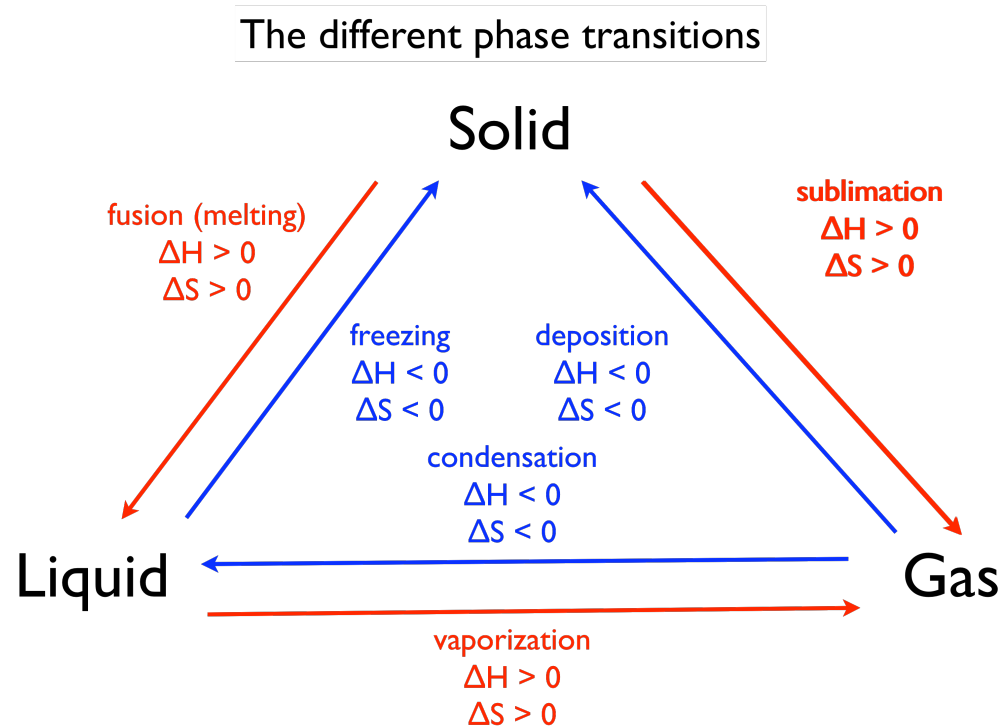# Lecture Notes 2: Physical Equilibria – Phase Diagrams

There are number of graphical means to help to understand the relationships between the different phases of a particular substance.   The first thing we need to do when looking at the transitions different phases is to establish some definitions.

There are three particular phases between which we will be examining discrete phase changes. These are solids, liquids, and gases. Each transition has a particular name. We can view them graphically below along with sign for the changes in enthalpy and entropy associated with each.

The different phase transitions

Solid

fusion (melting)
$\Delta H > 0$
$\Delta S > 0$

sublimation
$\Delta H > 0$
$\Delta S > 0$

freezing
$\Delta H < 0$
$\Delta S < 0$

deposition
$\Delta H < 0$
$\Delta S < 0$

condensation
$\Delta H < 0$
$\Delta S < 0$

Liquid

Gas

vaporization
$\Delta H > 0$
$\Delta S > 0$

For example, the transition form liquid to gas is called vaporization.   Vaporization is endothermic (uphill in energy), and this transition leads to an increase in entropy.   The reverse transition of a gas going to a liquid is condensation. Since condensation is simply the reverse of vaporization, the changes in enthalpy and entropy will be exactly the same, but opposite in sign. So $\Delta H_{condensation} = -\Delta H_{vaporization}$.   Typically, you will only find tabulated values for the endothermic transitions. It would be redundant to list values for the exothermic transitions.

Let's take a deeper look at the thermodynamics. In particular, we can examine the relationship between the enthalpy and the temperature during phase transitions.

