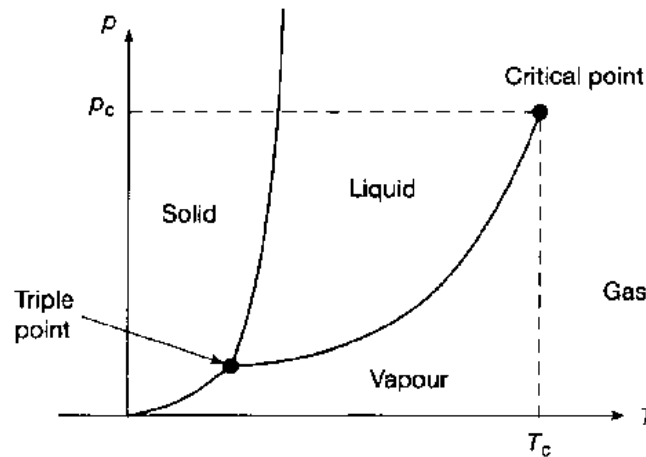


Phase transitions – brief overview

- A typical phase diagram of a p-v-T system:



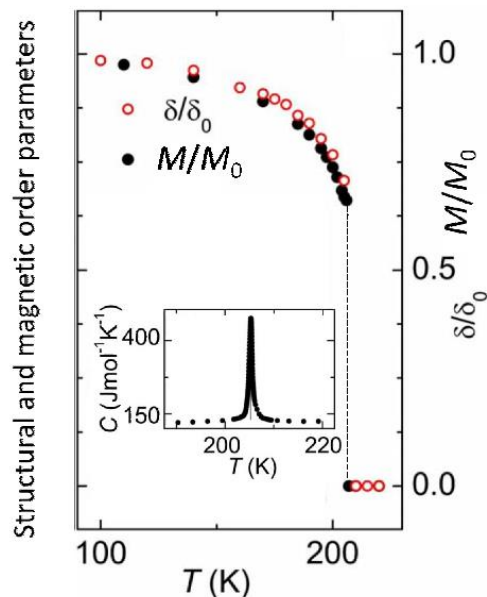
- The solid lines (called coexistence curves) = boundaries between distinct phases
- Along these curves two phases can coexist

N.B.: A phase is a region of a material throughout which all physical properties of the material (such as its density, index of refraction, magnetization, and chemical composition) are uniform.

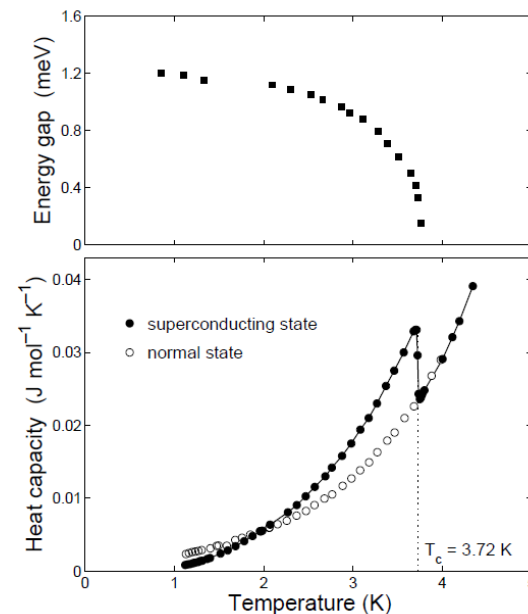
Phase transitions – brief overview

- At present we recognize two types of phase transitions
- **First-order transitions** – density or other “order parameter” changes discontinuously through the transition; they involve a latent heat; a peak in the heat capacity occurs
 - All phase changes (freezing, melting, boiling, condensation, etc.), changes in the crystal lattice (such as the α - β transformation of quartz or kaolin-metakaolin change in ceramics), or changes in the magnetization of magnets
 - Used in civil engineering – **phase-change materials** (high latent heat, able to store/release large amounts of energy)
- **Second-order transitions** – density (order parameter) stays constant, there is a discontinuity in the heat capacity – usually do not occur in civil engineering applications
 - Conductor-superconductor change, fluid-superfluid change, ferromagnet-paramagnet change

1st order magnetic/structural transition
in a superconductor:

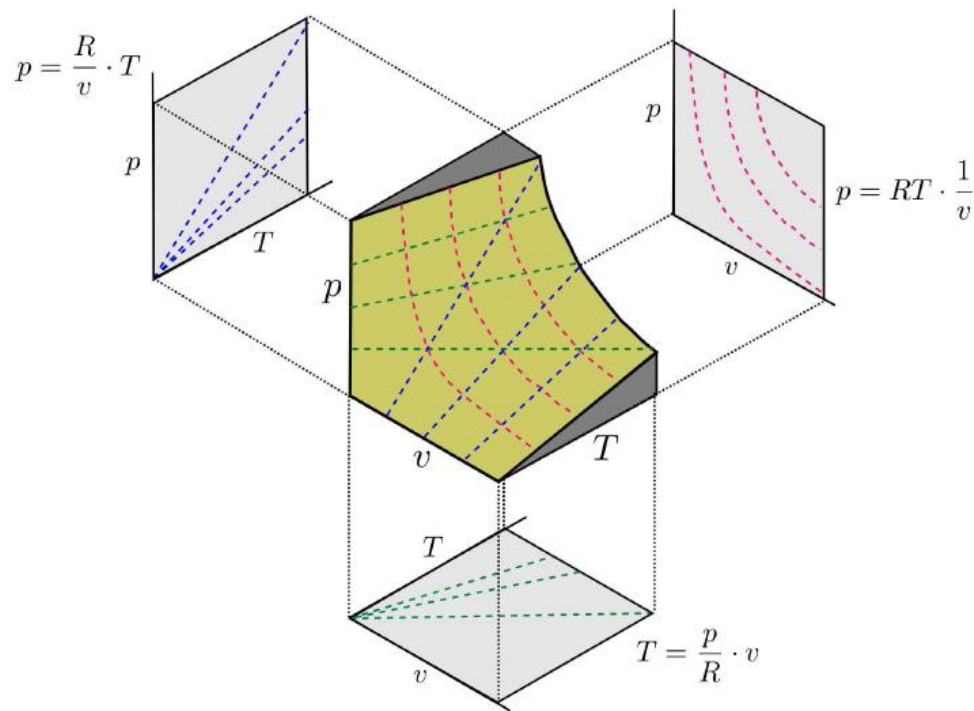


2nd order superconducting transition in tin:



Phase transitions – brief overview

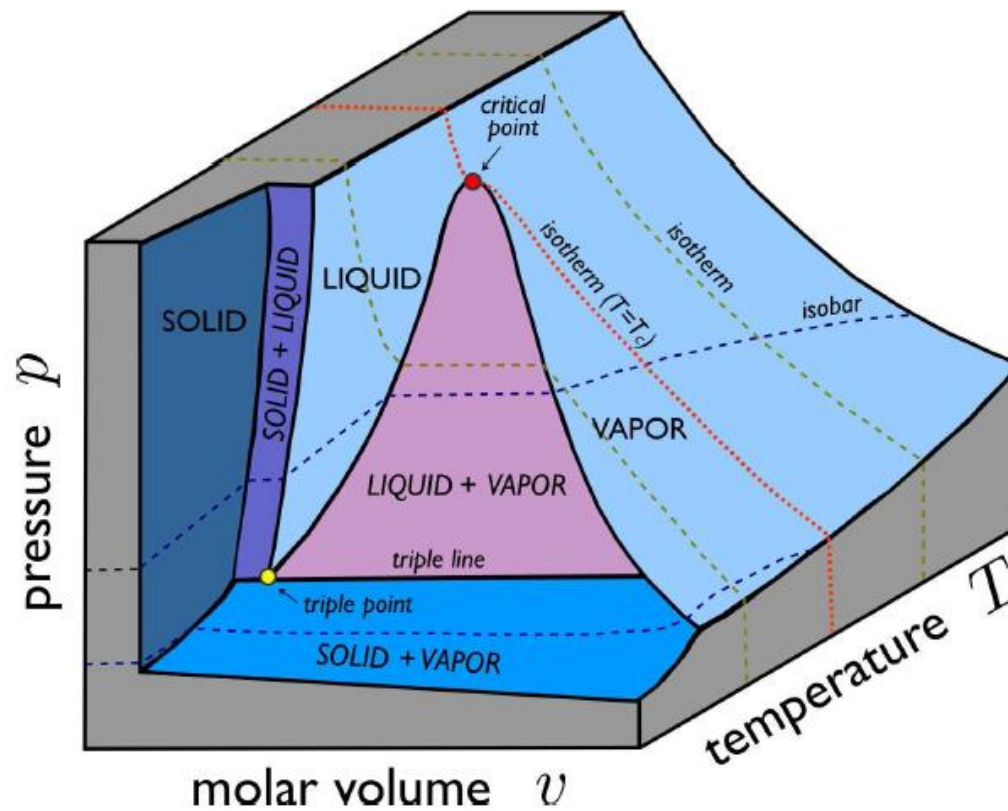
- Equation of state for the **ideal gas**: $p v = R T$
 - p = pressure, v = molar volume, T = temperature (in Kelvins), $R = 8.314$ (gas constant)
- p - v - T diagram/surface + its projections onto p - T , p - v , and T - v planes:



