**ROHIINI COLLEGE OF ENGINEERING AND TECHNOLOGY**
**ME 3391 ENGINERING THERMODYNAMICS**
**DIGITAL NOTES**



**UNIT -IV**

**Pure substance**

A substance that has a fixed chemical composition throughout the system is called a pure substance. Water, hydrogen, nitrogen, and carbon monoxide, for example, are all pure substance. A pure substance can also be a mixture of various chemical elements or compounds as long as the mixture is homogeneous. Air, a mixture of several compounds, is often considered to be a pure substance because it has a uniform chemical composition. "A mixture of two or more phases of a 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."

**PVT Surface**

Pressure can be expressed as a function of temperature and specific volume: $p = p(T, v)$. The plot of $p = p(T, v)$ is a surface called $p$-$v$-$T$ surface. Figure 3.1 shows the $p$-$v$-$T$ surface of a substance such as water that expands on freezing.
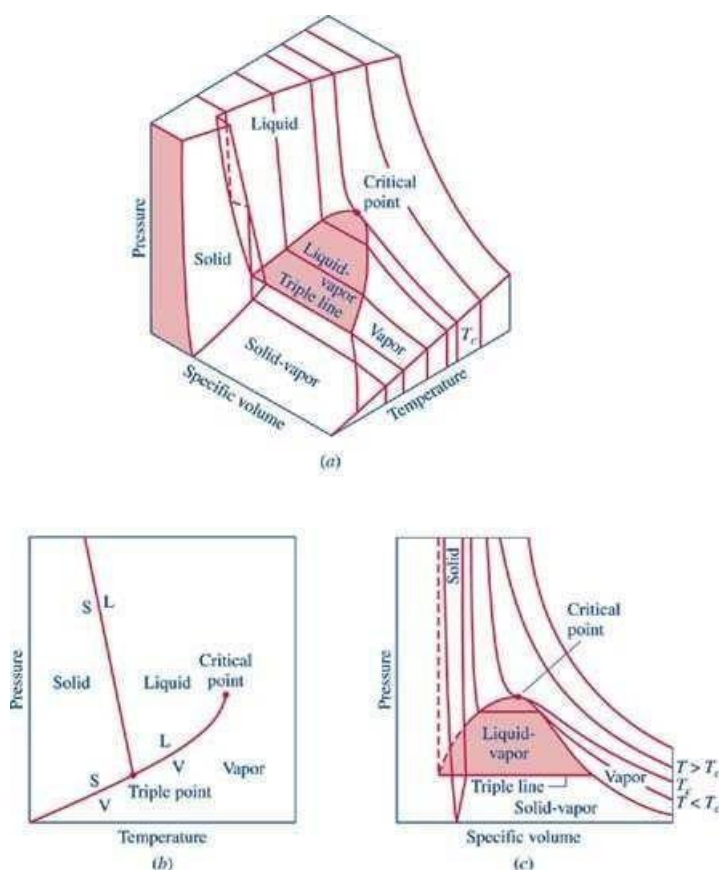


**Figure 3.1** $p$-$v$-$T$ surface and projections for a substance that expands on freezing.

(a) 3-D view (b) $p$-$T$ diagram (c) $p$-$v$ diagram[2].

The location of a point on the *p-v-T* surface gives the values of pressure, specific volume, and temperature at equilibrium. The regions on the *p-v-T* surface labeled *solid*, *liquid*, and *vapor* are single-phase regions. The state of a single phase is determined by any two of the properties: pressure, temperature, and specific volume. The two-phase regions where two phases exist in equilibrium separate the single-phase regions. The two-phase regions are: liquid-vapor, solid-liquid, and solid-vapor. Temperature and pressure are dependent within the two-phase regions. Once the temperature is specified, the pressure is determined and vice versa. The states within the two-phase regions can be fixed by specific volume and either temperature or pressure.

The projection of the *p-v-T* surface onto the *p-T* plane is known as the phase diagram as shown in Figure 3.1 (b). The two-phase regions of the *p-v-T* surface reduce to lines in the phase diagram. A point on any of these lines can represent any two-phase mixture at that particular temperature and pressure. The triple line of the *p-v-T* surface projects onto a point on the phase diagram called the triple point. Three phases coexist on the triple line or the triple point.

