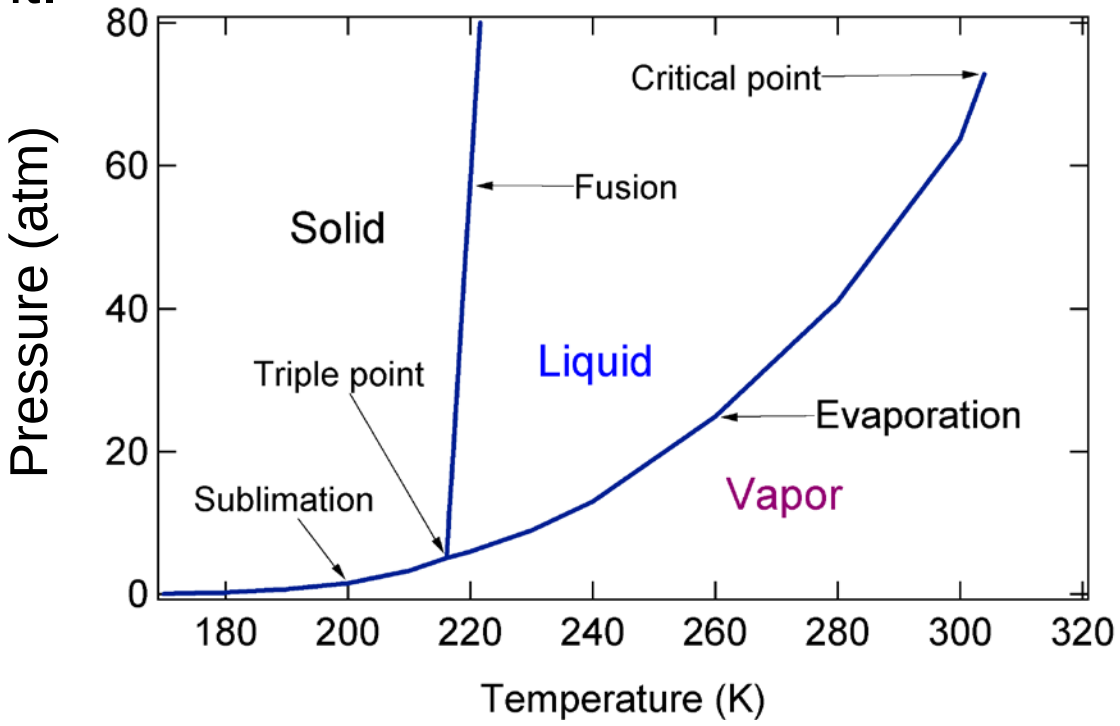
Definition of a phase diagram

A phase diagram is a representation of the states of matter, solid, liquid, or gas as a function of temperature and pressure. In the Figure shown below the regions of space indicate the three phases of carbon dioxide. The curved lines indicate the coexistence curves. Note there is a unique triple point.



Degrees of freedom

Within any one of the single-phase regions both temperature and pressure must be specified. Because two thermodynamic variables can be changed independently we say that the system has two degrees of freedom. Along any of the coexistence curves the pressure and temperature are coupled, i.e. any change in the temperature implies a change in pressure to remain on the line. Thus, along the curves there is only one degree of freedom. The triple point is a unique point in phase space and there is only one set of values of pressure and temperature consistent with the triple point. Thus, we say that at the triple point the system has zero degrees of freedom. If we follow the liquid-vapor coexistence curve towards higher temperature we find that it ends at the critical point. Above the critical point there is no distinction between liquid and vapor and there is a single fluid phase.

The phase rule

In the general case where we have more than one component (C), and the possibility for multiple phases (P) to coexist, Gibb's formulated the phase rule. The number of degrees of freedom, F is given by:

$$F = C - P + 2$$

For a single component (such as the CO_2 phase diagram above) the phase rule is:

$$F = 3 - P$$

If the system is in a single phase region (e.g. liquid, vapor etc.) there are two degrees of freedom. This is because temperature and pressure can be independently varied. However, at a coexistnce boundary (P = 2) then F = 1. If we vary T then the pressure must vary in a dependent way that we will show in this lecture. The triplet point has F = 0 since three phases coexist at that point.