PROPERTIES OF PURE SUBSTANCE

Pure Substance

A substance that has a fixed chemical composition throughout is called a pure substance such as water, air, and nitrogen.

A pure substance does not have to be of a single element or compound. 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 different phases. There are three principal phases: *solid*, *liquid*, and *gas*.

A phase: is defined as having a distinct molecular arrangement that is homogenous throughout and separated from others (if any) by easily identifiable boundary surfaces.

A substance may have several phases within a principal phase, each with a different molecular structure. For example, carbon may exist as graphite or diamond in the solid phase, and ice may exist in seven different phases at high pressure.

Note: Molecular bonds are the strongest in solids and the weakest in gases.

Solid: the molecules are arranged in a three-dimensional pattern (lattice) throughout the solid. The molecules cannot move relative to each other; however, they continually oscillate about their equilibrium position.

Liquid: the molecular spacing in liquid phase is not much different from that of the solid phase (generally slightly higher), except the molecules are no longer at fixed positions relative to each other.

Gas: the molecules are far apart from each other, and a molecular order does not exist. Gas molecules move randomly, and continually collide with each other and the walls of the container they are in.

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

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. Depending on the prevailing pressure, the matter will pass through various phase transformations. At P_0:

1. Solid

2. Mixed phase of liquid and solid

3. Sub-cooled or compressed liquid (means it is not about to vaporize)

4. Wet vapor or saturated liquid-vapor mixture, the temperature will stop rising until the liquid is completely vaporized.

