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UNIT II

Properties of Pure Substances

Pure Substance

A pure substance is a system which has a-

- homogeneous chemical composition
- Homogeneous chemical aggregation.
- Invariable in chemical aggregation.

A pure substance need not have to be of a single element or compound. It is 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.

Phases of a Pure Substance

A pure substance may exist in three different phases.

Solid: Strong molecular bonds.

Liquid: Molecules are not fixed relative to each other for a long duration.

Gas: Lowest molecular bond and molecules are very distant from each other.

Molecules in the gas phase are at a considerably higher energy level than they are in liquids or solid phases.

Types: Wet steam, Dry steam, superheated steam

Wet Steam: When steam contains water particles then it is called as Wet steam

Dry Steam: When wet steam is further heated at a constant volume then all water particles get converted into vapor and resulted steam is called dry steam.

Superheated Steam: When dry saturated steam is further heated and temperatures are increased then steam obtained is superheated. This steam is mostly used in Power generation.

Uses of steam:

- Power generation
- Heat engines (i.e. steam engines train)

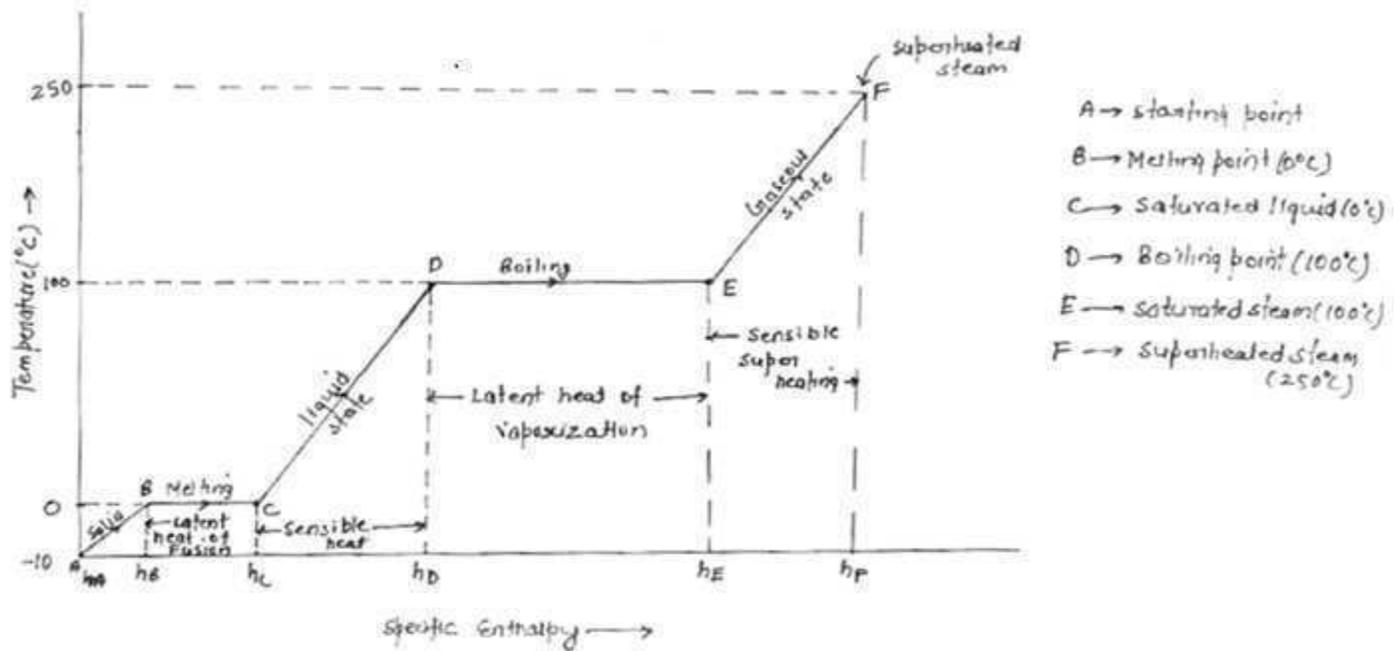
Phase-Change Processes of Pure Substances

