



When the initial state of the system is (-20 °C) and (0.613 kPa), the heating process results in increasing the temperature until it reaches (0.01 °C). Further heating may result in some of the ice becoming vapor and some becoming liquid. Therefore, at these conditions it is possible to have three phases in equilibrium. This point is called **triple point**, which is **defined as the state in which the three phases of a pure substance may be present in equilibrium**.

When the **heating** process is carried out at a **pressure higher** than the triple point pressure, the substance would pass from **solid** phase to **liquid** phase and then from liquid phase to **vapor** phase at **higher temperature**.

1.4.3 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 = constant lines on this diagram have a downward trend, as shown in Figure (1.3).

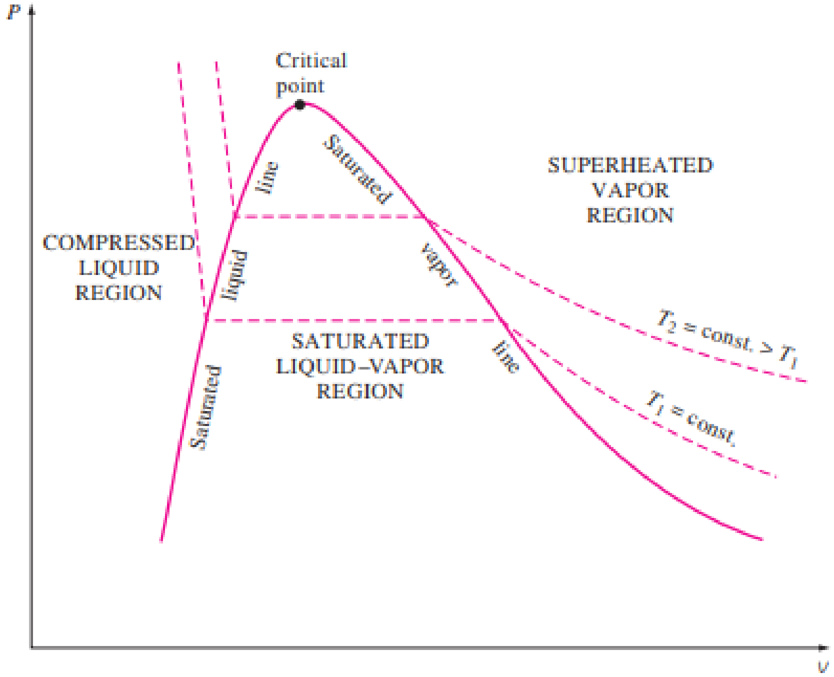


Figure (1.3) P-V diagram of a pure substance.

HOMEWORK :

1- Define
  a- subcooled liquid
  b- compressed liquid
  c- quality
  d- superheated vapor
2- write the condition of the
  a- subcooled liquid.
  b- compressed liquid.
  c- superheated vapor.

3- sketch
  a- T-v diagram of constant pressure.
  b- P-v diagram of constant temperature.