



Module

3

Lecture

3

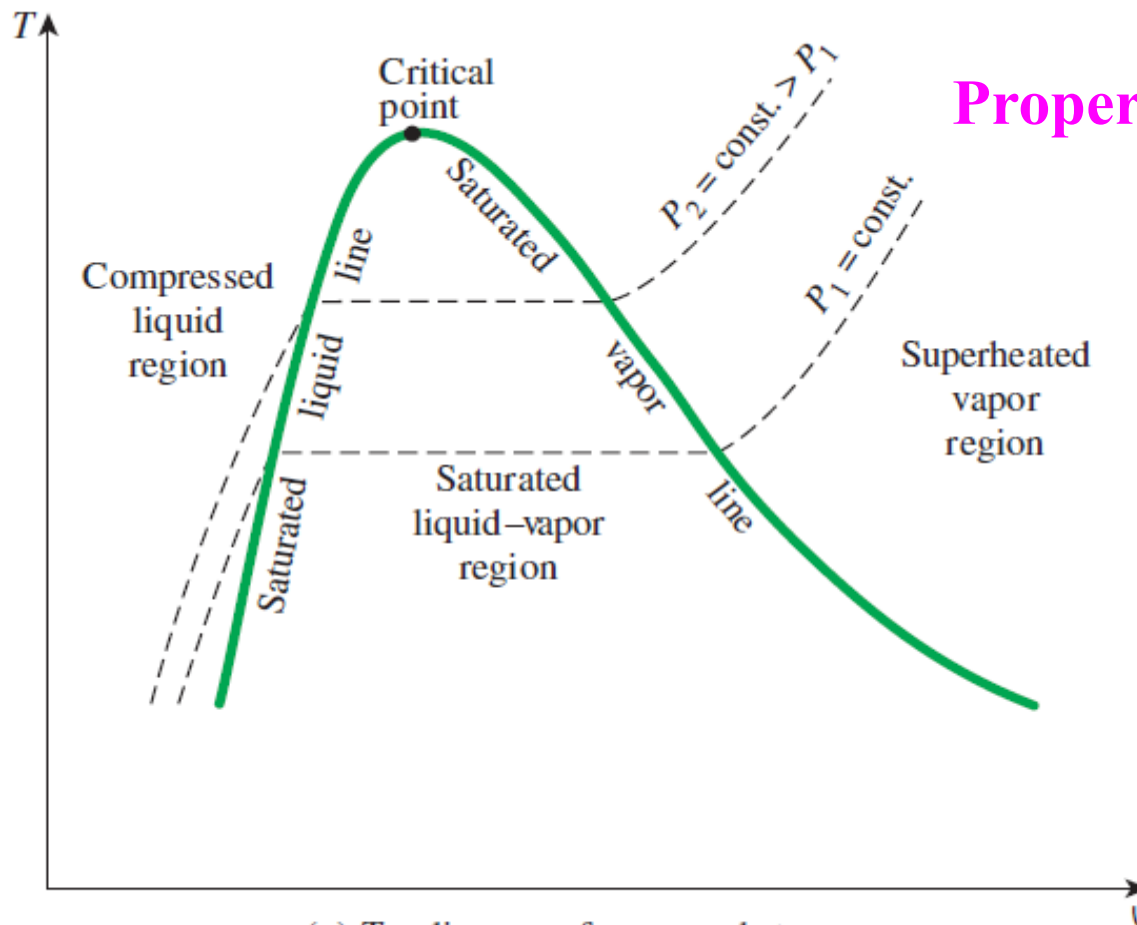
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Thermodynamics

Properties of Pure Substances

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(a) T - v diagram of a pure substance

Properties of Pure Substances (Contd...)