5. Superheated vapor (a vapor that is not about to condense).

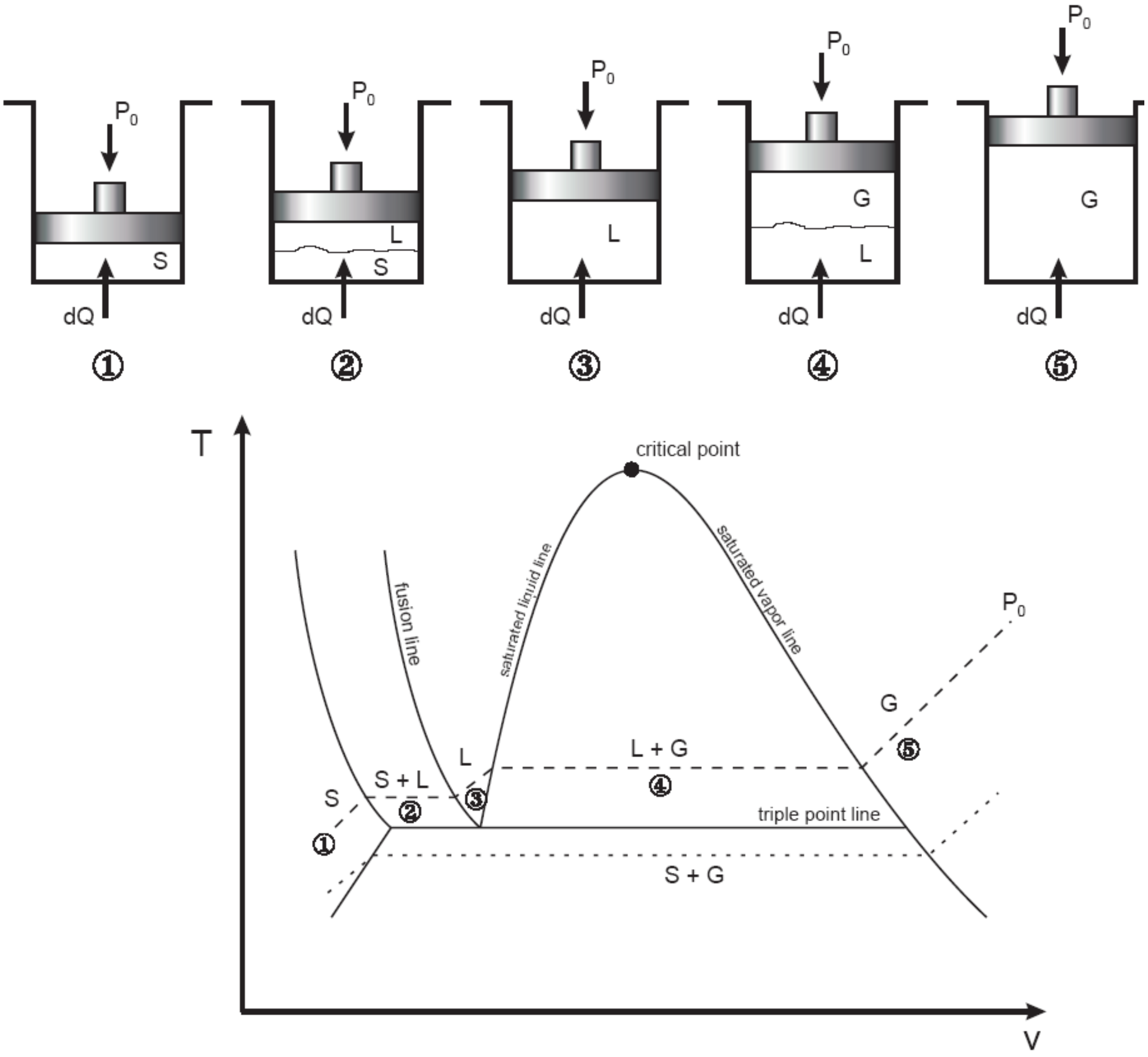

Fig. 1: *T*-*v* diagram for the heating process of a pure substance.

At a given pressure, the temperature at which a pure substance starts boiling is called the saturation temperature, T_{sat}.

Likewise, at a given temperature, the pressure at which a pure substance starts boiling is called the saturation pressure, P_{sat}.

During a phase-change process, pressure and temperature are dependent properties,

$$T_{sat} = f\,(P_{sat}).$$

<u>The critical point</u> is the point at which the liquid and vapor phases are not distinguishable.

<u>The triple point</u> is the point at which the liquid, solid, and vapor phases can co-exist together. On *P*-*v* or *T*-*v* diagrams, these triple-phase states form a line called the triple line.

Table 1: Critical and triple point for water and oxygen.

	Critical Point		Triple Point	
	P (atm)	*T* (K /°C)	*P* (atm)	*T* (K /°C)
H_2O	218	647.30/(374.14)	0.006	273.17 (0.01)
O_2	50.13	154.80/(−118.36)	0.0015	54.16/(−219)

Vapor Dome

The general shape of a *P*-*v* diagram for a pure substance is very similar to that of a *T*-*v* diagram.

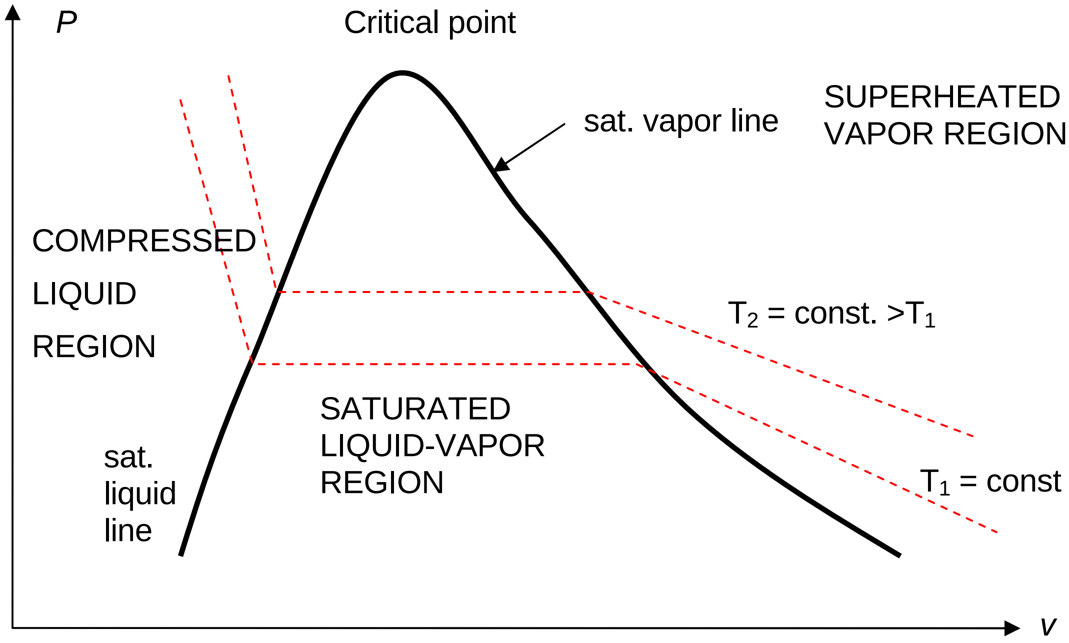

Fig. 2: P-v diagram of a pure substance.