Remember, heat can be tricky. When there is no chemistry or phase transitions, then energy flowing into a system in the form of heat will lead to a temperature change. However, when there is chemistry or a phase transition, then energy will flow in and the temperature can stay constant. Why doesn't the temperature go up? The energy coming in results in higher potential energy not higher kinetic energy. What is the higher potential energy? Breaking up the IMF between the molecules.

This can be easily seen in a heating curve that plots the temperature of a system as a function of the heat flow into the system. Initially the system is a solid, then it has a melting transition, then it is a liquid, then has a vaporization transition, and then it is a gas.
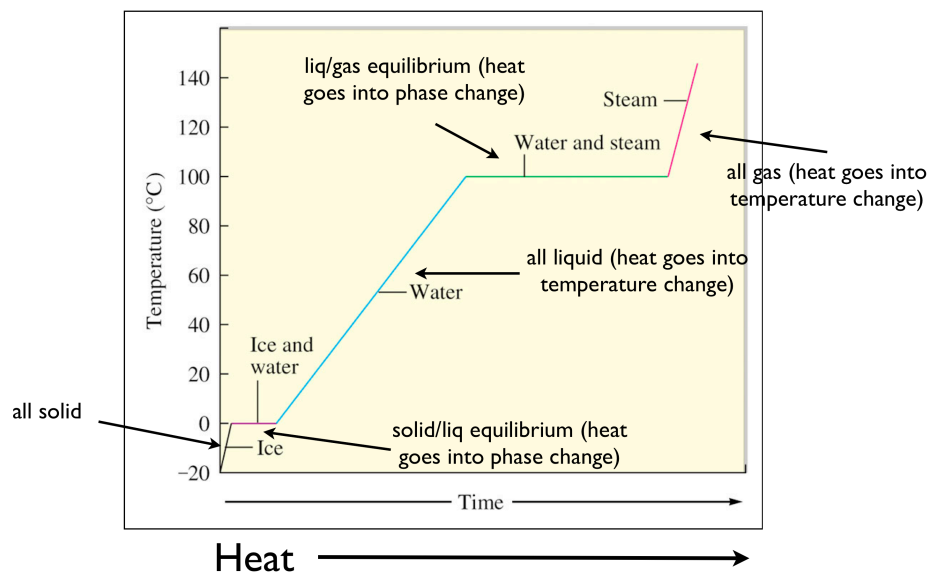
This can be seen in the diagram on the left that shows the heating curve for water. Initially, the system is solid water. As the heat flows in, the temperature of the ice increases.

The slope of this line is the heat capacity of solid water. Since this is at constant pressure $q = \Delta H = mC\Delta T$. For those who have forgotten, q is the heat, m is the mass, C is the specific heat capacity, and ΔT the change in the temperature. As this graph is a plot of T vs q, the slope is actually 1/mC.

Then the solid melts. During this time the temperature is constant. The length of the line is the amount of heat required to melt the solid. The is ΔH_{fusion}. ΔH_{fus} usually has units of kJ mol^{-1}, thus the actual length of line will be n (ΔH_{fus}) since you'll need to multiply by the number of moles of solid to get the total heat of the phase transition. Then the temperature increases. The slope of this line is again related to the heat capacity. However, this time it is the heat capacity of the liquid. The temperature is again constant during the vaporization transition. Then we see an increase in temperature related to the heat capacity of the gas.

The diagram you mostly find associated with different phases of a substance is the so-called "phase diagram". This diagram shows the regions of stability of different phases as a function of temperature and pressure. The interfaces between these regions will be the phase transition lines.

