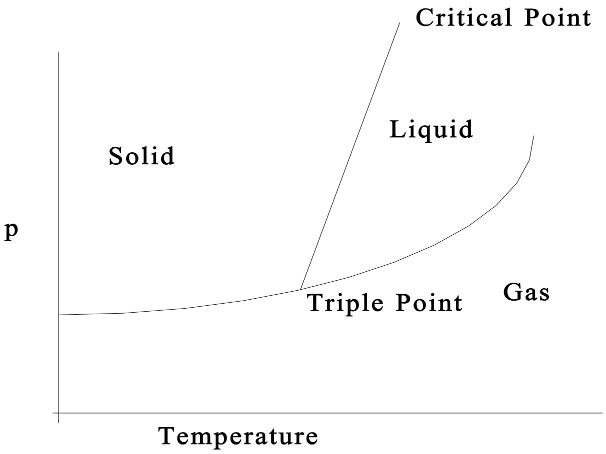
Lecture 20

At this point, we've developed the tools and basic concepts necessary to apply thermodynamics to a number of different systems, with the ultimate goal of describing chemically reacting systems. The simplest such real processes to apply our thermodynamics to **are physical transformations of one component systems**. This is because our main tool in predicting the spontaneity of these physical transformations is the chemical potential μ, and μ is most simply defined for one component systems as

$$\mu = \frac{G}{n}.$$

Before we use our thermodynamic techniques to describe these phase transitions we should precisely define some terms relating to phase transitions and reacquaint ourselves with phase diagrams.

Typical changes of phase include the familiar boiling and freezing. In addition, there are phase transitions in which the crystal structure of a solid changes. The transformation of graphite (s) → diamond (s)



is one such transformation. We use a **phase diagram** as a device to summarize our knowledge under what conditions a given phase of a sample, either a pure substance or a mixture, is stable. A typical phase diagram would look like this. Pressure is usually on the y-axis and temperature on the x-axis. The diagram consists of a series of lines demarking regions, each region corresponding to a different phase. In this diagram the region corresponding to the lowest pressures at high temperature is the vapor phase (insert vapor). The other high temperature phase is the liquid phase (insert liquid), and the final phase is the solid phase (insert solid).

The lines separating these regions are called **phase boundaries**. In addition to separating phases, these **phase boundaries show the pressures and temperatures at which two phases coexist at equilibrium**. For example: along the line separating the liquid and vapor phases liquid and vapor are in equilibrium. This is particularly important because **in order to apply thermodynamics to phase transitions we must have equilibrium conditions**. Remember that we said at the beginning of our studies that thermodynamics can tell us what transitions are possible, as long as they are from one system in equilibrium to another system in equilibrium. Note that at a given pressure there is only one temperature at which the liquid and the vapor will coexist at equilibrium. If we place a liquid in a closed evacuated vessel at a given temperature, the liquid will begin to evaporate, and will continue to do so until equilibrium is achieved. This results in an equilibrium pressure called the **vapor pressure** of the liquid. Thus the liquid-vapor coexistence curve can also be viewed as a curve of vapor pressure versus temperature.

In open vessels the behavior is somewhat different. Vaporization occurs from the surface of the liquid at most temperatures. However, there is a temperature at which the vapor pressure of the liquid is equal to the external pressure. At this temperature free vaporization can occur throughout the liquid. This temperature is called the **boiling temperature**. A consequence of this definition of the boiling temperature is that the boiling temperature is dependent on the external pressure. There are two special cases of the boiling temperature at specific pressures. One of these is the **normal boiling point** - the boiling point of a pure substance at one atmosphere. The second of these is based on the new standard of pressure, the bar. It is called **standard boiling point** and is defined as the boiling temperature of a pure substance at one bar. Since 1 bar is slightly less than 1 atm, the standard boiling point will be slightly less than the normal boiling point. For example: the normal boiling point of $H_2O(l)$ = 100°C, while the standard boiling point = 99.6°C.