T - v diagram

Fig. 3.11: T - v diagram of a pure substance

@ Constant Pressure

$T > T_{\text{sat}} \Rightarrow$ “superheated vapor”

$T = T_{\text{sat}} \Rightarrow$ “two-phase liquid-vapor”

$T < T_{\text{sat}} \Rightarrow$ “compressed liquid”

P - v diagram

@ Constant Temperature

$P < P_{\text{sat}} \Rightarrow$ “superheated vapor”

$P = P_{\text{sat}} \Rightarrow$ “two-phase liquid-vapor”

$P > P_{\text{sat}} \Rightarrow$ “compressed liquid”

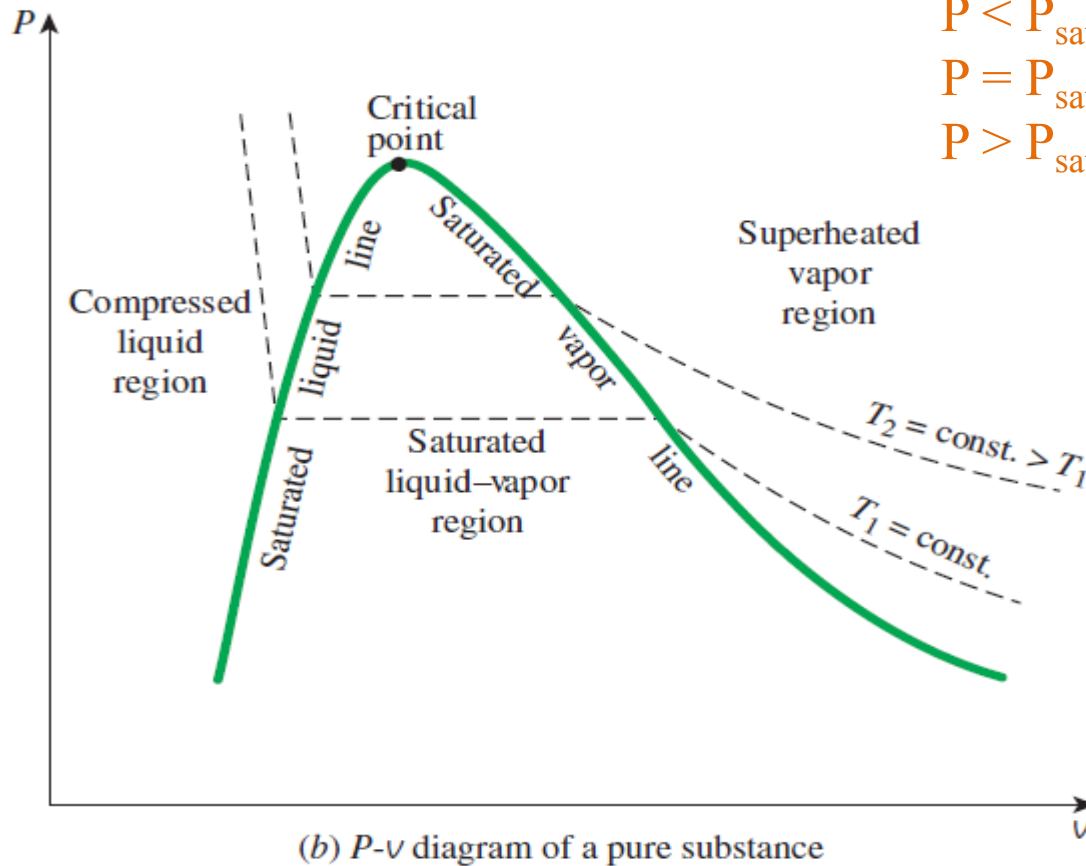


Fig. 3.12: P - v diagram of a pure substance

Extending the Diagrams to Include the Solid Phase

- The two equilibrium diagrams developed so far represent the equilibrium states involving the liquid and the vapor phases only.
- However, these diagrams can easily be extended to include the solid phase as well as the solid–liquid and the solid–vapor saturation regions. The basic principles discussed in conjunction with the liquid–vapor phase change process apply equally to the solid–liquid and solid–vapor phase change processes.
- Most substances contract during a solidification (i.e., freezing) process. Others, like water, expand as they freeze.
- The P - v diagrams for both groups of substances are given in Figs. 3.14 (a) and 3.14 (b).
- These two diagrams differ only in the solid–liquid saturation region. The T - v diagrams look very much like the P - v diagrams, especially for substances that contract on freezing.

