

ESO 201A: Thermodynamics
2016-2017-I semester

Properties: part 2

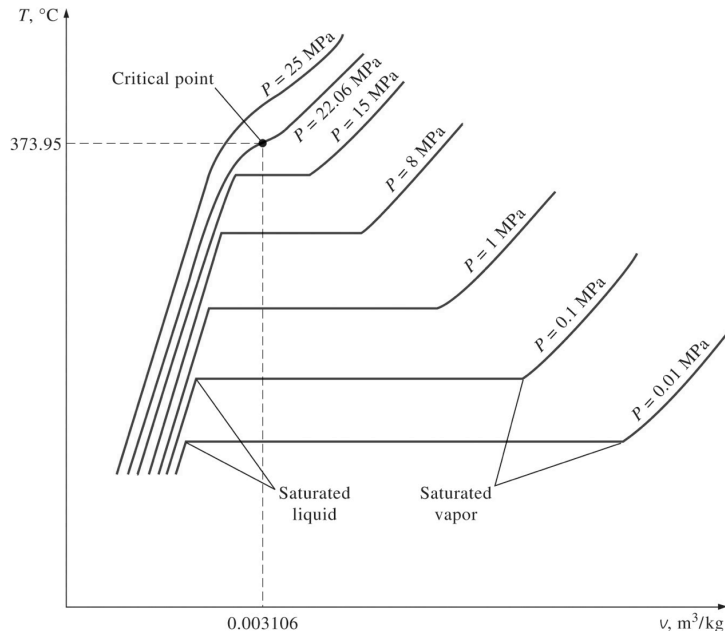
Dr. Jayant K. Singh
Department of Chemical Engineering
Faculty Building 469,
Telephone: 512-259-6141
E-Mail: jayantks@iitk.ac.in
home.iitk.ac.in/~jayantks/ESO201/index.htm

Learning objective

1. Introduce the concept of a pure substance.
2. Discuss the physics of phase change processes.
3. Illustrate the P-v, T-v and P-T property diagram, and P-v-T surfaces of pure substances.
4. Obtaining thermodynamic properties of a pure substance from a property table.
5. Define Ideal gas equation of state and demonstrate its use.
6. Introduce to compressibility.
7. Present the commonly used equation of states.

Property diagram for phase change process

- The variations of properties during phase-change processes are best studied and understood with the help of property diagrams such as the T - v , P - v , and P - T diagrams for pure substances.

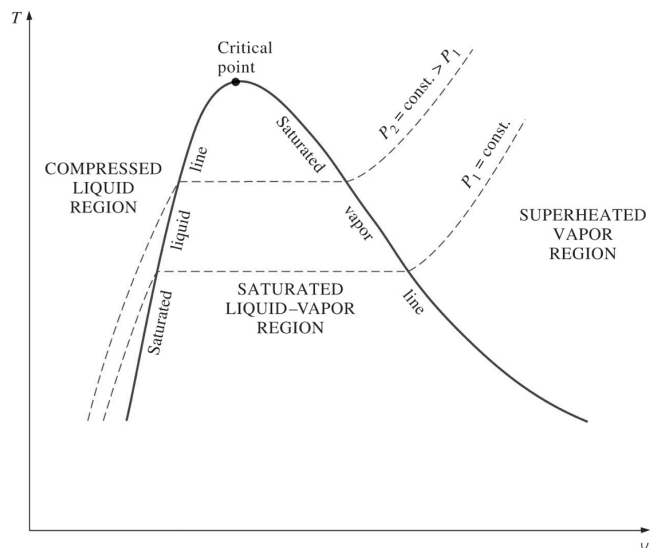
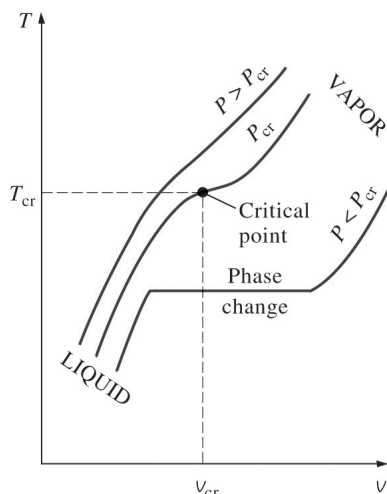


T - v diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

3

Property diagram for phase change process

- saturated liquid line
- saturated vapor line
- compressed liquid region
- superheated vapor region
- saturated liquid-vapor mixture region (wet region)