- p - v - T surfaces for real materials are more complex – the presence of phase changes

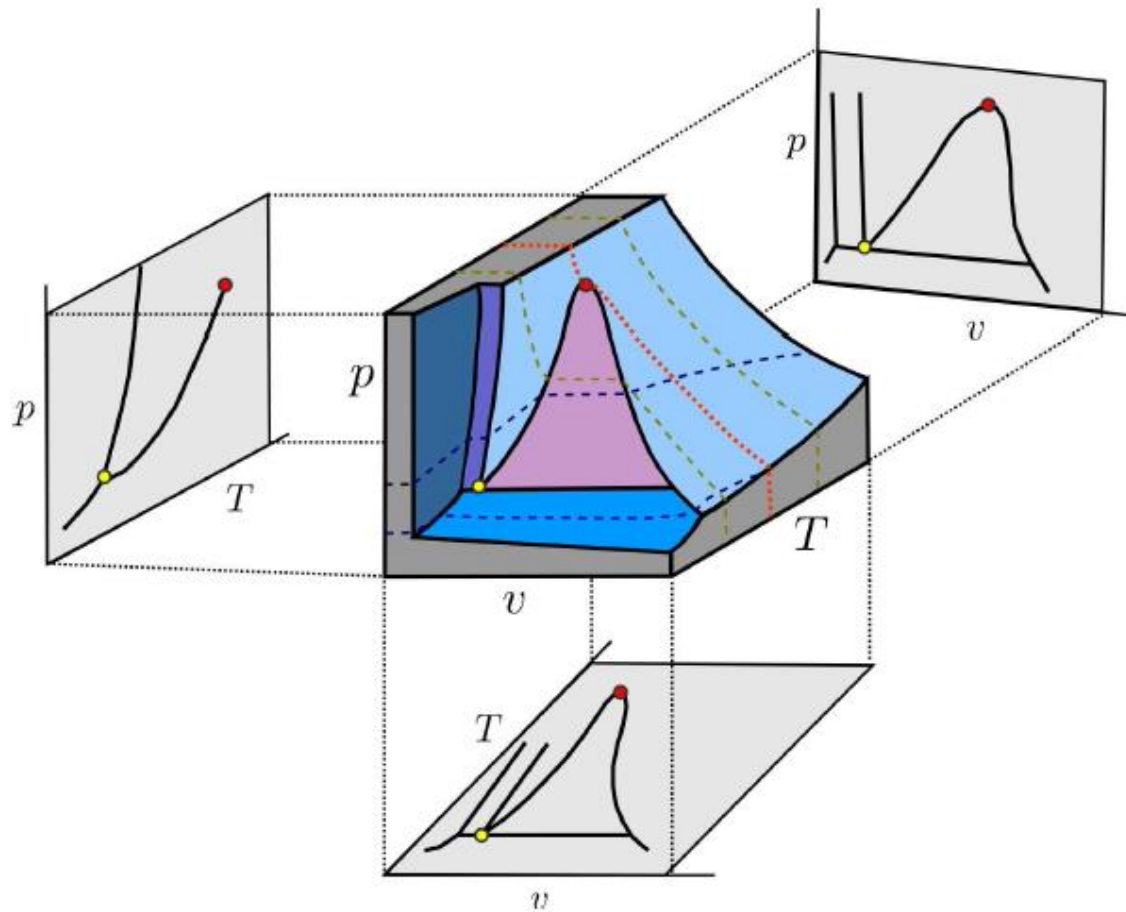
Phase transitions – brief overview

- p-v-T surface for a real material:



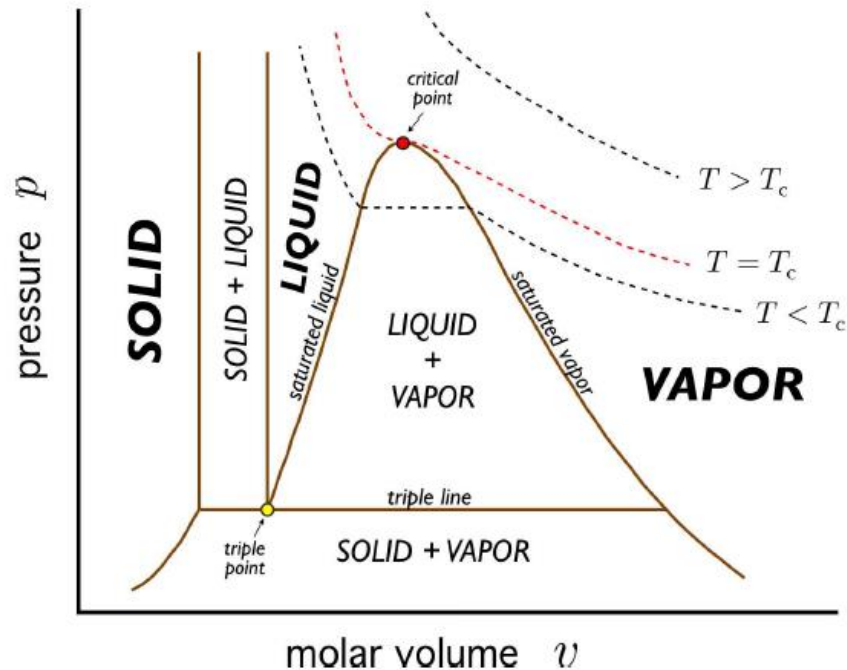
Phase transitions – brief overview

- p - v - T surface for a real material + its projections:



Phase transitions – brief overview

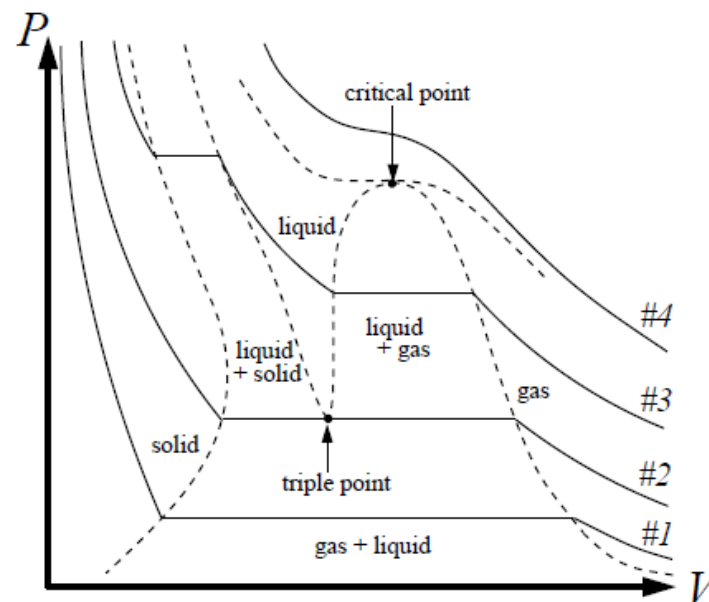
- Projection of the p-v-T surface onto the p-v plane:



- High T isotherms – as for the ideal gas
- Low T isotherms (below a certain critical temperature T_c) – isotherms are discontinuous
 - Exactly at T_c : the isotherm is horizontal at a critical molar volume v_c so that the isothermal compressibility, $\kappa = - (1/v) (\partial v / \partial p)$, diverges (also heat capacity and other quantities)
 - Below T_c : the isotherms have a flat portion = two-phase region where liquid and vapor **coexist**

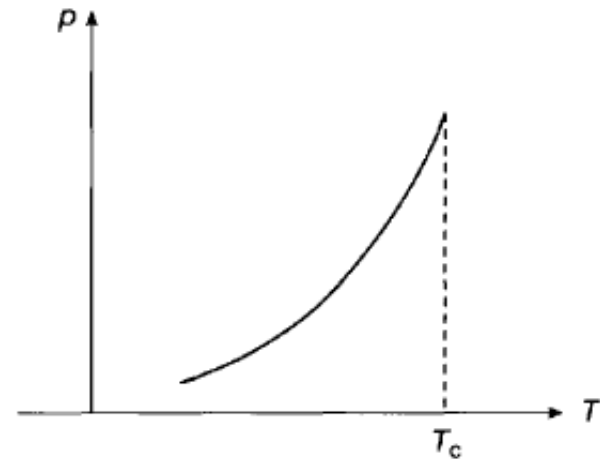
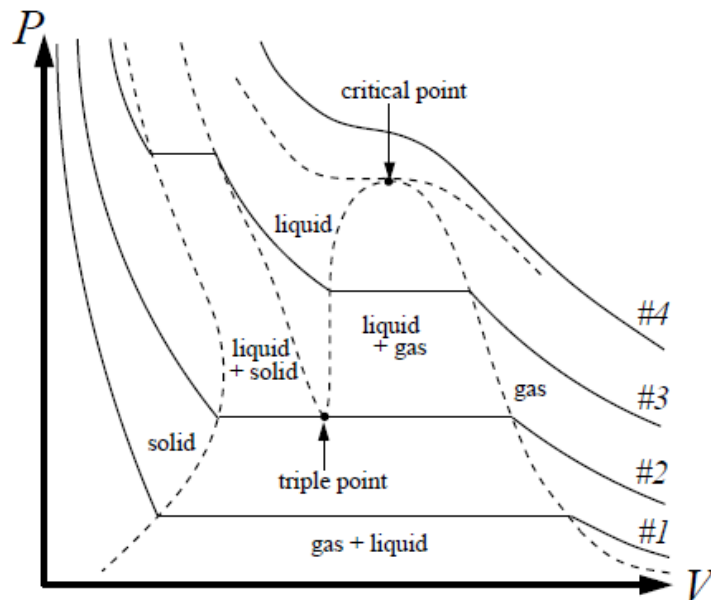
Phase transitions – brief overview