Consider a process where a pure substance starts as a solid and is heated up at constant pressure until it all becomes gas. Consider atmospheric pressure that is $p=1.01325 \text{ bar}$ -

- Solid phase
- Mixed phase of liquid and solid (At 0°C)
- Sub-cooled or compressed liquid (means the region where $t_{\text{actual}} < t_{\text{sat}}$)

4. Wet vapors, the temperature will stop rising until the liquid is completely vaporized and this region is called wet region. ($t_{\text{actual}} = t_{\text{sat}}$)

5. Superheated vapor region. ($t_{\text{actual}} > t_{\text{saturated}}$)



graph/map not to scale

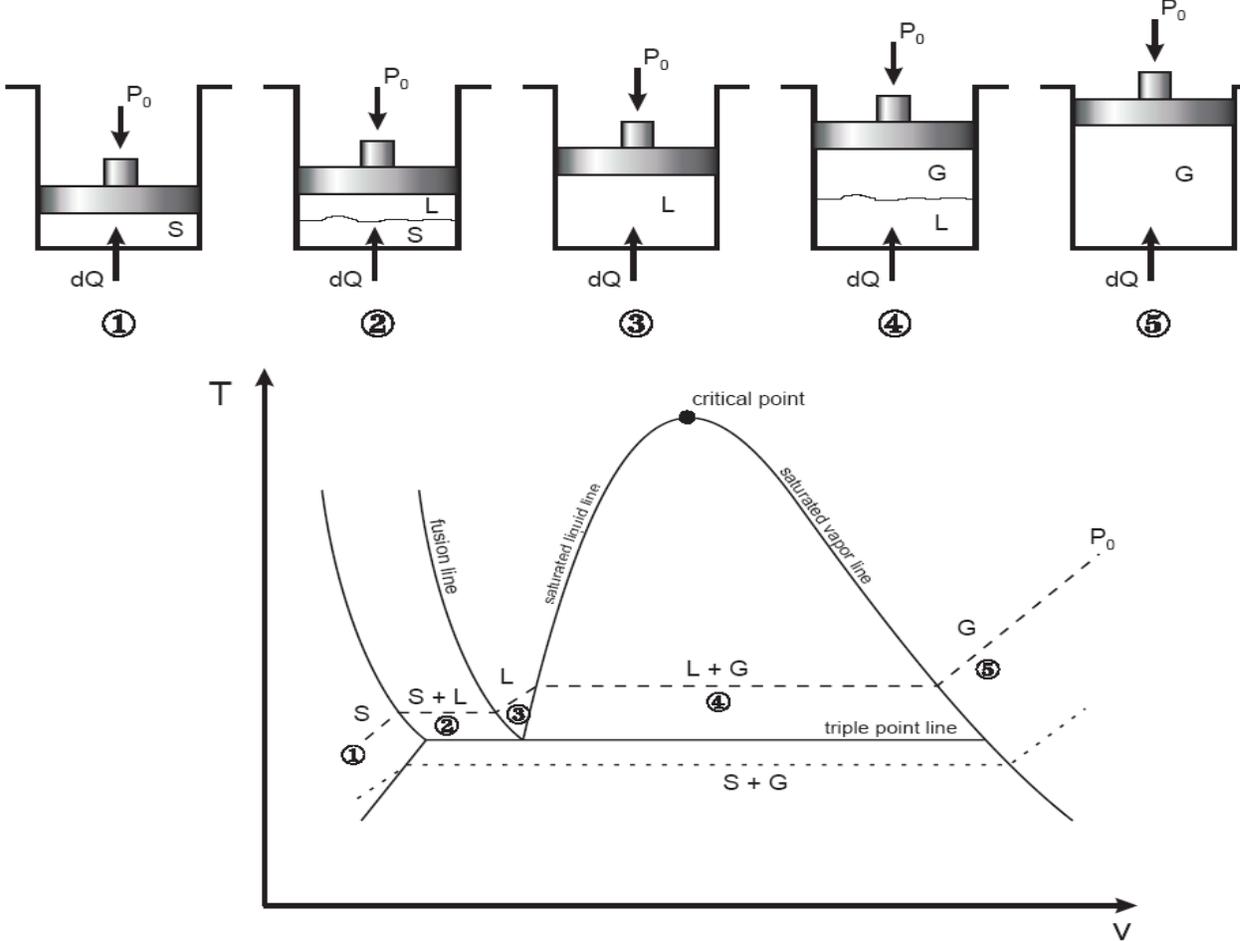


Fig. 1: T-v diagram for the heating process of a pure substance.

- ◆ At a given pressure, the temperature at which a pure substance starts boiling is called the saturation temperature, $T_{\text{sat}}.$