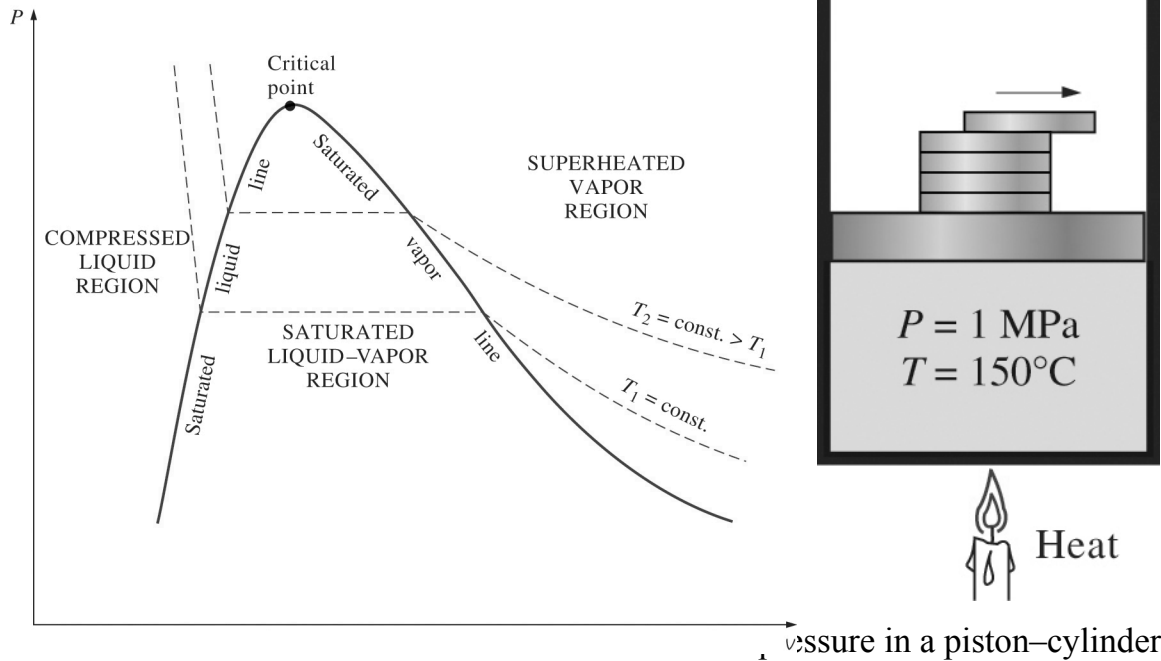


T - v diagram of a pure substance.

At supercritical pressures ($P > P_{cr}$), there is no distinct phase-

Critical point: The point at which the saturated liquid and saturated vapor states

P-v diagram



P-v diagram of a pure substance.

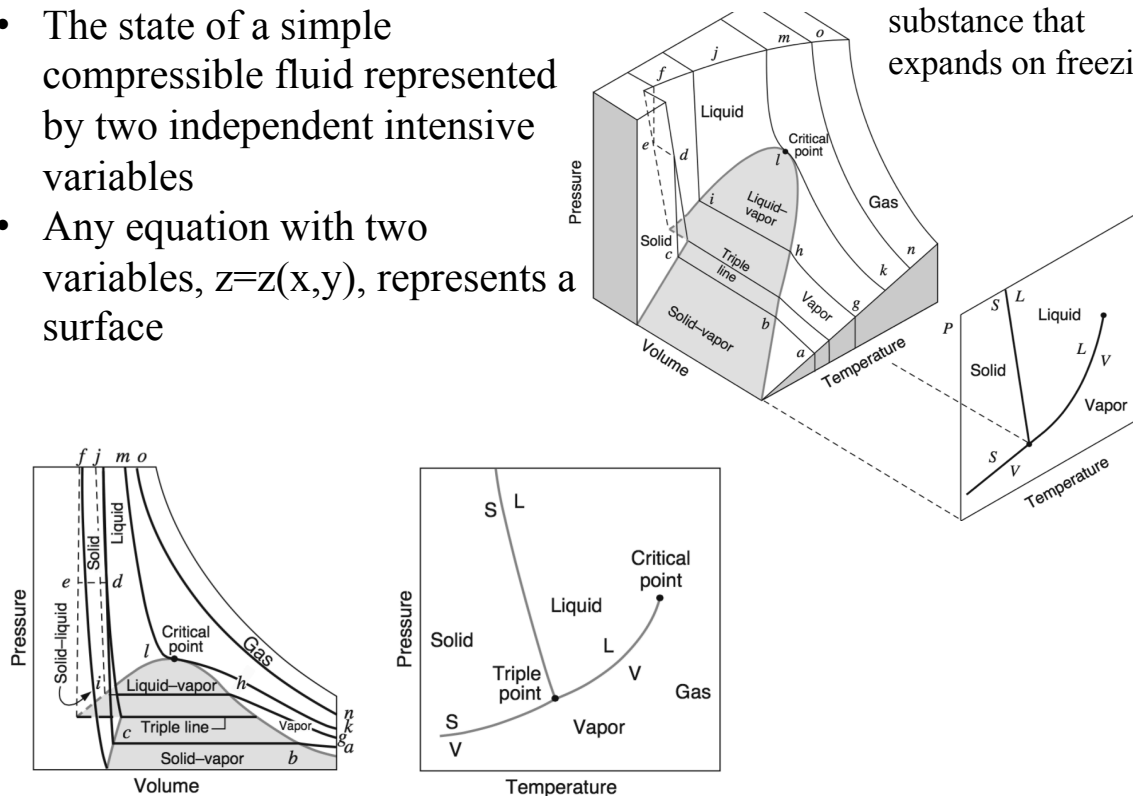
Pressure in a piston-cylinder device can be reduced by reducing the weight of the piston.