The constant temperature lines of the *p-v* diagram are called the isotherms. For any specified temperature less than the critical temperature, the pressure remains constant within the two- phase region even though specific volume changes. In the single-phase liquid and vapor regions the pressure decreases at fixed temperature as specific volume increases. For temperature greater than or equal to the critical temperature, there is no passage across the two-phase liquid-vapor region.
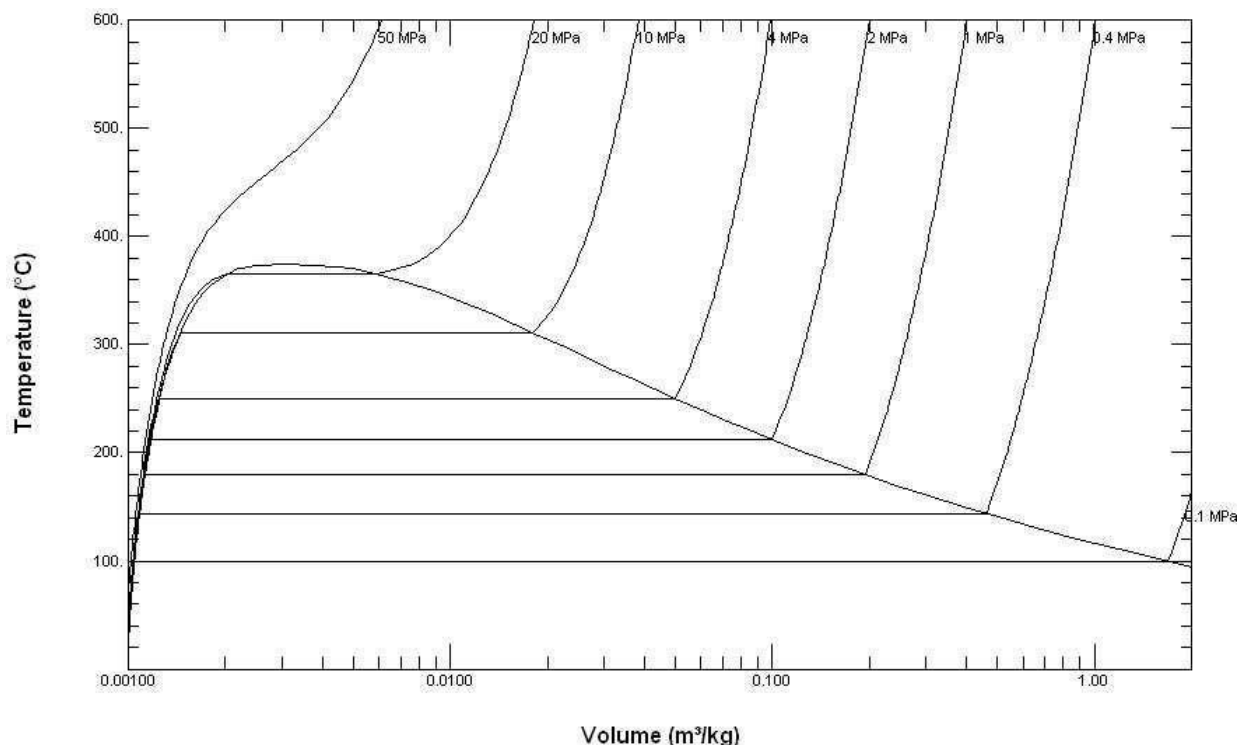


**Figure 3.1-2** *T-v* diagram for water (to scale).

Figure 3.1-2 is a *T-v* diagram for water. For pressure greater than or equal to the critical pressure, temperature increases continously at fixed pressure as the specific volume increases and there is no passage across the two-phase liquid-vapor region. The isobaric curve marked 50 MPa in Figure 3.1-2 shows this behavior. For pressure less than the critical value, there is a two-phase region where the temperature remains constant at a fixedpressure as the two- phase region is traversed. The isobaric curve with values of 20 MPa or less in Figure 3.1-2 shows the constant temperature during the phase change.

At 100°C, the saturated volumes of liquid and vapor water are 1.0434 cm³/g and 1,673.6 cm³/g, respectively. The quality of steam is the mass fraction of water vapor in a mixture of liquid and vapor water. The specific volume of 100°C steam with a quality of 0.65 is given by

$$v = (1 - 0.65)v^L + 0.65\ v^V = (0.35)(1.0434) + (0.65)(1{,}673.6) = 1088.2\ \text{cm}^3/\text{g}$$

**Phase Behavior:**

We will consider a phase change of 1 kg of liquid water contained within a piston-cycinder assembly as shown in Figure 3.2-1a. The water is at 20°C and 1.014 bar (or 1 atm) as indicated by point (1) on Figure 3.2-2.
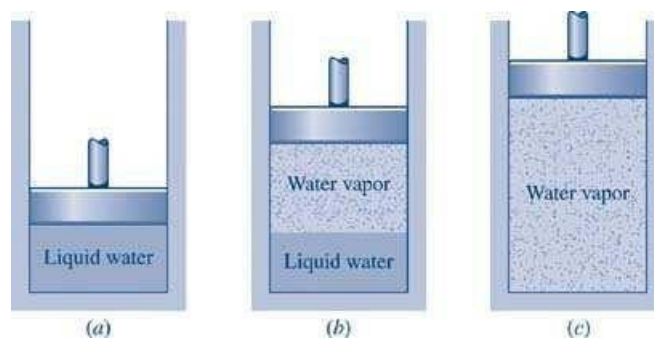


