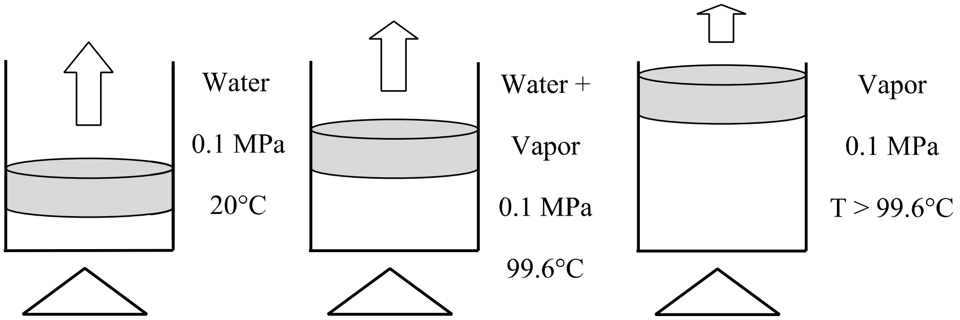
6. Pure Substance

It is the substance that has a homogenous and invariable chemical composition. It may exist in more than one phase, but the chemical composition is the same in all phases, such as a mixture of ice and liquid water or a mixture of water and steam. Sometimes a mixture of gases such as air is considered a pure substance as long as there is no change of phase, since it exhibits the same characteristics as a pure substance.

Equilibrium in a Pure Substance

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.

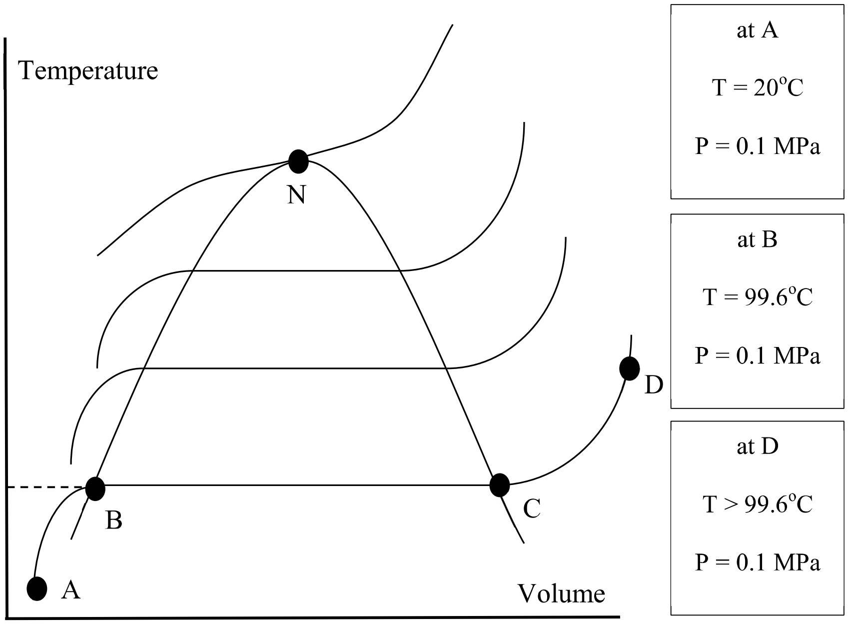
If a substance exists as liquid at the saturation temperature and pressure, it is called a **saturated liquid**. If the temperature of the liquid is lower than the saturation temperature for the existing pressure, it is called either a **subcooled liquid** (implying that the temperature is lower than 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).

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. 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 a **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.

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 increases 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.