5

Thermodynamic surface

- The state of a simple compressible fluid represented by two independent intensive variables
- Any equation with two variables, $z=z(x,y)$, represents a surface

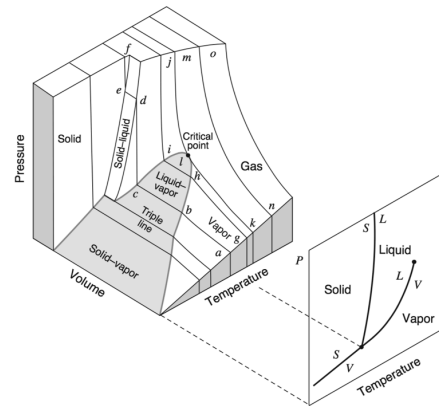
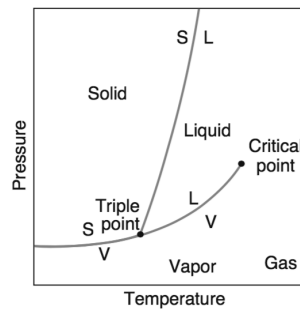
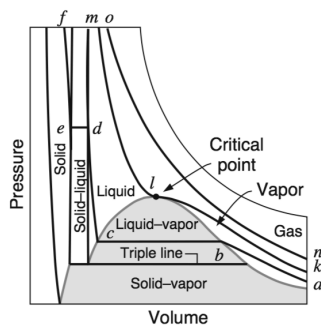
P-v-T surface of a substance that expands on freezing



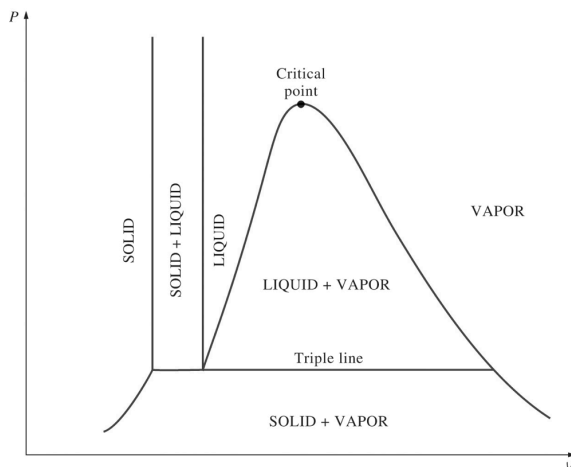
Thermodynamic surface

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.

