

Lecture 12

Properties of Pure Substances

Pure Substance

A pure substance has an invariable chemical composition and may exist in more than one phase.

Examples:

1. Water (solid, liquid, and vapor phases)
2. Mixture of liquid water and water vapor
3. Carbon dioxide, CO_2
4. Nitrogen, N_2
5. Mixtures of gases, such as air, as long as there is no change of phase

Phases of a pure substance

A **phase** is identified as having a distinct molecular arrangement that is homogeneous throughout and separated from the others by easily identifiable boundary surfaces. A substance that has uniform thermodynamic properties throughout is said to be **homogeneous**.

There are three principal phases namely solid, liquid, and gas, each with a different molecular structure. Within a phase for example solid, the substance may exist in several phases. Carbon in solid phase exists as graphite or diamond, each with a different molecular arrangement.

The molecules in a solid are arranged in a three-dimensional pattern that is repeated throughout. The molecules in a solid are close, so the attractive forces between them are large which keep the molecules in a solid together.

Molecules in a solid oscillate at their position. The velocity of oscillation depends on temperature. At high temperatures the intermolecular forces are overcome by the molecules and group of molecules break away forming a liquid. This is how melting happens.

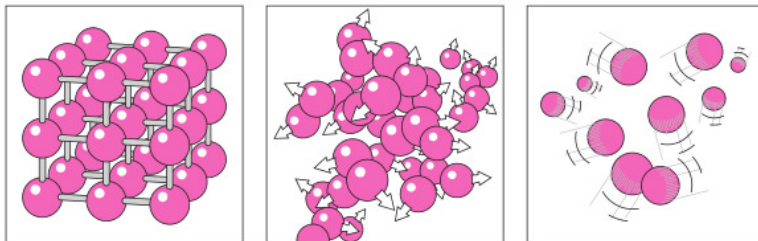


Fig: Structures of Solid, liquid and vapour

Molecular arrangement in the liquid is also similar to solids. The difference is that they are not in fixed positions i.e. they can translate and rotate.

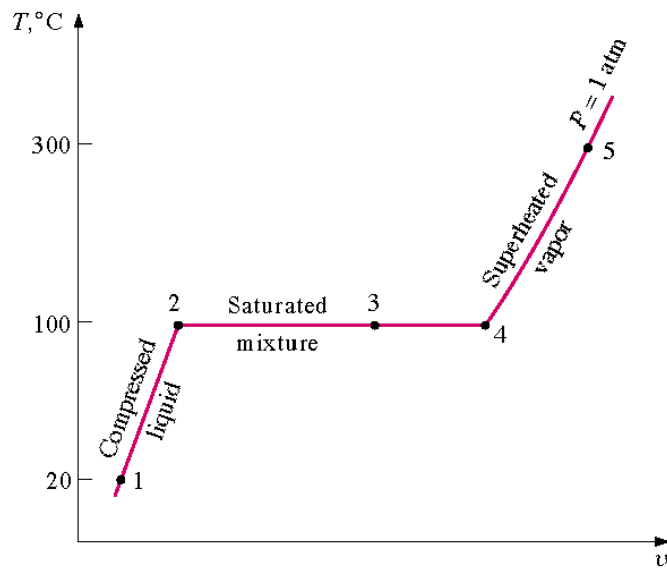
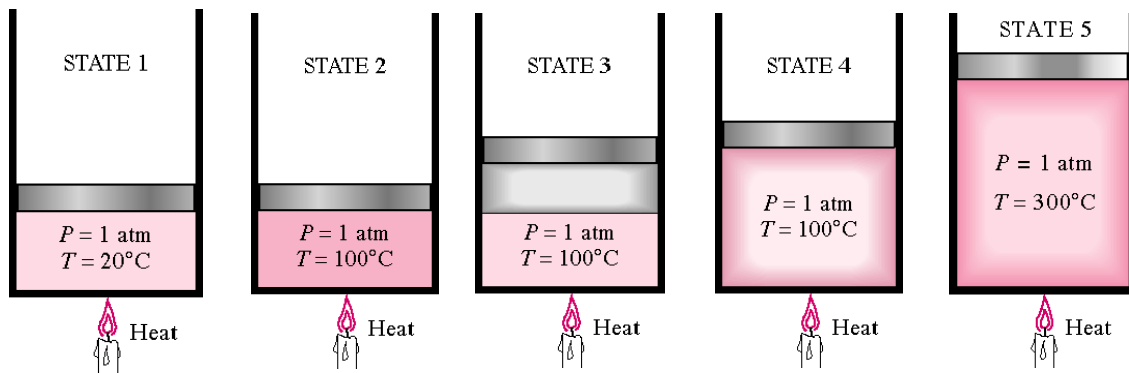
Intermolecular forces in liquid are weak as compared to solids.