- ◆ Likewise, at a given temperature, the pressure at which a pure substance starts boiling is called the saturation pressure, $P_{\text{sat}}.$
- ◆ In a phase-change operation, pressure and temperature are dependent properties, $T_{\text{sat}} = f(P_{\text{sat}}).$
- ◆ The critical point is the point at which the liquid and vapor phases are not distinguishable
- ◆ The point at which the solid, liquid, and vapor phases can co-exist is called triple point. On T-v or P-v diagrams, this triple-phase state appears as a line called the triple line.

Table 1 Critical and triple point for water and oxygen.

Compound	Critical Point		Triple Point	
	P (atm)	T (K / °C)	P (atm)	T (K / °C)
H ₂ O	218	647.30/(374.14)	0.006	273.17 (0.01)
O ₂	50.136	154.80/(-118.36)	0.0015	54.16/(-219)

Vapor Curve

The general shape of a P-v diagram and a T-v diagram are very similar for a pure substance.

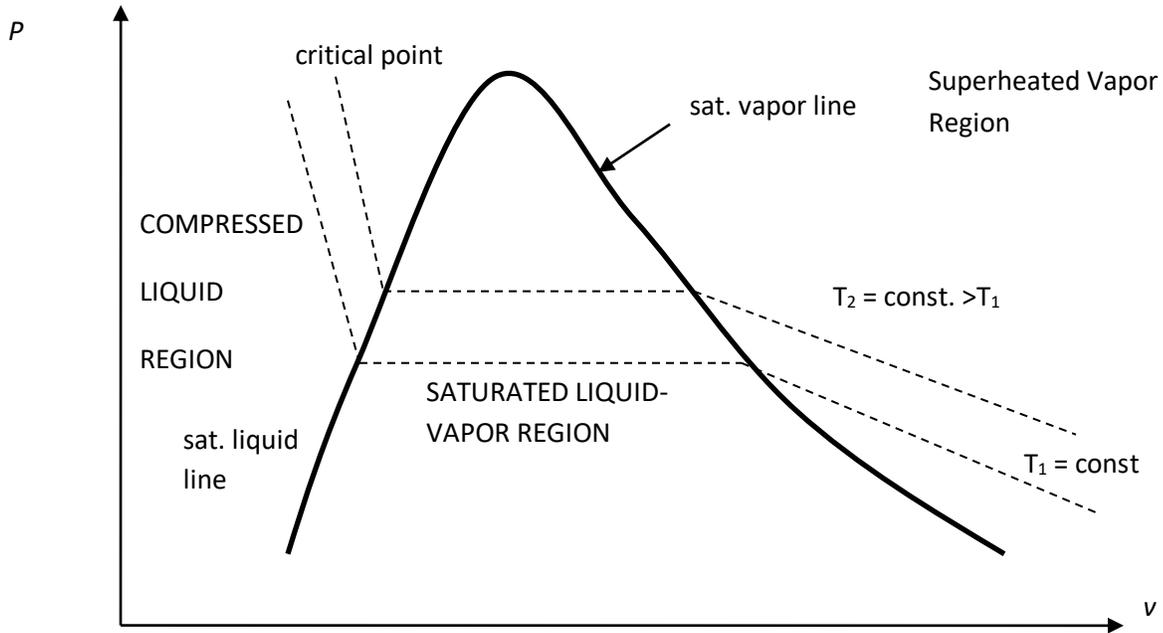


Fig. 2: P-v diagram of a pure substance.