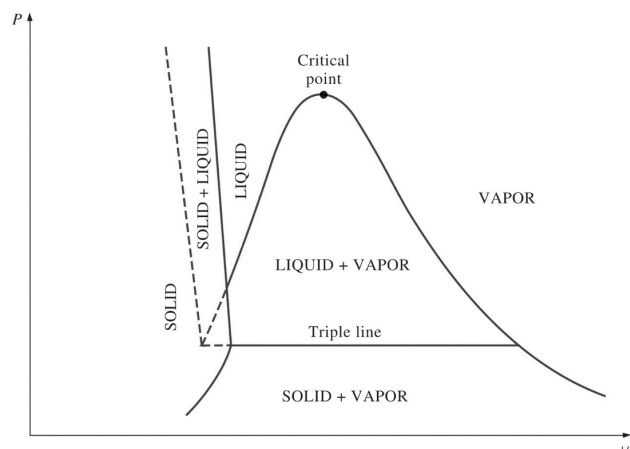
P - v - T surface of a substance that contracts on freezing



Extending P - v diagrams to include solid phase

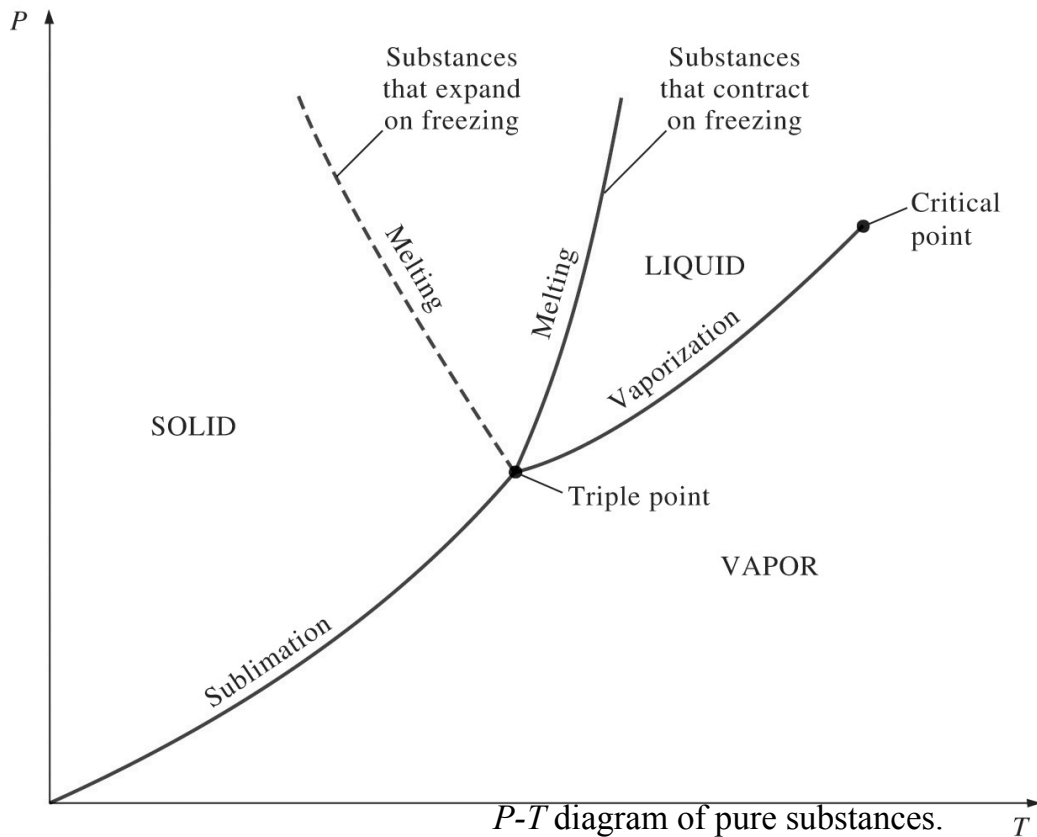


P - v diagram of a substance that contracts on freezing.



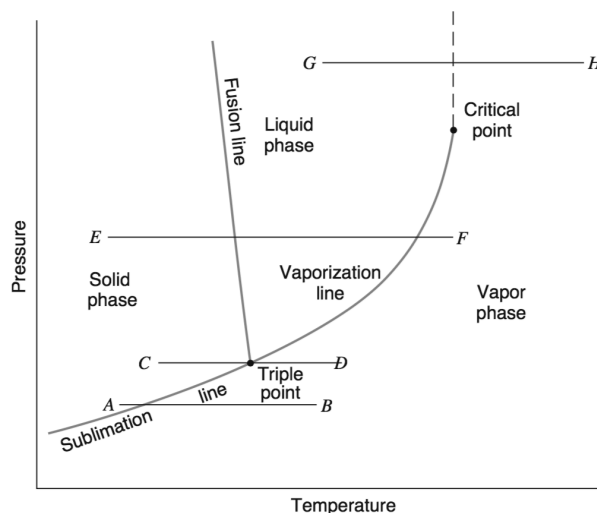
P - v diagram of a substance that expands on freezing (such as water).