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.

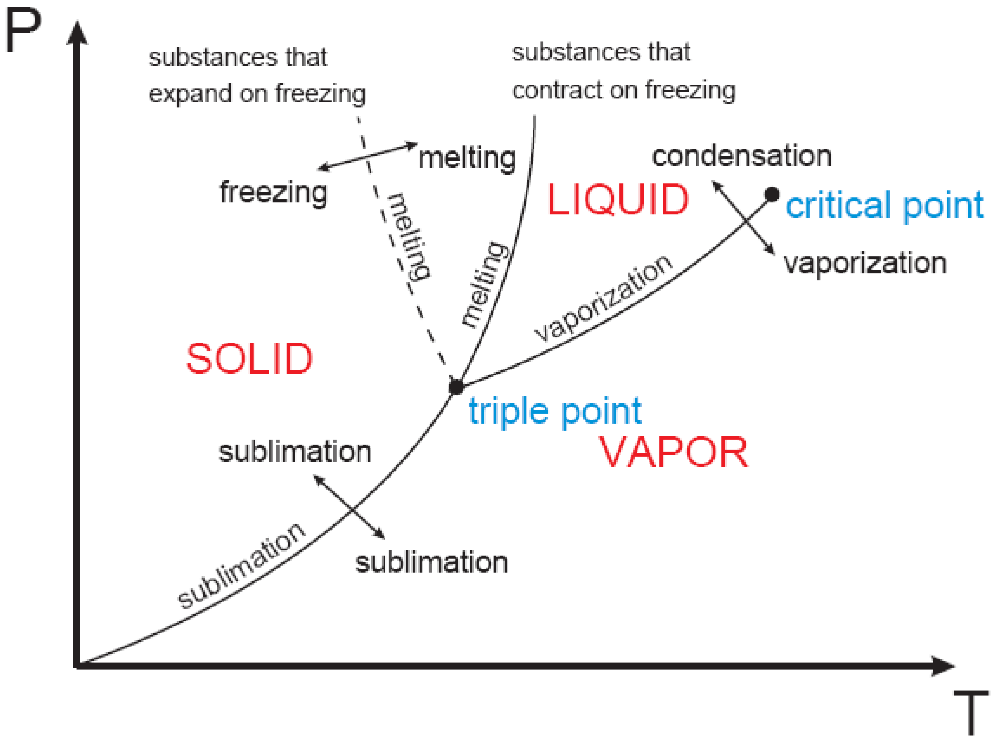

Fig. 3: phase diagram of pure substances.

There are two ways that a substance can pass from solid phase to vapor phase: i) it melts first into a liquid and subsequently evaporates; ii) it evaporates directly without melting (sublimation).

- The sublimation line separates the solid and the vapor.
- The vaporization line separates the liquid and vapor regions
- The melting or fusion line separates the solid and liquid.
- These three lines meet at the triple point.
- If $P < P_{TP}$, the solid phase can change 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 evaporates.
- Matter (like CO_2) which has a triple point above 1 *atm* sublimate under atmospheric conditions (dry ice)
- For water (as the most common working fluid) we are mainly interested in the liquid and vapor regions. Hence, we are mostly interested in boiling and condensation.

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 Table A-4 Cengel book.

The subscript "*f*" is used to denote properties of a saturated liquid and "*g*" for saturated vapor. Another subscript, "*fg*", denotes the difference between the saturated vapor and saturated liquid values of the same property.

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.