The P-T or Phase Change Diagram

This is called phase diagram since all three phases are separated from each other by three lines. Most pure substances exhibit the same behavior.

- ◆ One exception is water. Water expands upon freezing.

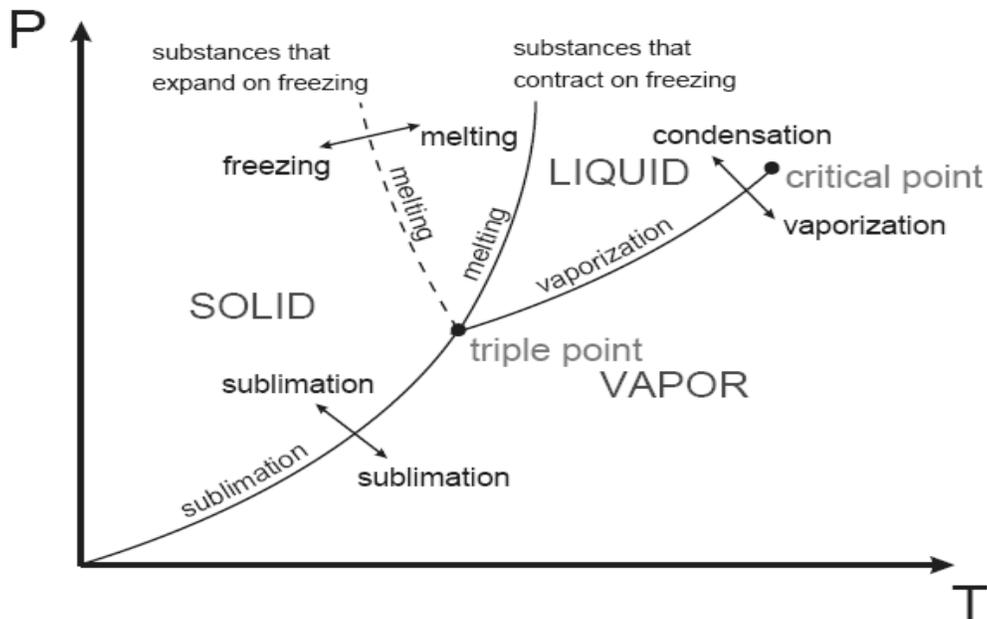


Fig. 3: phase diagram of pure substances.

A substance can transform from solid phase to vapor phase in two ways-

- i) First melting into a liquid and then evaporating into vapor,
 - ii) Direct evaporation without melting (sublimation as in camphor).
- ◆ The sublimation line distinguishes the solid and the vapor.
 - ◆ The vaporization line distinguishes the liquid and vapor regions.
 - ◆ The melting or fusion line differentiates the solid and liquid.
 - ◆ Triple point is a junction where these three lines meet.
 - if $P < P_{TP}$, the solid phase can transform directly to a vapor phase
 - At $P < P_{TP}$ the pure substance cannot exist in the liquid phase. Normally ($P > P_{TP}$) the substance melts into a liquid and then it gets evaporated.
 - Compounds (like CO_2) which has a triple point above 1 atm can sublime under atmospheric conditions (dry ice)
 - For water (as the most common working fluid) we are mainly interested in the liquid and vapor regions.

Property Tables

For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations. Thus, properties are frequently presented in the form of tables, (SEE Steam table)

The subscript “f” is used to denote properties of a saturated liquid and “g” for saturated vapor. The subscript, “fg”, indicates the algebraic difference between the same properties of saturated vapor and saturated liquid. For example:

v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor

v_{fg} = difference between v_g and v_f ($v_{fg} = v_g - v_f$)

Enthalpy: is a property defined as $H = U + PV$ (kJ) or $h = u + Pv$ (kJ/kg) (per mass unit).