- Along isotherm #1: The system starts in the gas state, it becomes a mixture of gas and solid, and then crosses into the solid state (gas-solid phase transition)
- Along isotherm #2 (at **triple point**): The system starts in the gas state, it becomes a mixture of gas, liquid, and solid, and then crosses into the solid state
- Along isotherm #3: The system starts in the gas state and undergoes a phase transition into the liquid state, and then another phase transition into the solid state
- Along isotherm #4: The system starts in the gas state and then crosses continuously (without a phase transition) into a liquid state
 - The point at which this first becomes possible is called the **critical point**



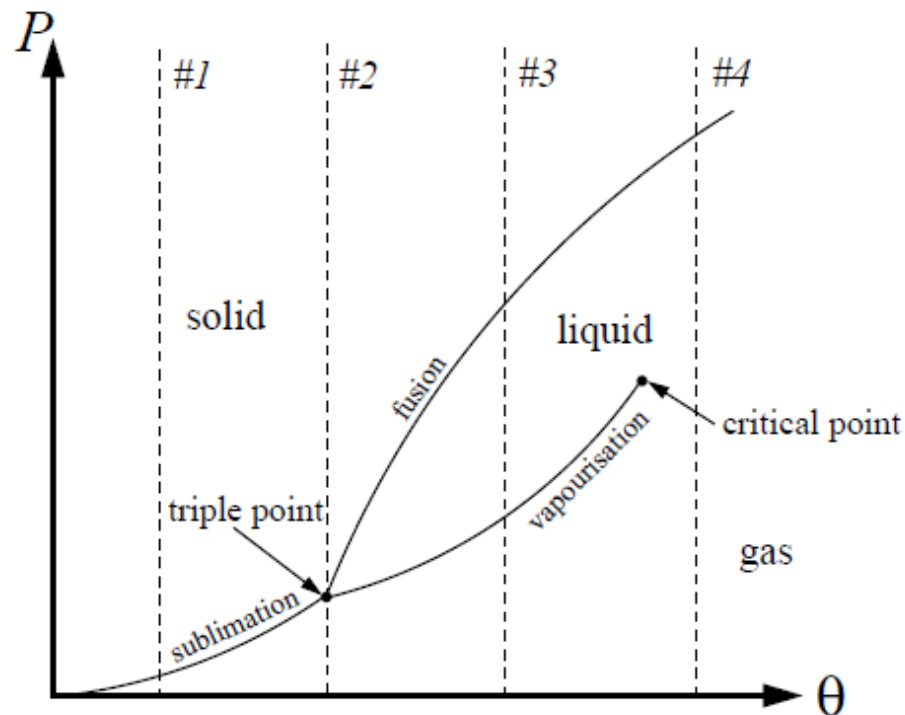
Phase transitions – brief overview

- Thus, the pressure p at which liquid and vapor coexist is a function of T
 - If T of a liquid is raised while keeping p above the liquid constant, it will no longer be in equilibrium and will evaporate
 - If we want to keep it in equilibrium, we must increase p
- Equilibrium pressure is therefore an increasing function of $T \rightarrow$ liquid-vapor coexistence line
 - Above this line, only liquid exists in equilibrium
 - Below it, only vapor exists in equilibrium
 - The coexistence curve ends at a maximum temperature T_c called the critical temperature