- The fact that water expands upon freezing has vital consequences in nature.
- If water contracted on freezing as most other substances do, the ice formed would be heavier than the liquid water, and it would settle to the bottom of rivers, lakes, and oceans instead of floating at the top.
- The sun's rays would never reach these ice layers, and the bottoms of many rivers, lakes, and oceans would be covered with ice year round, seriously disrupting marine life.
- We are all familiar with two phases being in equilibrium, but under some conditions all three phases of a pure substance coexist in equilibrium (Fig. 3.13).

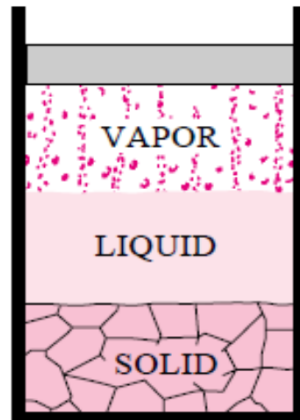
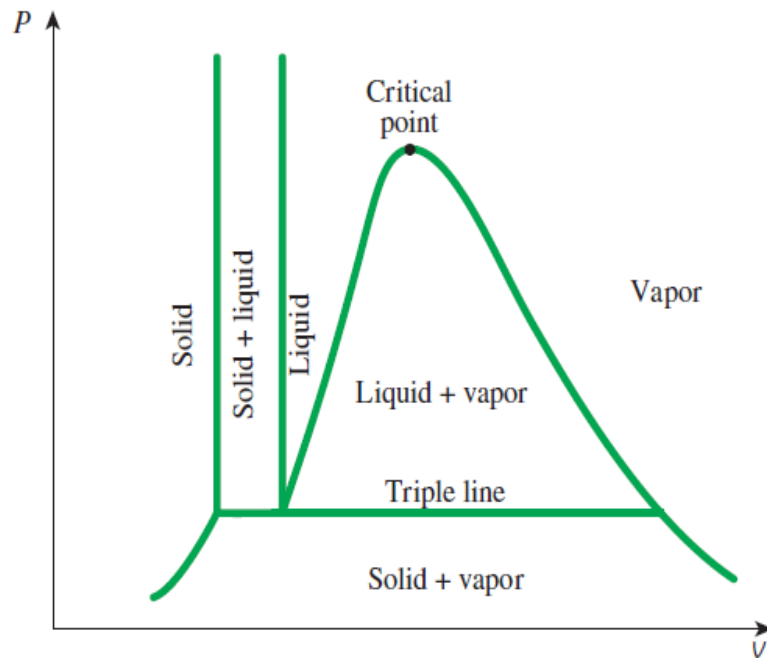
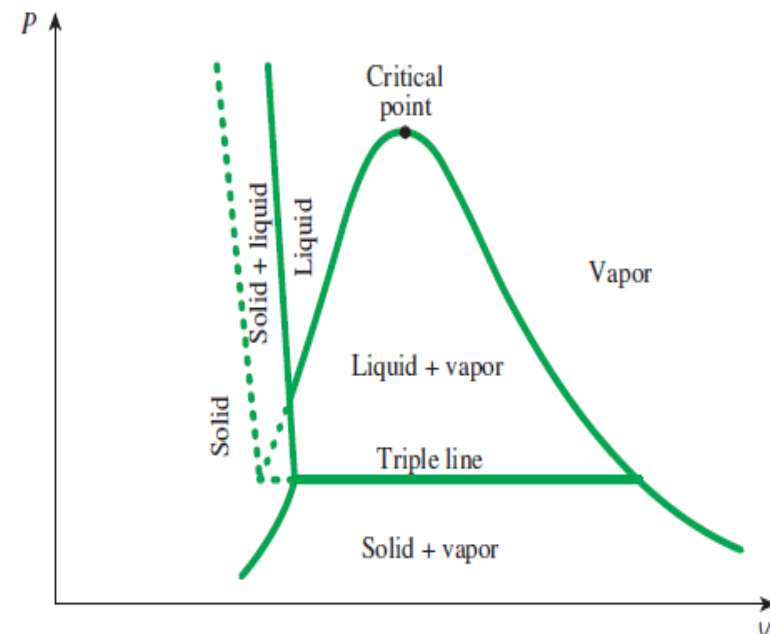