Enthalpy of vaporization (or latent heat): represents the amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure. It decreases as the temperature or pressure increase, and becomes zero at the critical point.

1- Saturated Liquid-Vapor Mixture

During vaporization, a mixture of part liquid part vapor exists. To analyze this mixture, we need to know the proportions of the liquid and vapor in the mixture. Dryness fraction or quality of steam is the ratio of the mass of saturated vapor to the mass of the total mixture. It is denoted by x:

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}} \quad m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$

Saturated liquid-vapor mixture is treated as a combination of two sub-systems (two phases). The properties of the “mixture” are the average properties of the saturated liquid-vapor mixture.

$$V = V_f + V_g$$

$$m_t v_{ave} = m_f v_f + m_g v_g$$

$$m_f = m_t - m_g \rightarrow m_t v_{ave} = (m_t - m_g) v_f + m_g v_g$$

dividing by m_t

$$v_{ave} = (1 - x) v_f + x v_g \quad \text{and} \quad x = m_g / m_t$$

$$v_{ave} = v_f + x v_{fg} \quad (m^3 / kg)$$

or,

$$x = \frac{v_{ave} - v_f}{v_{fg}}$$

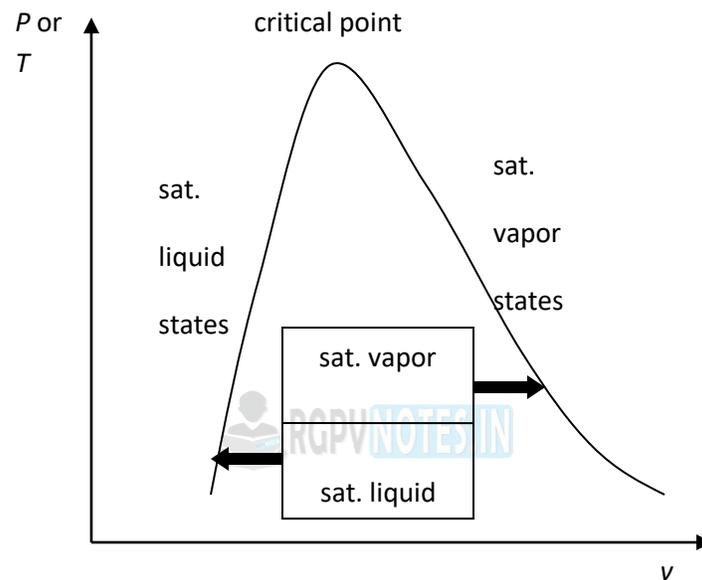


Fig. 4: The relative amounts of liquid and vapor phases (quality x) are used to calculate the mixture properties.

Similarly,

$$u_{ave} = u_f + x u_{fg}$$

$$h_{ave} = h_f + x h_{fg}$$

Or in general, it can be written as $y_{ave} = y_f + x y_{fg}$. Note that:

$$0 \leq x \leq 1$$

$$y_f \leq y_{ave} \leq y_g$$

Note: pressure and temperature are dependent in the saturated mixture region.

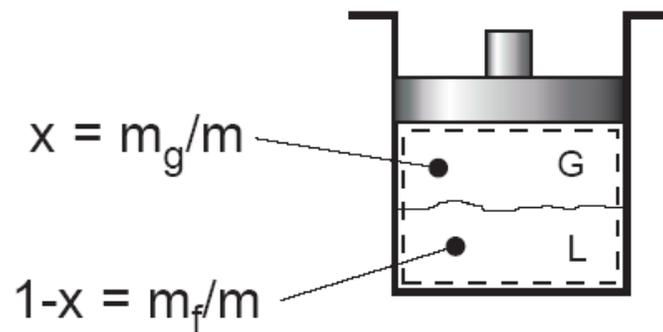


Fig. 5: Quality defined only for saturated liquid-vapor mixture.

2- Superheated Vapor

If $T \gg T_{\text{critical}}$ or $P \ll P_{\text{critical}}$, then the vapor can be approximated as an "ideal gas".