P-T diagram of pure substances

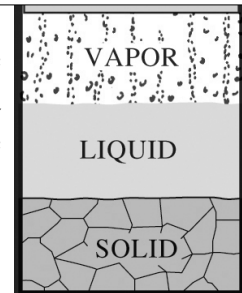


9

Phase transformation



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



- Sublimation line: solid-vapor coexistence
- Fusion line: solid-liquid coexistence
- Vaporization line: liquid-vapor coexistence
- Triple point: All the three phases at equilibrium
- Above critical point no distinction between vapor and liquid phases



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

For water,
 $T_{tp} = 0.01^\circ\text{C}$
 $P_{tp} = 0.6117 \text{ kPa}$

Latent heat

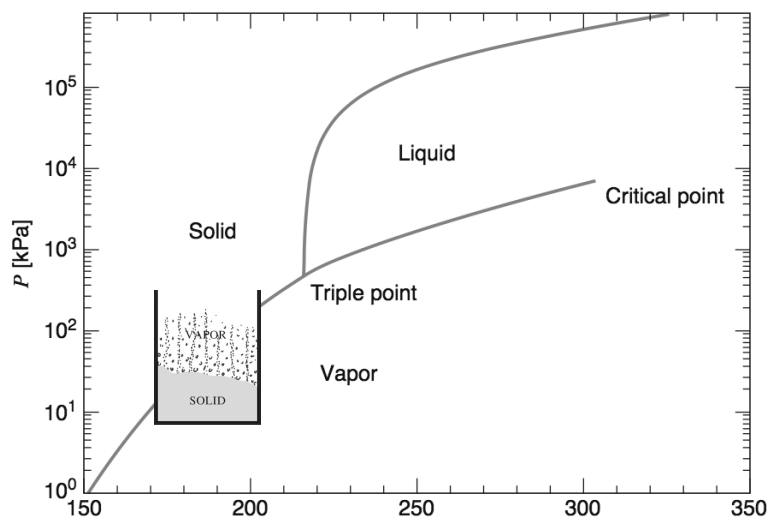
- **Latent heat:** The amount of energy absorbed or released during a phase-change process
 - **Latent heat of fusion**
 - **Latent heat of vaporization**
 - **Latent heat of sublimation**
- The magnitudes of the *latent heats* depend on the temperature or pressure at which the phase change occurs.
 - At 1 atm pressure, the latent heat of fusion of water is 333.7 kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.

TABLE 3-2

Variation of the standard atmospheric pressure and the boiling (saturation) temperature of water with altitude

Elevation, m	Atmospheric pressure, kPa	Boiling temperature, °C
0	101.33	100.0
1,000	89.55	96.5
2,000	79.50	93.3
5,000	54.05	83.3
10,000	26.50	66.3
20,000	5.53	34.7

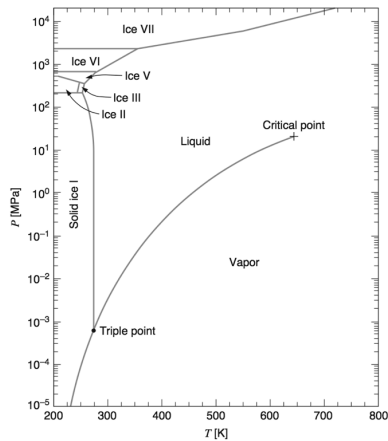
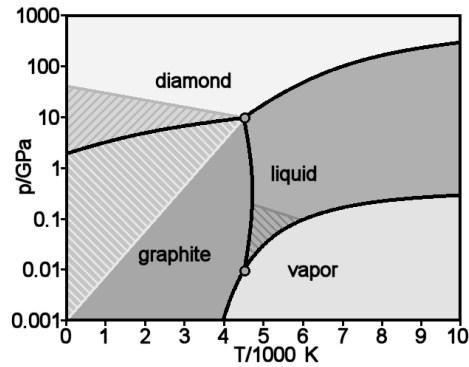
CO₂ phase diagram