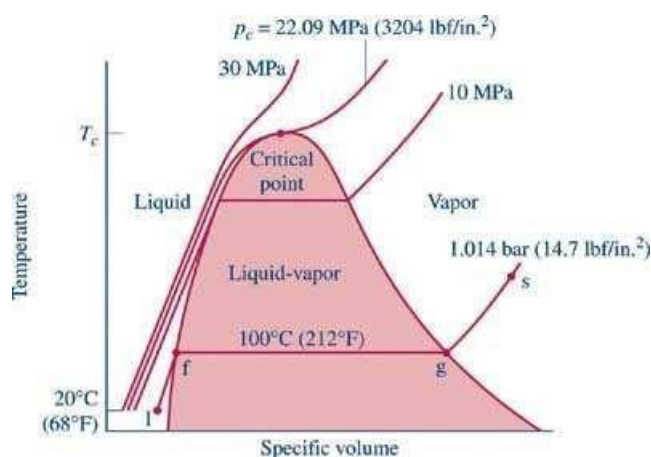**Figure 3.2-1** Phase change at constant pressure for water[3]



**Figure 3.2-2** Sketch of *T-v* diagram for water

As the water is heated at constant pressure, the temperature increases

with a slight increase in specific volume until the system reaches point (f). This is the saturated liquid state corresponding to 1.014 bar. The saturation temperature for water at 1.014 bar is 100°C. The liquid states along the line segment 1-f are called *subcooled* or *compressed* liquid states. When the system is at the saturated liquid state (point f in Figure 3.2-2) any additional heat will cause the liquid to evaporate at constant pressure as shown in Figure 3.2-1b. When a mixture of liquid and vapor exists in equilibrium, the liquid phase is a saturated liquid and the vapor phase is a saturated vapor.

Liquid water continues to evaporate with additional heat until it becomes all saturated vapor at point (g). Any further heating will cause an increase in both temperature and specific volume and the saturated vapor becomes superheated vapor denoted by point (s) in Figure 3.2-2. For a two-phase liquid-vapor mixture, the quality *x* is defined as the mass fraction of vapor in the mixture

$$x = \frac{m_{vapor}}{m_{vapor} + m_{liquid}}$$

When a substance exists as part liquid and part vapor at saturation conditions, its quality (x) is defined as the ratio of the mass of the vapor to the total mass of both vapor and liquid.

**Enthalpy–Entropy Chart**

An enthalpy–entropy chart, also known as the H–S chart or Mollier diagram, plots the total heat against entropy, describing the enthalpy of a thermodynamic system. A typical chart covers a pressure range of 0.01–1000 bar, and temperatures up to 800 degrees Celsius. It shows enthalpy H in terms of internal energy U, pressure p and volume V using the relationship H=U+pV or, in terms of specific enthalpy, specific entropy and specific volume.