3- Compressed (or Sub-cooled) Liquid

The properties of a liquid are relatively independent of pressure (incompressible).

A general approximation is to treat compressed liquid as saturated liquid at the given saturation temperature.

The property most affected by pressure is enthalpy. For enthalpy use the following approximation:

$$h \approx h_f + v_f (P - P_{\text{sat}})$$

PVT Surface

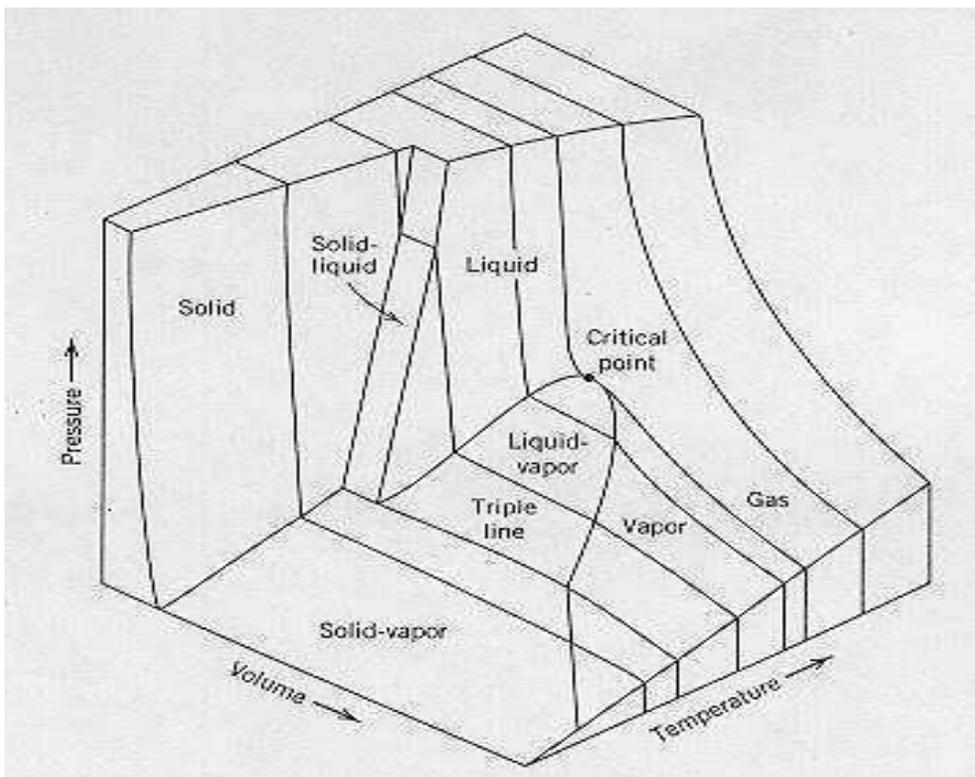
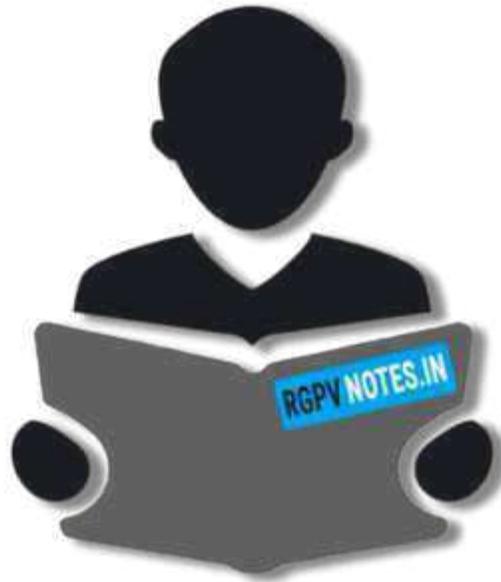


Fig.6 PVT Surface

The location of any point on the p-v-T surface gives the values of pressure, temperature and specific volume at equilibrium. The regions on the p-v-T surface labeled solid, liquid and vapor are single-phase regions.





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