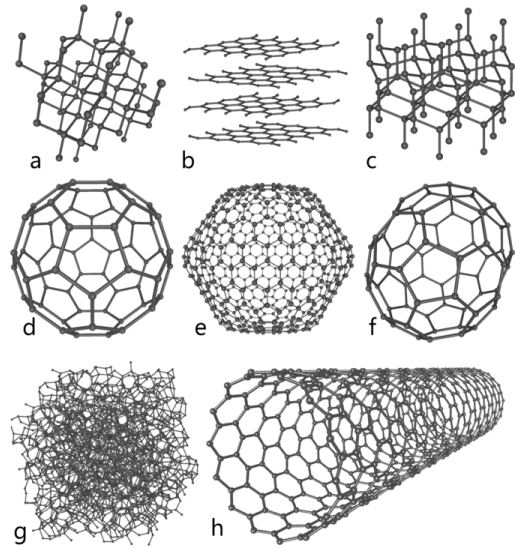
- Triple point pressure is greater than the normal atmospheric pressure
- Thus at atmospheric pressure the phase transition is sublimation
- Referred as dry ice.



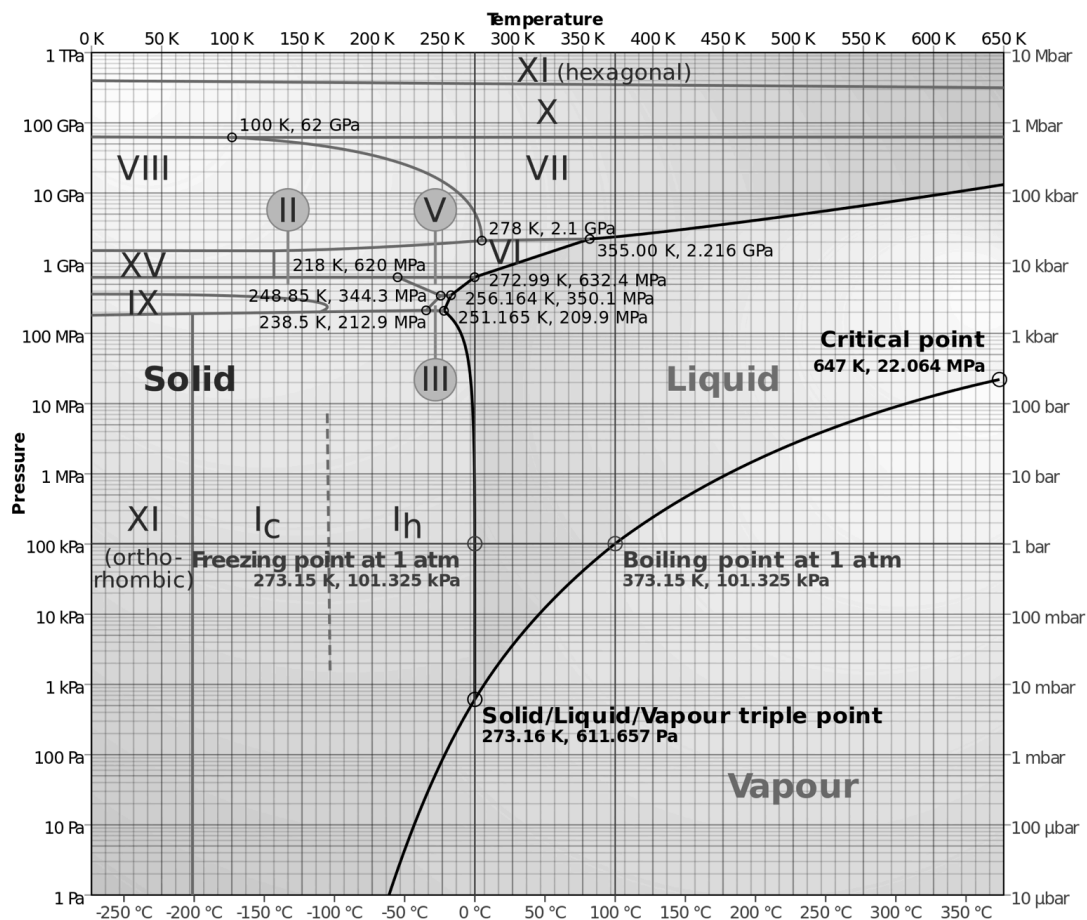
Allotropes: carbon phase diagram



Allotropes of Carbon

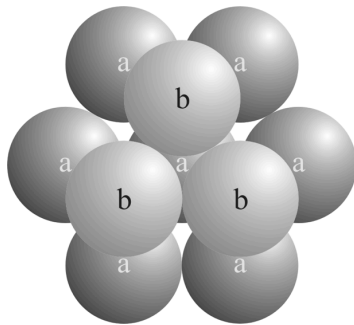


A pure substance can have a number of triple points, but only one triple point has a solid, liquid, and vapor equilibrium.