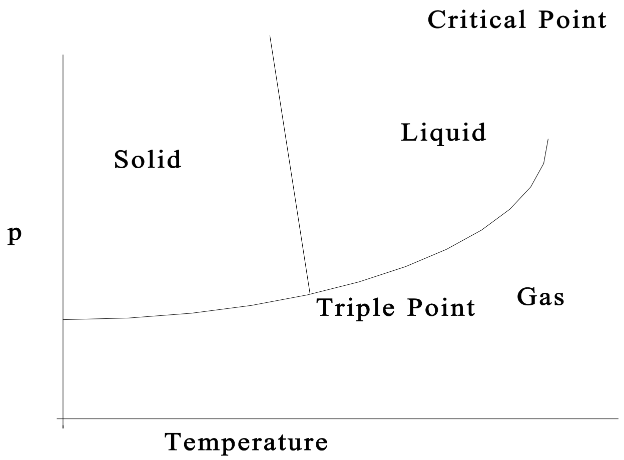
The line separating the liquid and solid phases represents the line of coexistence between liquids and solids, the pressures and temperatures at which the two phases are in equilibrium. Again, as was the case for liquids we see that at any given pressure there is only one temperature at which the solid and liquid are at equilibrium. This temperature is the **melting temperature,** which is of course the same as the **freezing temperature** at the same pressure, since the two processes merely represent the same phase transition in different directions. The **normal melting temperature** is the melting temperature of a pure substance at one atmosphere pressure. The **standard melting temperature** is the melting temperature of a pure substance at 1 bar pressure.

The line between solid and vapor denotes the pairs of pressures and temperatures at which these two phases are in equilibrium. A phase transition at these temperatures goes directly from solid to vapor or vice versa. Such a solid-vapor phase transition is called **sublimation**. Solid CO_2 is one substance that sublimates at room temperature and atmospheric pressure. It is the absence of a liquid phase in the vaporization of solid CO_2 at atmospheric pressure that has earned it the name dry ice. However, any substance can sublime under the correct conditions. For example, water ice sublimes under the conditions present in most freezers. (This can be demonstrated by freezing water in a Dixie Cup and leaving it in a freezer for a month or so.)

There is one point on the phase diagram where all three phases coexist at equilibrium. This point is called the **triple point** (write on diagram) of a substance. Note that unlike the equilibrium between two phases, in which there is a line along which the two phases are in equilibrium, there is only one point in which solid, liquid, and vapor are simultaneously in equilibrium. The fact that there is only one triple point for a given set of three phases is a consequence of the Gibbs phase rule, which we will discuss later. The triple point of water is at a temperature of 273.16 K and a pressure of 6.11 mbar. This point is the lowest pressure at which a liquid phase can exist, and also the lowest temperature at which the liquid can exist. If the pressure or temperature is at all different from these values then only two of the phases will be in equilibrium.

Notice that when I drew the liquid-vapor phase boundary, it does not extend to all temperatures and pressures. That is because at certain pressures and temperatures there is no phase boundary between the vapor and liquid. The temperature at which this occurs is our old friend the critical point. The temperature at which the curve is truncated is the critical temperature T_c.

There is one final point I'd like to make about these phase diagrams. Notice that the slope of the liquid-solid curve is positive, that is, as pressure increases, the melting point increases. This makes common sense. In effect the pressure tends to hold the solid together, while the temperature is the dispersing influence. However, for one important substance, H_2O, the phase diagram looks like this, with a negative slope for the liquid - solid coexistence curve. This is because of water's peculiar characteristic of occupying a larger volume in the solid phase (ice), than in the liquid phase. We will show later why this leads to the negative slope, but this negative slope is one of the peculiar characteristics of water that makes it so important to our form of life.



Lectures 21-22

Now let's look at how thermodynamics can account for the various features of the phase diagram. Changes of phase that are not along the phase boundaries occur when a substance moves from a less stable state to a more stable state. Since at constant T and p the Gibbs Free Energy is the measure of stability, this is the same as saying that the system moves toward the minimum of the Gibbs Free Energy. Since the chemical potential for a one-component system is the same as the molar Gibbs Free Energy, this is the same as saying that **the substance will move toward the minimum in the chemical potential**. This in turn suggests that at constant T and p, if we are in a region of the phase diagram where the solid phase is stablest, that $\mu_{solid} < \mu_{liquid}, \mu_{gas}$. Similarly we can argue that in the region where the liquid phase is stablest that its chemical potential is lowest, while in the region where the gas phase is stablest that its chemical potential is lowest.