At higher temperatures these weak intermolecular forces are also overcome and subsequently gas is formed. The molecules in the gas are far apart and there is no molecular order. The molecules in the gas phase are at a higher energy level as compared to the liquid phase. Or we have to give energy to the molecules to convert from liquid to gaseous phase.

PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

Constructing a T-v diagram

Let's consider the results of heating liquid water from 20°C , 1 atm while keeping the pressure constant.



Process 1-2

The temperature and specific volume will increase from the **compressed liquid**, or **subcooled liquid**, state 1, to the **saturated liquid** state 2.

Process 2-3

- At state 2 the liquid has reached the temperature at which it begins to boil, called the **saturation temperature**, and is said to exist as a **saturated liquid**.
- Properties at the saturated liquid state are noted by the subscript **f** and $v_2 = v_f$.
- During the **phase change** both the **temperature and pressure remain constant**
- At state 3 the liquid and vapor phase are in equilibrium and any point on the line between states 2 and 3 has the same temperature and pressure.

Process 3-4

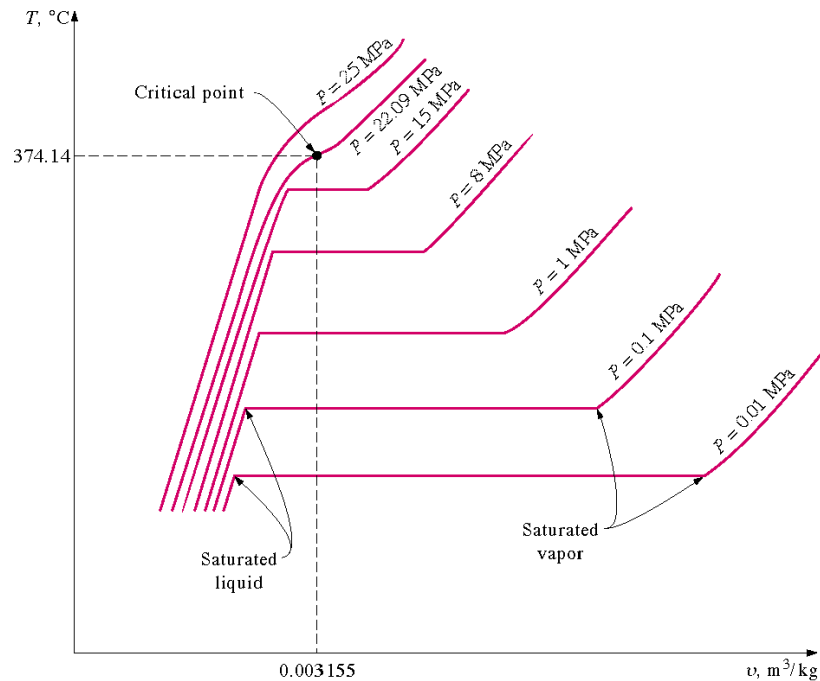
- At state 4 a saturated vapor exists and vaporization is complete. The subscript **g** will always denote a saturated vapor state. Note $v_4 = v_g$.
- The **saturation pressure** is the pressure at which phase change will occur for a given temperature.

- In the saturation region the **temperature and pressure are dependent properties**; if one is known, then the other is automatically known.

Process 4-5

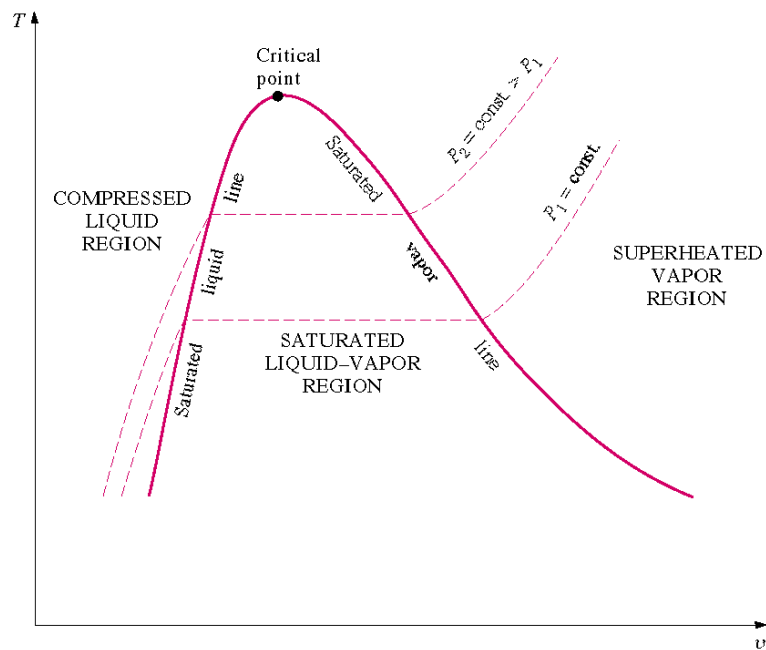
- If the constant pressure heating is continued, the temperature will begin to increase above the saturation temperature, 100 °C in this example, and the volume also increases.
- State 5 is called a **superheated state** because T_5 is greater than the saturation temperature for the pressure and the vapor is not about to condense