Fig. 3.13: At triple-point pressure and temperature, a substance exists in three phases in equilibrium

- On P - v diagram, these triple-phase states form a line called the *triple line*.
- The states on the triple line of a substance have the same pressure and temperature but different specific volumes.
- The triple line appears as a point on the P - T diagrams and, therefore, is often called the *triple point*.
- For water, the triple-point temperature and pressure are 0.01°C and 0.6113 kPa, respectively.



(a) P - v diagram of a substance that contracts on freezing



(b) P - v diagram of a substance that expands on freezing (such as water)

Fig. 3.14: P - v diagram of a pure substance

- That is, all three phases of water will exist in equilibrium only if the temperature and pressure have precisely these values.
- No substance can exist in the liquid phase in stable equilibrium at pressures below the triple-point pressure.
- The same can be said for temperature for substances that contract on freezing. However, substances at high pressures can exist in the liquid phase at temperatures below the triple-point temperature.
- For example, water cannot exist in liquid form in equilibrium at atmospheric pressure at temperatures below 0°C , but it can exist as a liquid at 20°C at 200 MPa pressure. Also, ice exists at seven different solid phases at pressures above 100 MPa.

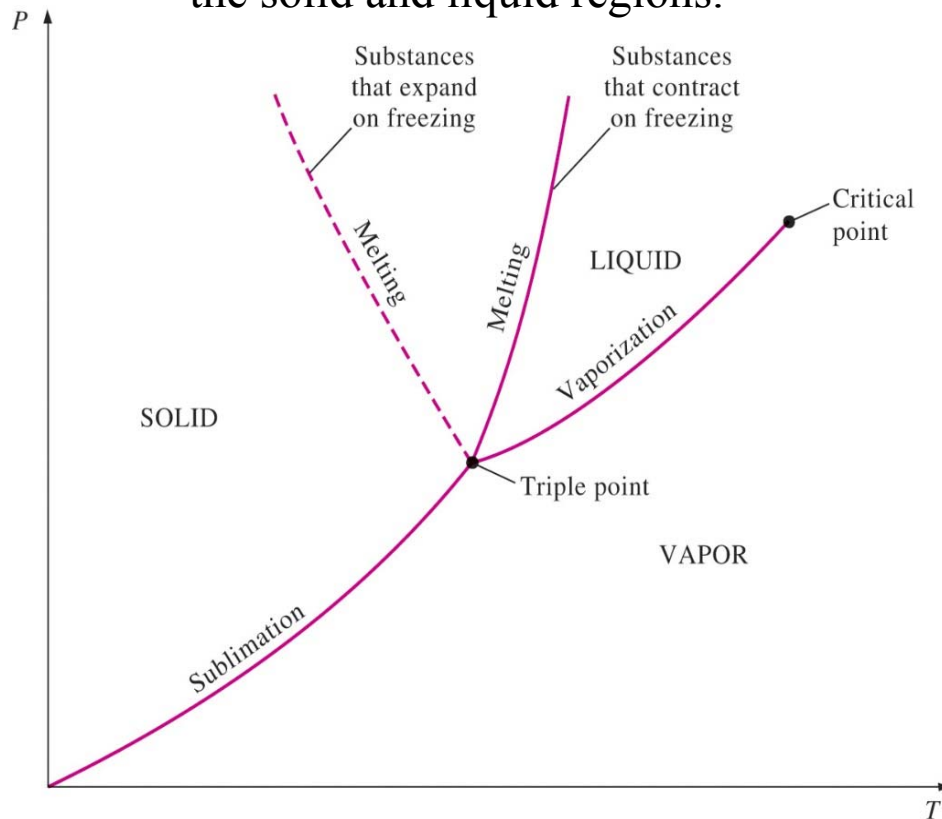
- There are two ways a substance can pass from the solid to vapor phase: either it melts first into a liquid and subsequently evaporates, or it evaporates directly without melting first.
- The latter occurs at pressures below the triple point value, since a pure substance cannot exist in the liquid phase at those pressures (Fig. 3.15). Passing from the solid phase directly into the vapor phase is called *sublimation*.
- For substances that have a triple-point pressure above the atmospheric pressure such as solid CO₂ (dry ice), sublimation is the only way to change from the solid to vapor phase at atmospheric conditions.