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. The ratio of the mass of vapor to the mass of the total mixture is called quality, *x*:

$$x = \frac{\mathrm{m}_{\text{vapor}}}{\mathrm{m}_{\text{total}}} \qquad m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$

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.

$$V = V_f + V_g$$

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

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

dividing by m_t

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

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

or,

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

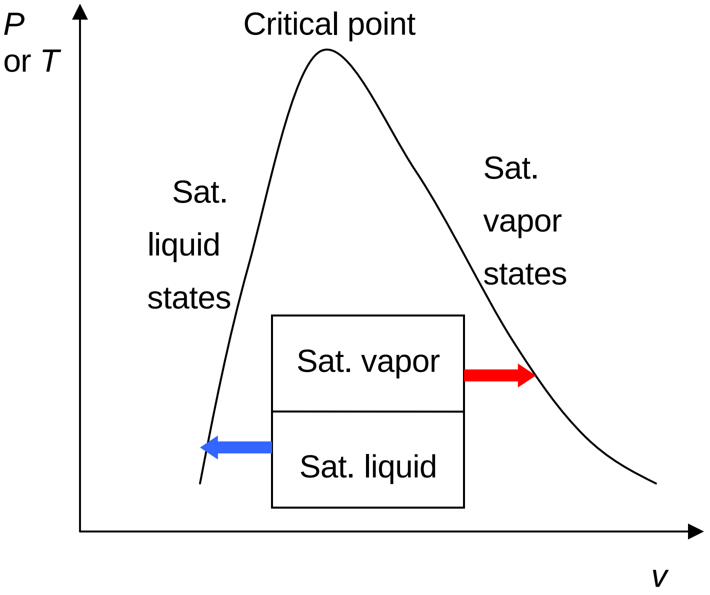

Fig. 4: The relative amounts of liquid and vapor phases (quality x) are used to calculate the mixture properties.

Similarly,

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

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

$$0 \le x \le 1$$
$$y_f \le y_{ave} \le y_g$$

<u>Note</u>: pressure and temperature are dependent in the saturated mixture region.

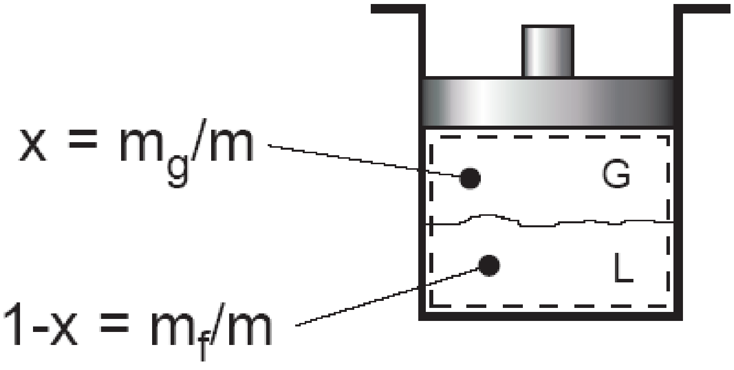

Fig.5: Quality defined only for saturated liquid-vapor mixture.

Superheated Vapor

Superheated region is a single phase region (vapor only), temperature and pressure are no longer dependent. See Table A-6 for superheated vapor properties. Compared to saturated vapor, superheated vapor is characterized by:

- Lower pressures ($P < P_{sat}$ at a given T)
- Higher temperatures ($T > T_{sat}$ at a given P)
- Higher specific volumes ($v > v_g$ at a given T or P)
- Higher internal energies ($u > u_g$ at a given T or P)
- Higher enthalpies ($h > h_g$ at a given T or P)

Note: If $T >> T_{critical}$ or $P << P_{critical}$, then the vapor is called “gas” and can be approximated as an “ideal gas”.

Compressed (or Sub-cooled) Liquid

The properties of a liquid are relatively independent of pressure (incompressible). In general, a compressed liquid is characterized by:

- Higher pressures ($P > P_{sat}$ at a given T)
- Lower temperatures ($T < T_{sat}$ at a given P)
- Lower specific volumes ($v < v_f$ at a given T or P)
- Lower internal energies ($u < u_f$ at a given T or P)
- Lower enthalpies ($h < h_f$ at a given T or P)

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

$$y \approx y_{f\,@T}$$

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

$$h \approx h_{f\,@T} + v_f \left(P - P_{sat}\right)$$

Note: Interpolation

Often the exact value of a required property cannot be found in property table. In such occasions, *linear interpolation* should be used. That is to fit a line connecting the two known points on either side of the desired value and then estimate the required value.