If we repeat the process for other constant pressure lines we get the following curves



- If all of the saturated liquid states are connected, the **saturated liquid line** is established.
- If all of the saturated vapor states are connected, the **saturated vapor line** is established.
- These two lines intersect at the **critical point**
- The critical-point properties of water are $P_{cr} = 22.06$ MPa, $T_{cr} = 373.95^\circ\text{C}$, and $v_{cr} = 0.003106$ m³/kg.
- The region between the saturated liquid line and the saturated vapor line is called by these terms: saturated liquid-vapor mixture region, wet region (i.e., a mixture of saturated liquid and saturated vapor), two-phase region, and just the saturation region.

Critical point, is defined as the point at which the saturated liquid and saturated vapor states are identical. At pressures above the critical pressure, there is not a distinct phase-change process. 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 has occurred

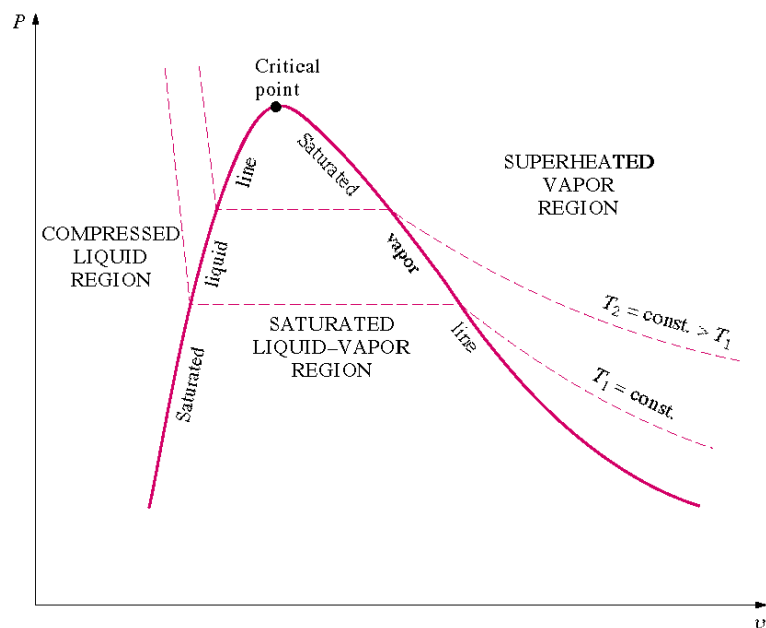


T-v diagram

- The region to the left of the saturated liquid line and below the critical temperature is called the compressed liquid region.
- The region to the right of the saturated vapor line and above the critical temperature is called the superheated region.

P-v diagram

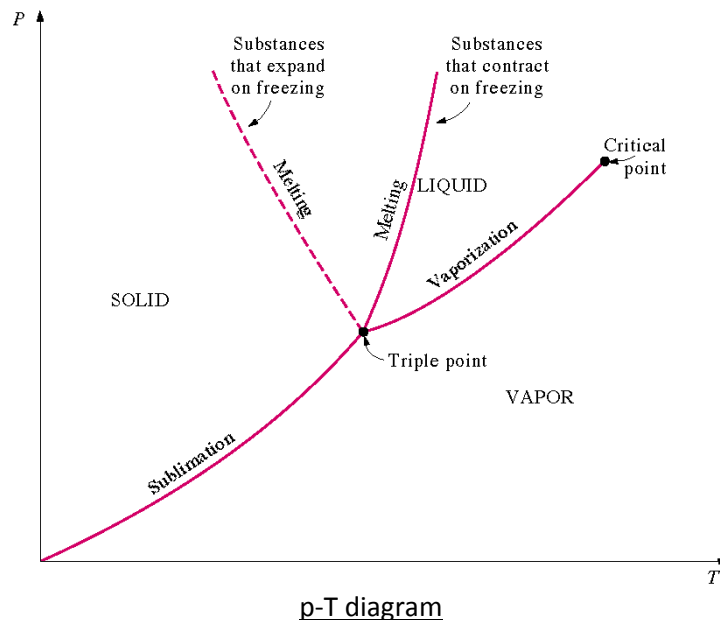
If we conduct the experiment by keeping the temperature constant we obtain the p-v diagram. Water is heated keeping the temperature constant. This can be achieved by reducing the pressure.