Ice structures

Hexagonal close-packing a-b-a-b..



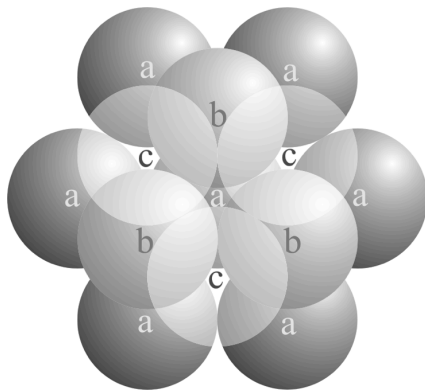
Ordinary ice Ih

Layers of atoms are stacked in the crystal, which gives snowflakes their six-fold geometry

Cubic close-packing

Cubic Ic

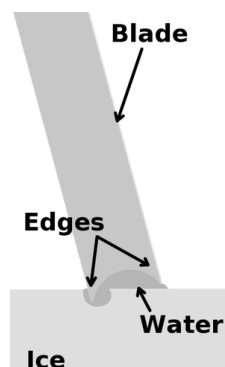
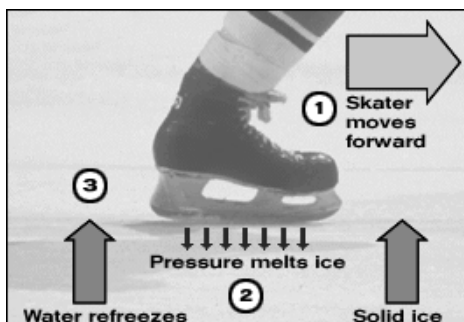
a-b-c-a-b-c..



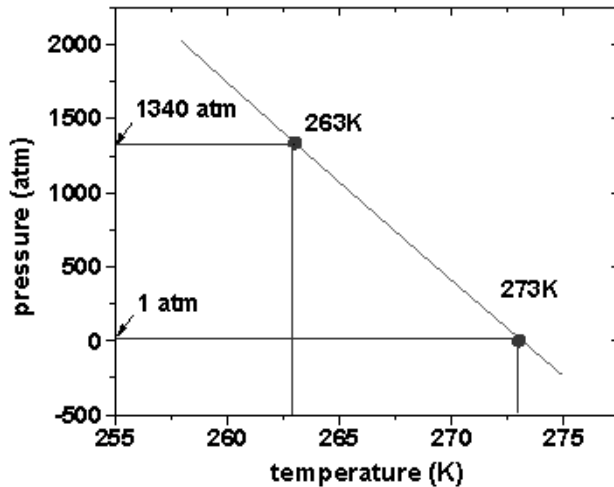
Ice XI has been found in Antarctic ice that's 100 to 10,000 years old. This ice is ferroelectric, meaning that it spontaneously become electrically polarized, just like a ferromagnet spontaneously magnetizes.

Regelation properties

- **Regelation is the phenomenon of melting under pressure and freezing again when the pressure is reduced**
- Regelation occurs only for substances, such as ice, that have the property of expanding upon freezing, for the melting points of those substances decrease with increasing external pressure.
- The melting point of ice falls by $0.0072\text{ }^{\circ}\text{C}$ for each additional atm of pressure applied. For example, a pressure of 500 atmospheres is needed for ice to melt at $-4\text{ }^{\circ}\text{C}$



Regelation properties



Is it really ice melting which allows skates to slide on ice!

Typical skater weight : 50 kg

Area of skate blade: 3mmx 200mm

$$\text{Pressure} = F/A = 816666.67 \text{ Pa} = 8.056 \text{ atm}$$

Next lecture

1. Introduce the concept of a pure substance.
2. Discuss the physics of phase change processes.
3. Illustrate the P-v, T-v and P-T property diagram, and P-v-T surfaces of pure substances.
4. **Obtaining thermodynamic properties of a pure substance from a property table.**
5. Define Ideal gas equation of state and demonstrate its use.
6. Introduce to compressibility.
7. Present the commonly used equation of states.