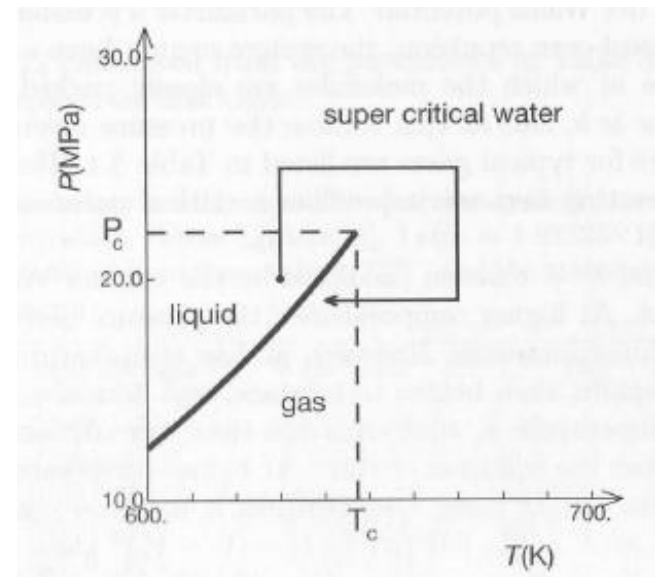
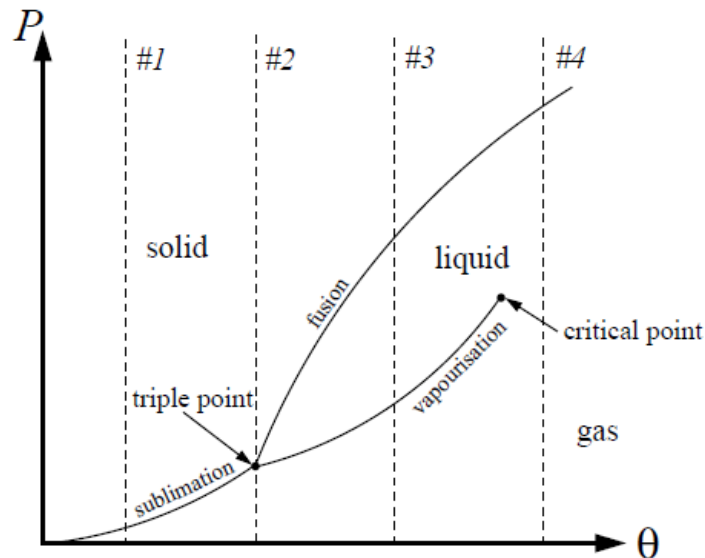
Phase transitions – brief overview

- For $T > T_c$ the gas cannot be condensed into liquid irrespective of how high the pressure is
 - This is not a problem for water for which $T_c = 647 \text{ K} = 374 \text{ C}$
 - But it is a problem for the liquefaction of air, for instance: $T_c (\text{O}_2) = 154 \text{ K} = -119 \text{ C}$ and $T_c (\text{N}_2) = 126 \text{ K} = -147 \text{ C}$
 - The problem is even greater for helium: $T_c (^4\text{He}) = 5.2 \text{ K}$ and $T_c (^3\text{He}) = 3.3$
 - So, to liquefy these gases, one needs to attain very low temperatures