Fig. 3.15: At low pressures (below the triple point value), solids evaporate without melting first (*sublimation*).

The P - T Diagram

- Fig. 3.16 shows the P - T diagram of a pure substance.
- 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.



- These three lines meet at the triple point, where all three phases coexist in equilibrium.
- The vaporization line ends at the critical point because no distinction can be made between liquid and vapor phases above the critical point.
- Substances that expand and contract on freezing differ only in the melting line on the P - T diagram.

Fig. 3.16: P - T diagram

P - v - T Surface

- The state of a simple compressible substance is fixed by any two independent, intensive properties.
- Once the two appropriate properties are fixed, all the other properties become dependent properties.
- Remembering that any equation with two independent variables in the form $z=z(x, y)$ represents a surface in space, we can represent the P - v - T behaviour of a substance as a surface in space, as shown in Figs. 3.17 and 3.18.
- Here T and v may be viewed as the independent variables (the base) and P as the dependent variable (the height).
- The single-phase regions appear as curved surfaces on the P - v - T surface, and the two-phase regions as surfaces perpendicular to the P - T plane.
- This is expected since the projections of two phase regions on the P - T plane are lines.

P-v-T Surface (Contd...)

- All the two-dimensional diagrams we have discussed so far are merely projections of this three-dimensional surface onto the appropriate planes.
- A P - v diagram is just a projection of the P - v - T surface on the P - v plane, and a T - v diagram is nothing more than the bird's-eye view of this surface.
- The P - v - T surfaces present a great deal of information at once, but in a thermodynamic analysis it is more convenient to work with two-dimensional diagrams, such as the P - v and T - v diagrams.

P - v - T Surface (Contd...)