p-v diagram

p-T diagram

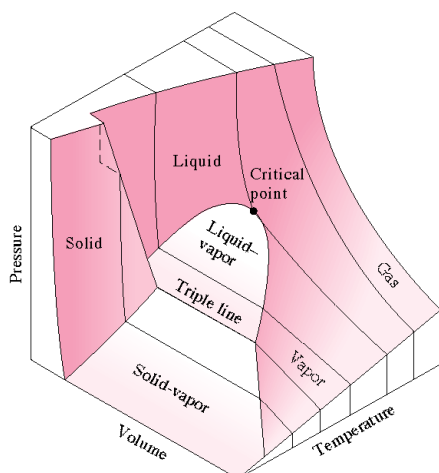
This diagram is often called the **phase diagram** since all three phases are separated from each other by three lines. The **sublimation line** separates the solid and vapor regions, the **vaporization line** separates the liquid and vapor regions, and the **melting** (or fusion) **line** separates the solid and liquid regions. All three lines meet at the triple point. At the triple point all the 3 phases i.e. solid, liquid and vapour coexists in equilibrium. For water, the triple-point temperature and pressure are 0.01°C and 0.6117 kPa, respectively



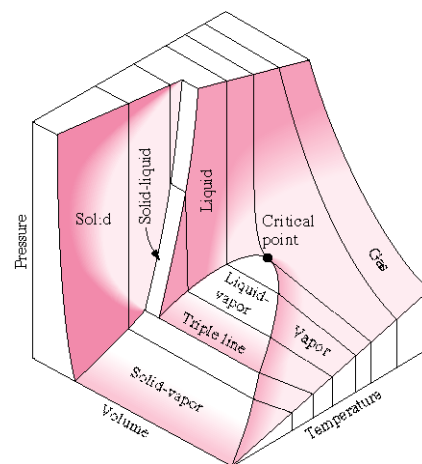
p-v-T surface

The state postulate for a simple, pure substance states that the equilibrium state can be determined by specifying any two *independent intensive properties*. Once the two appropriate properties are fixed, all the other properties become dependent properties.

If T and v are fixed as independent properties and pressure is plotted it represents a surface in space. This we call as the p-v-T surface.



P-V-T Surface for a Substance that expands upon freezing



P-V-T Surface for a Substance that contracts upon freezing

Temperature and volume are shown in the base and pressure is plotted as the height. The p-v-T surface for substances that expands on freezing and substances that contract on freezing are different.

All the points on this surface are equilibrium states. Single phase regions are curved and two phase regions are planes perpendicular to p-T plane. (Their projection on the p-T plane is a line i.e. the p-T diagram). Three phase region is a line, triple line.

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 and are calculated by using the relations between them and measurable properties. The results of these measurements and calculations for Temperature, pressure, volume, the specific internal energy u the specific enthalpy h and the specific entropy s data are available in tables in a convenient format.

- The subscript **f** denotes a saturated liquid state. eg: v_f h_f etc
- The subscript **g** denotes a saturated vapor state. eg: v_g h_g etc
- The subscript **fg** used in Tables refers to the difference between the saturated vapor value and the saturated liquid value region

$$u_{fg} = u_g - u_f$$

$$h_{fg} = h_g - h_f$$

$$s_{fg} = s_g - s_f$$

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

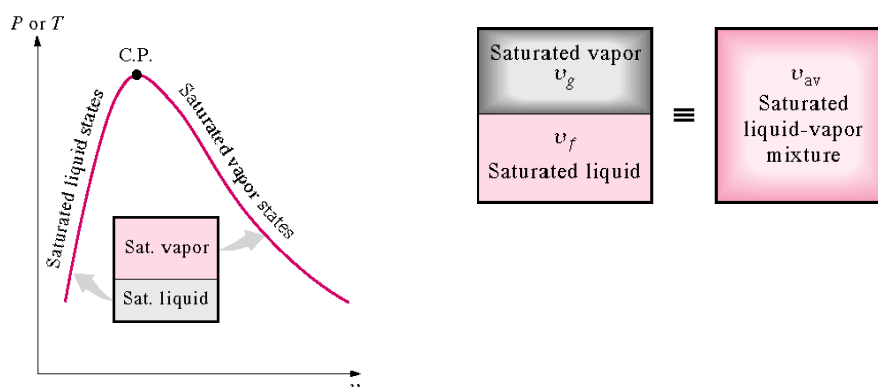
The property table for water and steam are known as **steam table**.