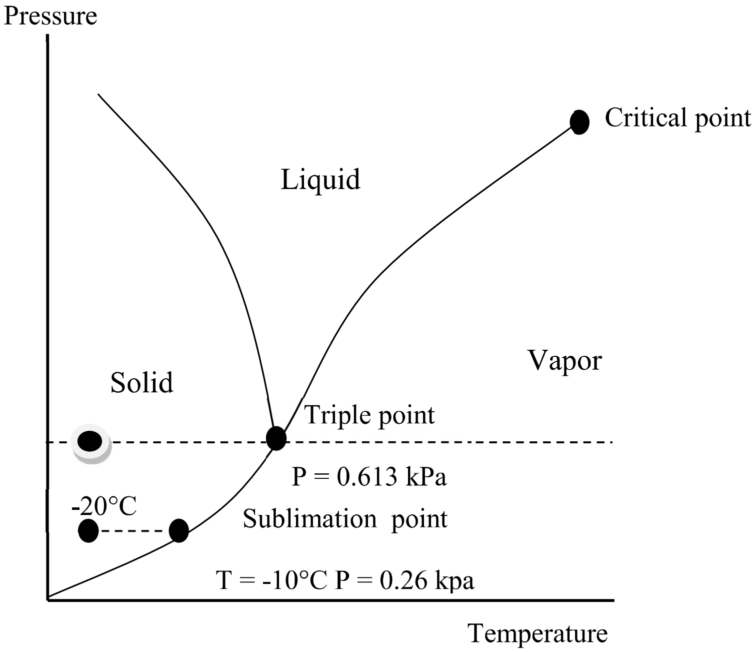
Similar lines may be drawn for heating processes at other pressure values. At a pressure of 22.09 MPa, we find that there is no constant temperature vaporization process. Instead point N is a point of inflection with zero slop. This point is called the critical point which is the point where the saturated 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**.

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 until -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.

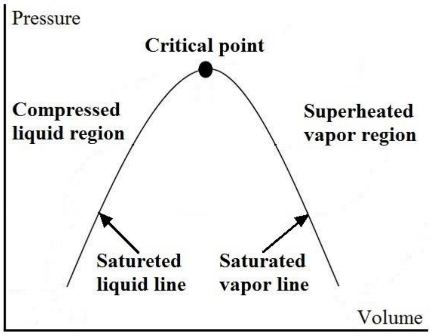


When the initial state of the system is -20°C and 0.613 kPa, the heating process results in increasing the temperature until it reaches 0.01°C. Further heating may result in some of the ice becoming vapor and some becoming liquid. Therefore at these conditions it is possible to have three phases in equilibrium. 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.

Water Properties Tables

The term steam is solely used for water vapor. 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 and are calculated by using the relations between them and measurable properties. The results of these measurements and calculations are presented in tables in a convenient format. In the following discussion, the steam tables are used to demonstrate the use of thermodynamic property tables.



Property tables of other substances are used in the same manner. 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.

1. Saturated liquid and vapor: when water is in the saturated phase, (table 2) and (table 3) are used to get the required properties. Both tables give the same information, the only difference is that in (table 2) properties are listed under temperature and in (table 3) under pressure. Therefore, it is more convenient to use (table 2) when temperature is given and (table 3) when pressure is given. Knowing only one property of the water, we can extract any other property from these tables. For saturated liquid, the properties with the subscript (f) are used. For saturated vapor, the properties with the subscript (g) are used. The properties with the subscript (fg) are the difference between the two phases $(g - f)$. For example: $h_{fg} = h_g - h_f$ which is called the **latent heat**.

2. Wet vapor: it is a state in which a mixture of both saturated vapor and liquid are present. To calculate the properties of water in this phase, a property known as the **dryness fraction (x)** is used alongside the saturation properties of (table 2) and (table 3).

Dryness Fraction can be defined as the mass of dry saturated vapor in 1 kg of a mixture of liquid and vapor. It is also called **vapor quality**.

$$x = \frac{m_v}{m_m} = \frac{m_v}{m_v + m_l} \qquad \dots\dots\dots\dots\dots\dots\dots (6.1)$$

For saturated liquid line $x = 0$ (which is said to have a quality of 0%)