For a substance **along a phase boundary the two phases exist in equilibrium**. Therefore **the difference in chemical potentials of the two phases is zero**. To show this, consider a liquid and a solid along a phase boundary. Let the chemical potential of the liquid = μ_l and the chemical potential for the solid = μ_S. If we transfer dn moles from the solid to the liquid, then $dG_l = \mu_l$ dn, $dG_S = -\mu_S$ dn and $dG_{TOT} = (\mu_l - \mu_S)$ dn. But we know that the two phases are in equilibrium along the phase boundary. We also know that $dG_{T,P} = 0$ for equilibrium. Since dn is not equal to 0, the only way that dG can equal 0 for this process is if $\mu_l = \mu_S$.

We have already pointed out that a substance will move toward the phase with the lowest chemical potential. At low temperatures, a solid will have the lowest chemical potential (HOW DO WE KNOW THIS?), but **the chemical potentials of the various phases will vary with temperature in different ways**, so it is useful to examine the way the chemical potential varies with T and p, the two variables in our phase diagram.

Let's begin by evaluating the change in μ with temperature, $(\frac{\partial \mu}{\partial T})_{p,n}$. Using our rules for the reduction of partial derivatives, we plug in the Gibbs-Duhem relation to get

$$(\frac{\partial \mu}{\partial T})_{p,n} = (\frac{-\frac{S}{n}\partial T + \frac{V}{n}\partial p}{\partial T})_{p,n} = -\frac{S}{n} = -\overline{S}$$

This shows that **as T increases, the chemical potential of a pure substance decreases with a slope equal to the molar entropy**. You can see from this that the chemical potential of a gas will decrease more quickly than that of a liquid of the same substance because the entropy of the gas is greater than that of the liquid, i.e., because S(g) > S(*l*). Q: WHICH WILL DECREASE FASTER WITH TEMPERATURE, THE CHEMICAL POTENTIAL OF A LIQUID OR A SOLID?

Our other variable in the phase diagram is p, so it is equally useful to consider the effect of changing pressure on μ. We've already stated that when pressure increases for most substances, a phase transition from solid to liquid is less likely so we suspect that the slope will be positive. This is confirmed, once again by looking at the Gibbs-Duhem relation for $(\frac{\partial \mu}{\partial p})_{T,n}$.

$$(\frac{\partial \mu}{\partial p})_{T,n} = (\frac{-\frac{S}{n}\partial T + \frac{V}{n}\partial p}{\partial p})_{T,n} = \frac{V}{n} = \overline{V}$$

For most substances, $\overline{V}(l) > \overline{V}(s)$, so increasing the pressure raises the temperature for melting. However, ice at low pressures has a higher molar volume as a solid than as a liquid, so an increase in pressure lowers the melting temperature. This is the reason the slope of the solid liquid coexistence curve for ice is negative. This results in several practical and strange qualities for ice. For example, the reason that we can skate across ice is that the pressure exerted by a narrow blade lowers the melting temperature of the ice and makes the surface slippery where the skate passes. With this last example, we have begun talking about the effect on the phase boundary of changes in temperature and pressure.

Now let’s calculate the temperatures and pressures at which two phases are in equilibrium, in other words, the **locations of our phase boundaries on a p-T graph**. Again we note that along these phase boundaries,

$$\mu_s = \mu_g \text{ or } \mu_s = \mu_l \text{ or } \mu_g = \mu_l.$$

To solve this problem, we’d have to consider the way in which the chemical potential depends on both T and P as expressed by the Gibbs-Duhem equation,