The phase diagram for CO_2 is shown below.
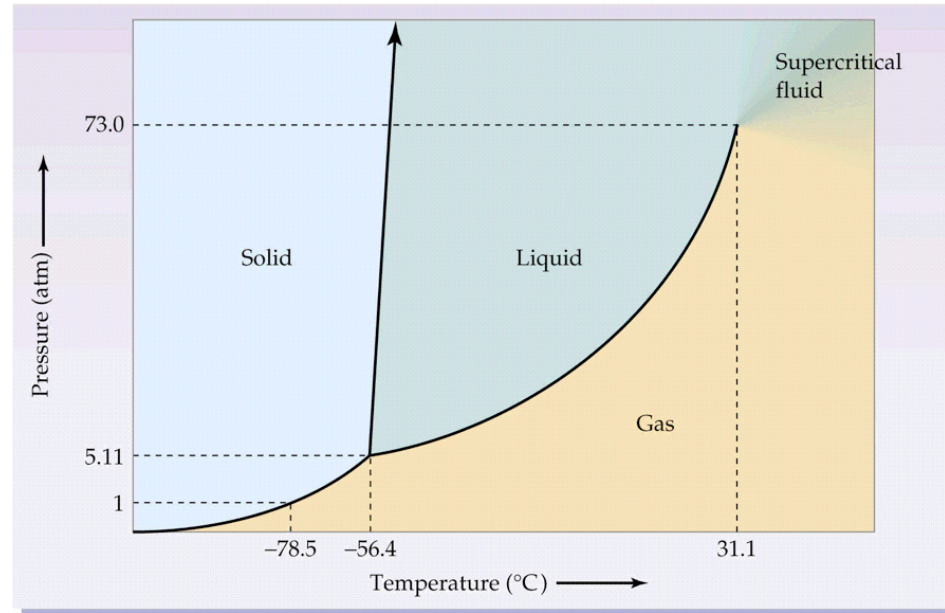
Things to notice on the diagram.

1. Given a pressure and a temperature you can find the stable phase (gas, solid, or liquid)

2. As pressure and temperature are varied CO2 behaves as expected:
-- As temperature increase you go from solid to liquid to vapor
-- As pressure increases you go from gas to solid or gas to liquid or liquid to solid

The key to a phase diagram is the phase transition lines. For example, in the lower left portion of the diagram is the sublimation line that divides the solid and the gas. At the interface between the solid and the liquid is the melting line. When interpreting a phase diagram it is critical to note that the pressure that is important for the gas is the partial pressure of the substance you are looking at. Thus, it is best to think about the pressure in this graph as the pressure of CO_2. This is very important as it means that the sublimation line and the vaporization line actually are the vapor pressure of the solid and the liquid. This is the temperature dependence that we determined with the Clausius-Clapeyron equation.

There are two other very special points on most diagrams.

The first is the triple point. This is the temperature and pressure at which three phases are in equilibrium. Typically, when we are talking about a triple point it is the solid, liquid, gas triple point. For CO_2 this is at a pressure of 5.11 atm and -56.4 °C. Many substances have more than one solid phase, and therefore they can have more than one triple point.

The other important point is the critical point. If you follow the vaporization curve up to high temperature and pressure you notice it simply stops. This is not because the person who made the diagram was lazy. It is because this is the critical point for the substance. At temperatures and pressures greater than this point, the definition of a liquid and a gas disappear and the substance exists as a super-critical fluid (SCF). What is a super-critical fluid? It is a fluid like a liquid and a gas (it takes the shape of its container), but it has a density that can vary between the two extremes of the liquid and the gas. This makes SCF extremely interesting. Typically, the molecules are either very close together or very far apart. In a SCF they can essentially be any where in between.

What happens when you go from a gas to a SCF? Essentially nothing. That is, the boundary between the liquid and the SCF and the gas and the SCF is and imaginary line defined by the critical point. This is not a phase transtion. I repeat. **Going from a gas to a SCF or a liquid to an SCF is not a phase transition.** Going form a liquid to a gas there is a discrete change in enthalpy, entropy, volume, density…..This is a phase transition. When you "cross the line" form a gas to an SCF there are not discrete changes. It is a continuous change. Thus if the diagram shows this boundary, it is usually with dotted lines to note it is different.

Note: it is fairly easy to make CO_2 a SCF. As a result, it is has wide industrial use as an SCF solvent.