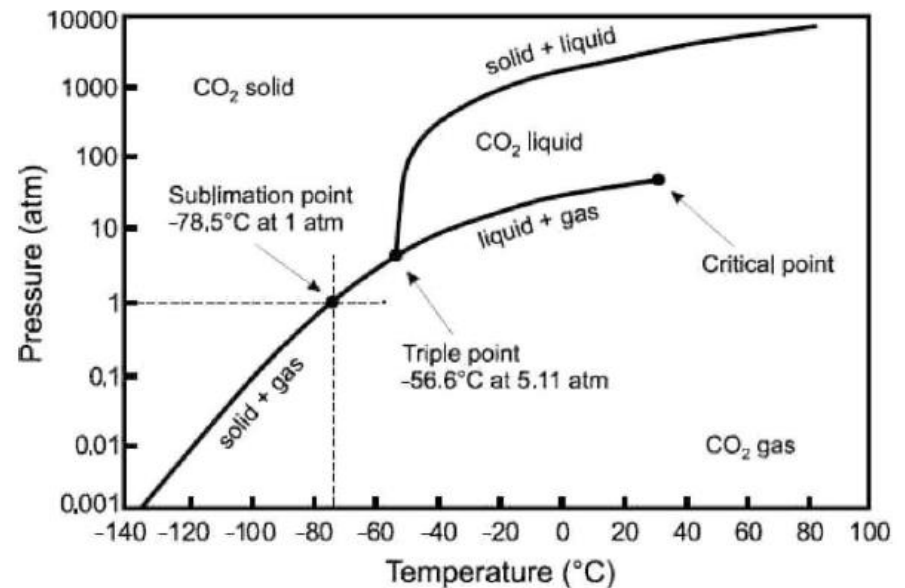
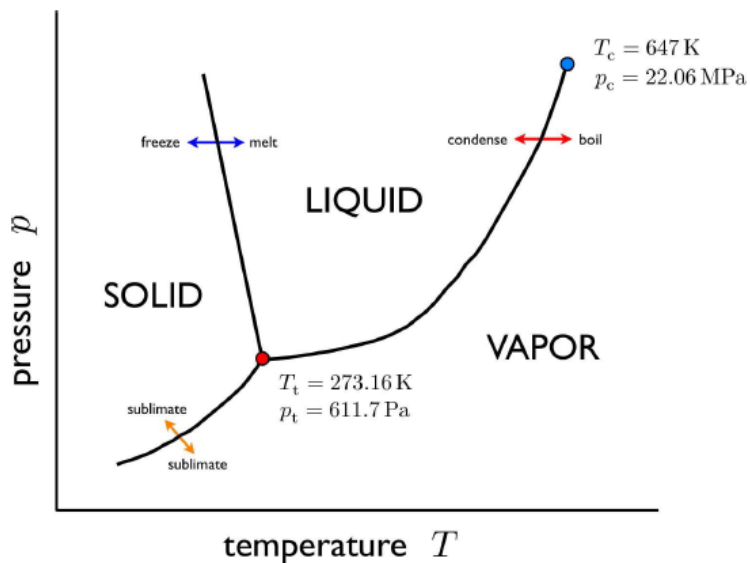
Phase transitions – brief overview

- Sublimation curve: solid and gas states are in equilibrium
- Fusion curve: solid and liquid states are in equilibrium
- Vaporization curve: liquid and gas states are in equilibrium
- Triple point: solid, liquid, and gas states are in equilibrium
 - The lowest p at which a liquid can exist
- Critical point: end point of the vaporization curve; continuous transition between gas and liquid possible beyond the critical point
 - For example, production of aerogels



Phase transitions – brief overview

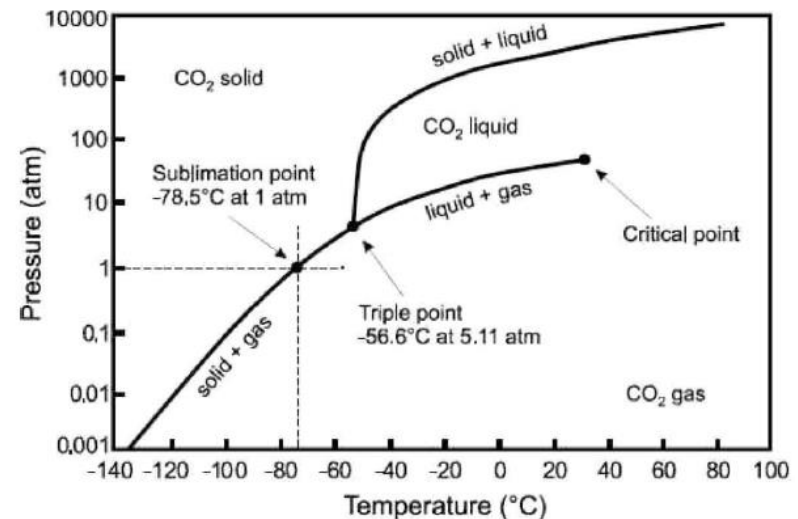
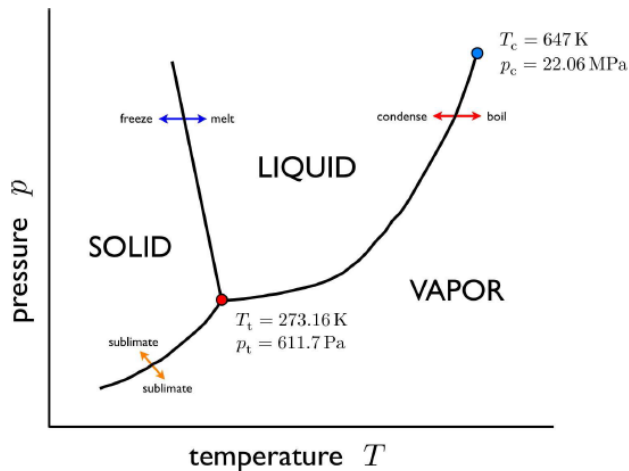
- Projection of the p-v-T surface onto the p-T plane for **water** and **CO₂**:



- Density changes discontinuously across the curves (for example, for the liquid water-ice transition the change is about 1000 times)