engineeringtoolbox.com
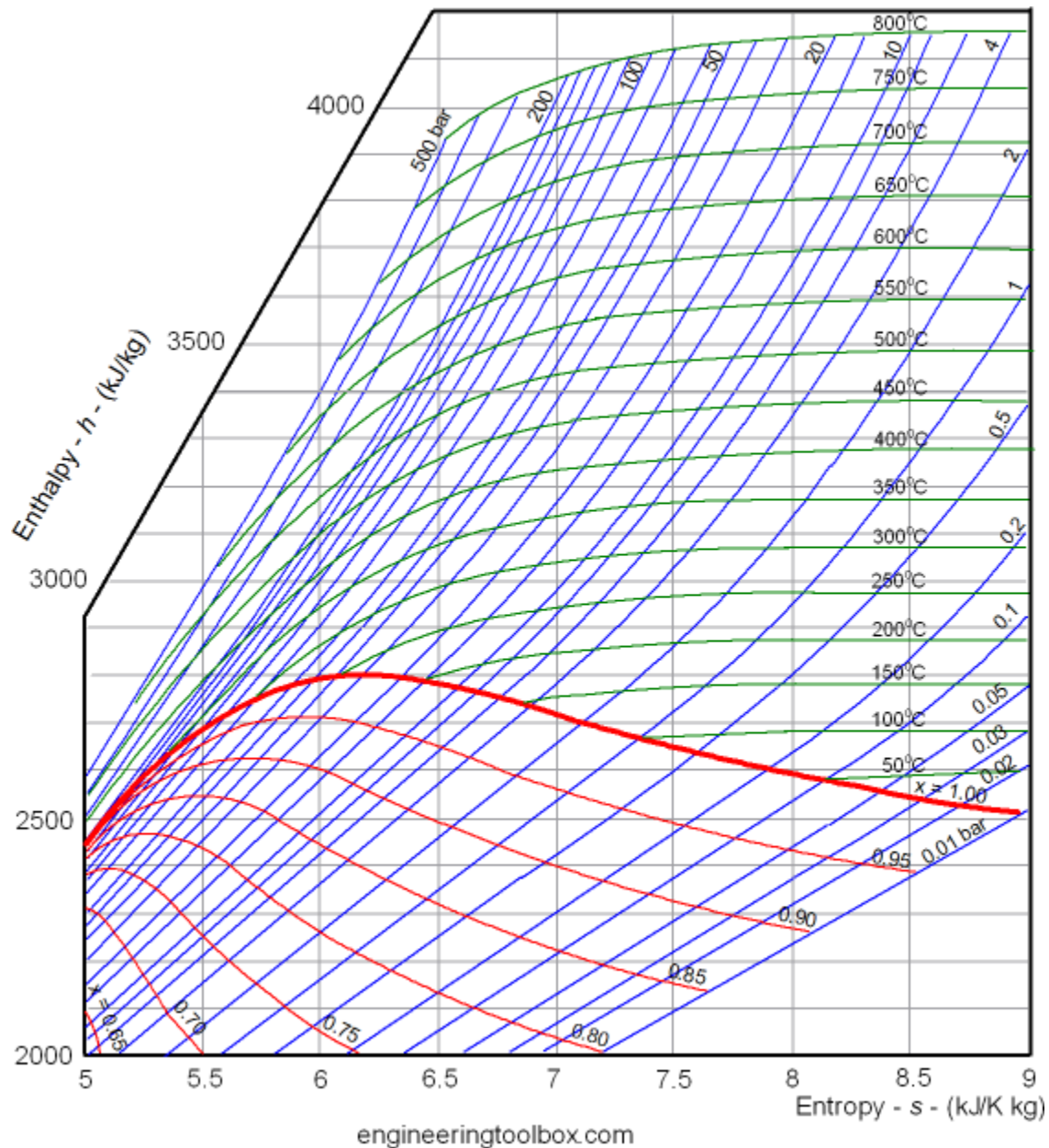
On the diagram, lines of constant pressure, constant temperature and volume are plotted, so in a two-phase region, the lines of constant pressure and temperature coincide. Thus, coordinates on the diagram represent entropy and heat.

A vertical line in the h–s chart represents an isentropic process. The process 3–4 in a Rankine cycle is isentropic when the steam turbine is said to be an ideal one. So the expansion process in a turbine can be easily calculated using the h–s chart when the process is considered to be ideal (which is the case normally when calculating enthalpies, entropies, etc. Later the deviations from the ideal values and they can be calculated considering the isentropic efficiency of the steam turbine used.

Lines of constant dryness fraction (x), sometimes called the quality, are drawn in the wet region and lines of constant temperature are drawn in the superheated region. X gives the

fraction (by mass) of gaseous substance in the wet region, the remainder being colloidal liquid droplets. Above the heavy line, the temperature is above the boiling point, and thedry (superheated) substance is gas only.

**Characteristics of the critical point:**

- ➢ For saturated phase often its enthalpy is an important property.
- ➢ Enthalpy-pressure charts are used for refrigeration cycle analysis.
- ➢ Enthalpy-entropy charts for water are used for steam cycle analysis.
- ➢ Note: Unlike pressure, volume and temperature which have specified numbers associated with it, in the case of internal energy, enthalpy (and entropy) only changes are required. Consequently, a base (or datum) is defined -as you have seen in the case of water.

Let V be total volume of liquid vapour mixture of quality x, Vfthe volume of saturated liquid and Vg the volume of saturated vapour, the corresponding masses being m, mf and mg respectively.

Now, m = mf + mg

V = Vf+ Vg

m v= mfvf+ mgvg

 **Saturation States**

When a liquid and its vapour are in equilibrium at certain pressure and temperature, only the pressure or the temperature i is s sufficient to identify the saturation state.
If pressure is given, the temperature of the mixture gets fixed, which is known as saturation temperature, or if the temperature is given, the saturation pressure gets fixed.
Saturation liquid or saturated vapour has only on independent variable, i.e. only one property is required to b known to fix up the state.

**Type of Steam**

Wet steam:

Wet steam is defined as steam which is partly vapour and partly liquid suspended in it. It means that evaporation of water is not complete.

Dry saturated steam:

When the wet steam is further heated, and it does not contain any suspended particles of water, it is known as dry saturated steam.

Superheated steam: When the dry steam is further heated at constant pressure, thus raising its temperature, it is called superheated steam.