Assume that two known points are: (x_1, y_1) and (x_2, y_2) and we need to estimate the value of y at point x. Using linear interpolation, we have:

$$y = ax + b$$

where

$$\begin{cases} a = \dfrac{y_1 - y_2}{x_1 - x_2} \\ b = \dfrac{x_1 y_2 - y_1 x_2}{x_1 - x_2} \end{cases}$$

Example

Determine the phase for each of the following water states using thermodynamics tables and indicate the relative position in P-v and T-v diagrams.

a) 120°*C* and 500 *kPa*
b) 120°*C* and 0.5 m^3/kg

Solution:

a) Enter Table A-4, Saturated Water - Temperature Table. The saturated pressure at this temperature is 198.67 *kPa*, since *P*=500 *kPa* > 198.67 *kPa*, we have a compressed liquid. We could also enter Table A-5, Saturated Water - Pressure Table, with 500 *kPa* and found the saturation temperature as 151.83°*C*, since *T* = 120°*C* < 151.83°*C*, we have subcooled liquid.

b) Enter Table A-4 with 120°*C* and notice

$$v_f = 0.001060 < v = 0.5 < v_g = 0.8913\ m^3/kg$$

So the state is a two phase mixture of liquid and vapor.

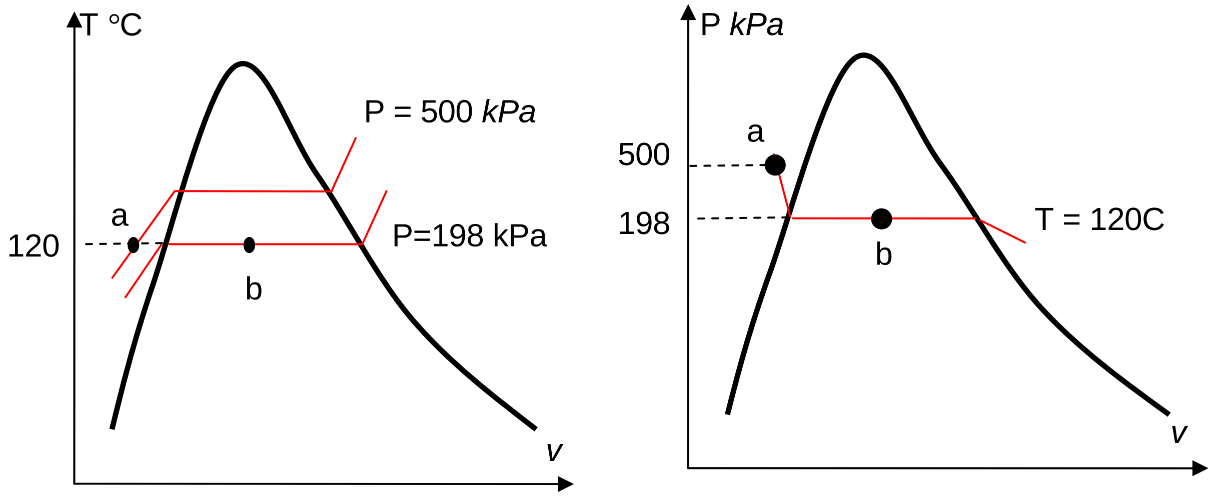

Fig. 6: *T-v* and *P-v* diagrams for example 1.

Example

A rigid vessel contains saturated vapor refrigerant R-134a at 20°*C*. Heat is transferred to the system until the temperature reaches 40°*C*. What is the final pressure?

Solution:

Since the volume and the mass of the refrigerant do not change during this process, the specific volume remains constant. From Table A-11, Saturated Refrigerant-134a – Temperature Table, we have:

$$v_1 = v_2 = 0.035969\ m^3/kg$$

Enter Table A-11 with 40°*C*, the saturated vapor specific volume reads $v_{g@40C} = 0.019952 < v_2 = 0.035969\ m^3/kg$, thus the final state is superheated vapor. Knowing temperature and specific volume, we enter Table A-13, Superheated Refrigerant-134a, interpolating between $P = 0.6$ and $0.7\ MPa$ at $T = 40$°C, we find:

$$P_2 = 0.658\ MPa$$