Phase transitions – brief overview

- For water: $T_t = 273.16 \text{ K}$ (0 C) and $p_t = 611.7 \text{ Pa}$
 - If the humidity of air is so low that the partial pressure of water is below p_t , then water vapor in the air solidifies when T drops below $T_t = 0 \text{ C}$ – hoar frost
 - T_t is above the melting temperature of water, and the melting temperature decreases with p (peculiarity of water)
- For CO_2 : $T_t = 216.8 \text{ K}$ (-56.6 C) and $p_t = 511 \text{ kPa}$
 - At atmospheric pressure 100 kPa , gaseous CO_2 does not liquefy when T is lowered but it solidifies – dry ice



Phase transitions – brief overview

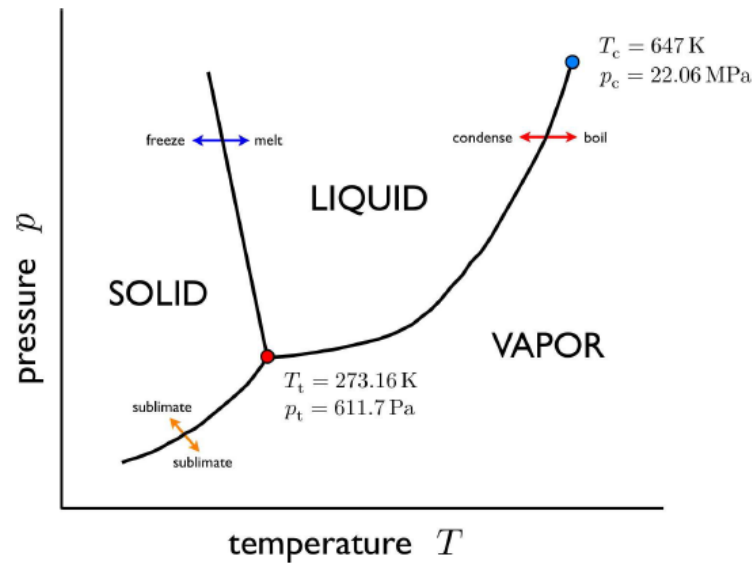
- **Gibbs phase rule:** state of a system of c components (chemical species) in f phases can be completely described by the $c - f + 2$ quantities
 - 2 is for pressure and temperature
- **Single-component system ($c = 1$):**
 - Single phase ($f = 1$) \rightarrow 2 quantities (such as p and T)
 - Coexistence of 2 phases ($f = 2$) \rightarrow 1 quantity, which corresponds to the line of coexistence
 - Coexistence of 3 phases ($f = 3$) \rightarrow 0 quantities, which corresponds to a point (triple point)
- $c - f + 2 \geq 0 \rightarrow$ maximal number of coexisting phases is $c + 2$
 - Single-component system ($c = 1$): 3 coexisting phases at most
 - Two-component system ($c = 2$): 4 coexisting phases at most
 - Etc.

Phase transitions – brief overview

- Clausius-Clapeyron equation for a coexistence curve:

$$\frac{dp}{dT} = \frac{\ell}{T \Delta v}$$

- ℓ = molar latent heat of transition (the heat ℓ must be supplied to change from one phase to another)
- $\Delta v = v_2 - v_1$ = change in the molar volumes of the two phases



Phase transitions – brief overview

- **Example 1:** liquid-vapor coexistence curve
- $v_{\text{vapor}} \gg v_{\text{liquid}}$ so that $\Delta v \approx v_{\text{vapor}} \approx RT/p$ (if the vapor behaves as the ideal gas)

$$\frac{dp}{dT} = \frac{\ell}{T \Delta v} \quad \text{reads} \quad \frac{dp}{p} = \frac{\ell}{R} \frac{dT}{T^2} \quad \text{so that} \quad p(T) = p_0 e^{\frac{\ell}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

- **Example 2:** liquid-solid coexistence curve for water
- For normal conditions ($T = 273.1 \text{ K}$ and $p = 100 \text{ kPa}$): $\ell = 333 \text{ kJ/kg}$, $v_{\text{liquid}} = 0.001 \text{ m}^3/\text{kg}$, $v_{\text{ice}} = 0.0011 \text{ m}^3/\text{kg}$ (ice is less dense than liquid water)
- Thus,

$$\frac{dp}{dT} = \frac{\ell}{T \Delta v} = \frac{333\,000}{273.1 \times (-0.0001)} = -12.2 \frac{\text{kPa}}{\text{K}}$$

- The melting curve has a **negative slope**
- For most materials the slope is positive