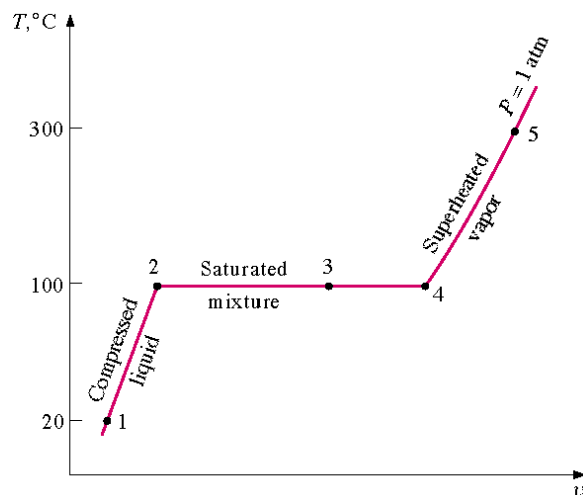
Quality(Dryness fraction) and Saturated Liquid-Vapor Mixture

When there is a mixture of saturated liquid and saturated vapor, the state of the system cannot be described by pressure and temperature since they are dependent properties. So to establish the state of the mixture we define a new parameter known as **quality** or **dryness fraction**.

$$x = \frac{\text{mass}_{\text{saturated vapor}}}{\text{mass}_{\text{total}}} = \frac{m_g}{m_f + m_g}$$

The dryness fraction is zero for the saturated liquid and one for the saturated vapor ($0 \leq x \leq 1$)





specific volume at state 3 can be calculated as follows

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

Let Y be any extensive property and let y be the corresponding intensive property, Y/m , then

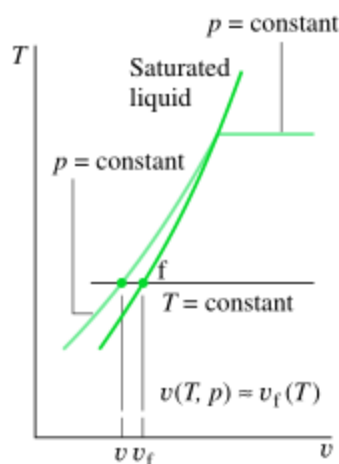
$$\begin{aligned} y &= \frac{Y}{m} = y_f + x(y_g - y_f) \\ &= y_f + x y_{fg} \end{aligned}$$

where $y_{fg} = y_g - y_f$

The term y_{fg} is the difference between the saturated vapor and the saturated liquid values of the property y ;

y may be replaced by any of the variables v , u , h , or s .

Evaluating Properties of Liquids and Solids



For liquids at a particular temperature the **specific volume** and **internal energy** is approximately equal to values at the **corresponding saturation temperature**

Specific Volume

$$v(T, p) \approx v_f(T)$$

Internal Energy

$$u(T, p) \approx u_f(T)$$

Enthalpy

$$h = u + pv$$

Therefore

$$h(T, p) \approx h_f(T) + \underline{v_f(T)[p - p_{sat}(T)]}$$

where p_{sat} denotes the saturation pressure at the given temperature.

Evaluating Δu and Δh for solids and liquids_ using incompressible substance model

To simplify evaluations involving **liquids or solids**, the specific volume (density) is often assumed to be constant and the specific internal energy assumed to vary only with temperature. A substance idealized in this way is called **incompressible**.

For a substance modeled as incompressible, the specific heats c_v and c_p are equal. $c_v = c_p = c$

Since internal energy is a function of temperature only

$$du = c dT$$

integrating the above expression assuming constant specific heat

$$u_2 - u_1 = c(T_2 - T_1)$$

Enthalpy depends on temperature and pressure

$$h = u + pv$$

$$du = du + p dv + v dp$$

integrating the above expression assuming constant specific heat and since specific volume is constant

$$h_2 - h_1 = c(T_2 - T_1) + v(p_2 - p_1)$$

*All the diagrams are from Yunus A. Cengel Michael A. Boles, Thermodynamics, Tata McGraw-Hill