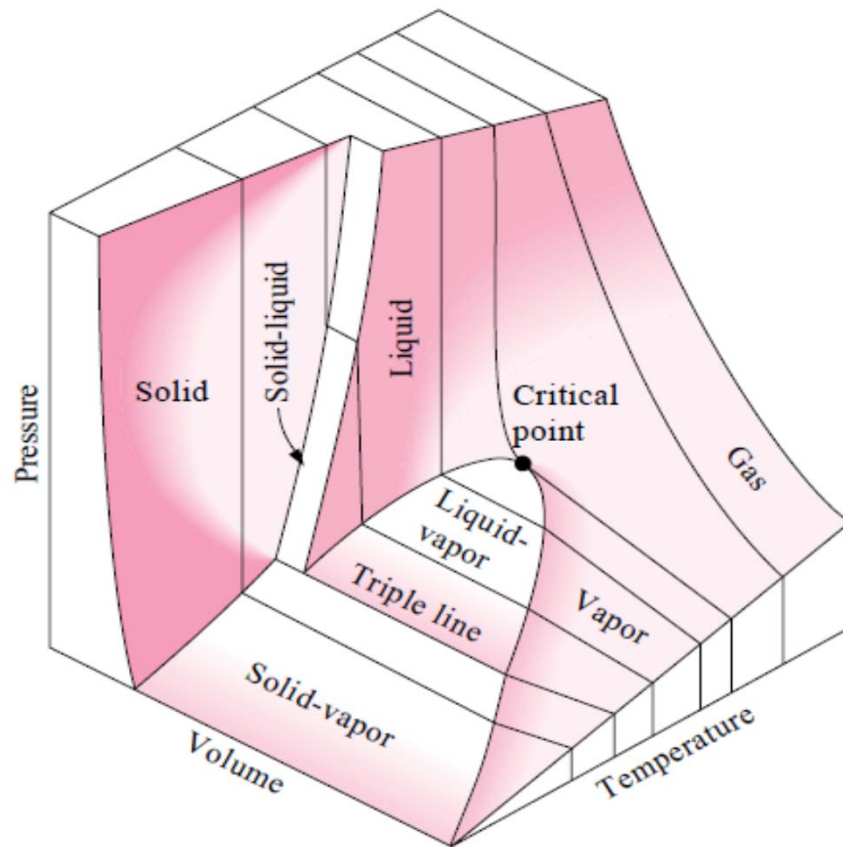


Fig. 3.17:
 P - v - T surface of a substance that *contracts* on freezing.

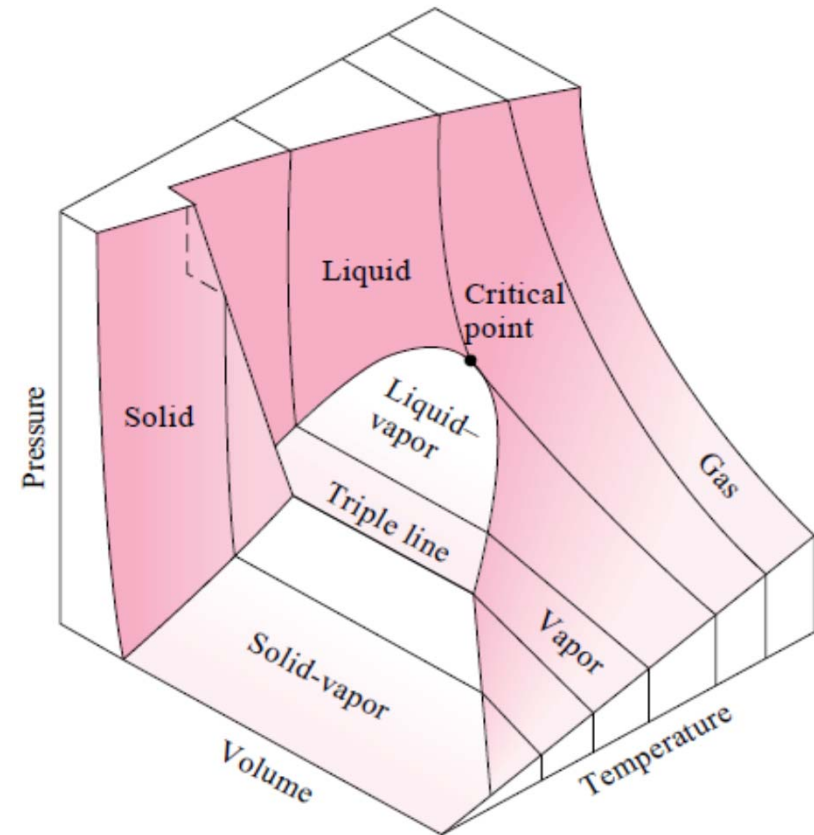


Fig. 3.18:
 P - v - T surface of a substance that *expands* on freezing (like water).

Thank You