Are all phase diagrams the same? No.
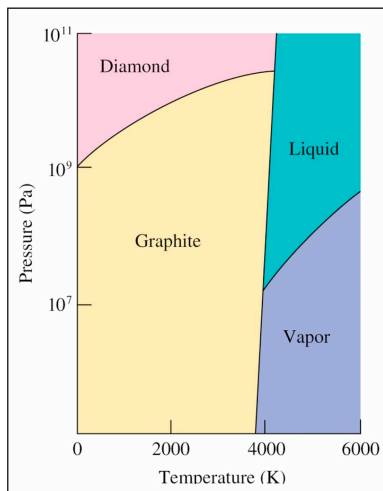
What can be different?
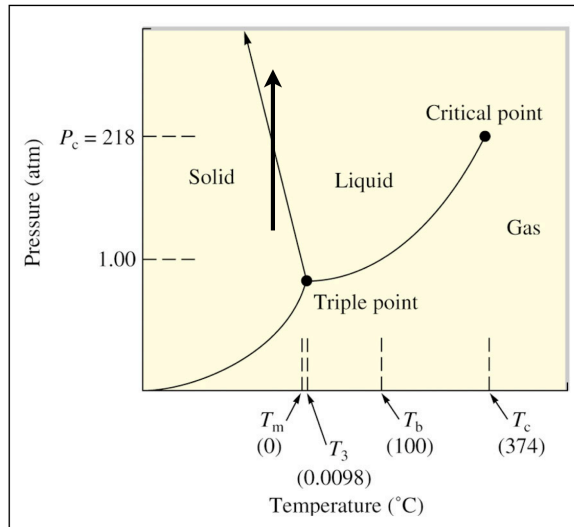
The first example is the most rare, and yet one of the most important. Water.

What is different for water? Water has the very odd property that its solid phase is less dense than its liquid phase. Ice floats. This is very very strange. It should really freak everyone out, but we are so used to the idea that it seems quite normal. It is not.

This has a consequence for the phase diagram of water.

The slope of the melting line for water is the opposite of everything else. When you increase the pressure, the melting point of water decreases rather than increases. However, increasing the pressure still moves you to the more dense phase. In this case it is liquid that is most dense.

What else can be different? Most substances have a number of different solid phases. These phases all have distinct packings of the molecules, known as crystal structures. For example, the phase diagram for carbon is at the left. Carbon has two crystal structures. The phase diagram depicts two regions of solid carbon: one in which graphite is the most stable form and another where diamond is thermodynamically stable.

Note: at room temperarure and pressure, diamonds are not stable (thankfully their transformation to graphite is very very slow). Note also that there are two triple points: one graphite, liquid, gas and one graphite, diamond, liquid.

What else can we determine from a phase diagram?

Since the vaporization line gives the vapor pressure of liquid, we can easily read off the normal boiling point. This is the temperature at which the vapor pressure of the liquid is 1 atm. We can also find the normal melting temperature, which is defined as the temperature at which the substance melts at 1 atm.

A final note on thermodynamics and phase transitions:

We can make connections between ΔH and ΔS and ΔG for different transitions.

For a phase transition, the two phases are in equilibrium. This means something from the thermodynamics standpoint. At equilibrium, the two phases will have the same free energy.

Thus at this point, $\Delta G = 0$

But we also know that $\Delta G = \Delta H - T\Delta S$

This means that at the phase transition temperature $\Delta H = T\Delta S$.

We can now relate these three. If we know the transition temperature and the enthalpy change for the transition we can find the entropy change. Alternatively if we know the enthalpy change and the entropy change we can find the transition temperature. Etc…

For example, given that the water boils at 100°C and that the enthalpy of vaporization for water is 40.7 kJ mol^{-1}, what is the entropy of vaporization for water?

$\Delta S = \Delta H/T = 40{,}700 \text{ J mol}^{-1}/373 \text{ K} = 109 \text{ J K}^{-1} \text{ mol}^{-1}$