$$d\mu = -\overline{S}\,dT + \overline{V}\,dp.$$

Let's solve this problem for the equilibrium between any two arbitrary phases, and then consider each of the three most common phase transitions in turn. Let’s call our two phases α and β. Now suppose that these two phases are at equilibrium at some pressure and temperature. We know that this means that $\mu_\alpha = \mu_\beta$. Now suppose that we change the pressure and temperature in such a way that a new equilibrium is established between the phases. Since the phases are in equilibrium, the new chemical potentials must also be equal, i.e., $\mu'_\alpha = \mu'_\beta$. If we take the difference between these two equations we find that $\mu'_\alpha - \mu_\alpha = \mu'_\beta - \mu_\beta$ or $\Delta\mu_\alpha = \Delta\mu_\beta$. In other words, **if we start out with two systems in equilibrium, and change their states in such a way that the two states stay in equilibrium, the change in the chemical potentials of the two systems will be the same**. If we rewrite this for a very small change in conditions, we get

$$d\mu_\alpha = d\mu_\beta.$$

Substituting the Gibbs-Duhem relation for $d\mu$ on each side yields

$$-\overline{S}_\alpha\,dT + \overline{V}_\alpha\,dp = -\overline{S}_\beta\,dT + \overline{V}_\beta\,dp.$$

Which is easily rearranged to

$$(\overline{V}_\beta - \overline{V}_\alpha)\, dp = (\overline{S}_\beta - \overline{S}_\alpha)\, dT.$$

If we solve for dp/dT and define $\Delta\overline{V} = \overline{V}_\beta - \overline{V}_\alpha$ and $\Delta\overline{S} = \overline{S}_\beta - \overline{S}_\alpha$, then we obtain the **Clapeyron equation,**

$$\frac{dp}{dT} = \frac{\Delta\overline{S}}{\Delta\overline{V}}$$

This is an **exact equation for the slope of the phase boundary**. It is immensely useful because if we know a single pressure and temperature at which two phases are in equilibrium, and know the way that the molar entropy difference and molar volume difference change with pressure and temperature, we can calculate all the other pressures and temperatures at which the two phases are in equilibrium. Since it is an exact equation, i.e., since no approximations are used in its derivation, it can be applied to any substance. It is our **fundamental equation when we consider phase transitions**.

Let's apply the Clapeyron equation to determine the way our three most common phase boundaries, the solid-liquid boundary, the liquid-vapor boundary, and the solid - vapor boundary, depend on pressure and temperature. The simplest is the **solid - liquid boundary**, so let’s treat it first.

We begin with the Clapeyron Equation.

$$\frac{dp}{dT} = \frac{\Delta\overline{S}}{\Delta\overline{V}}$$

We know that for a phase transition, $\Delta\overline{S} = \Delta\overline{H}/T$, so for a solid to liquid transition, this becomes,

$$\frac{dp}{dT} = \frac{\Delta\overline{H}_{fus}}{T\Delta\overline{V}}$$

Note that this is not an approximation and is therefore as universal as the Clapeyron equation. For all substances, $\Delta H_{fus} > 0$, because after all, it takes heat to melt something. $\Delta \overline{V}_{fus}$ is almost always positive but small, i.e., the molar volume of the liquid is almost always slightly larger than the molar volume of the solid. Therefore dp/dT, will almost always be steep and positive for the liquid solid coexistence curve. In other words, as the temperature rises, the pressure must increase rapidly for the two phases to stay in equilibrium. This is the way the solid - liquid coexistence line appears on most phase diagrams.

The exception to this rule of course is water, and we can now see why water's solid - liquid coexistence curve has a negative slope. Like other substances, the heat of fusion of water is positive. But for water, $\overline{V}_{ice} > \overline{V}_{H2Ol}$, so $\Delta \overline{V} < 0$ and

$$\frac{dp}{dT} = \frac{\Delta \overline{H}}{T \Delta \overline{V}} < 0$$

We can obtain the p-T curve for the solid - liquid coexistence curve by integrating the differential equation. We first rearrange our equation to get

$$dp = \frac{\Delta \overline{H}_{fus}}{\Delta \overline{V}} \frac{dT}{T}$$

and integrate both sides,

$$\int_{p_1}^{p_2} dp = \int_{T_1}^{T_2} \frac{\Delta \overline{H}_{fus}}{\Delta \overline{V}} \frac{dT}{T}$$

If we specify that the temperature range is small, then we can make two simplifying assumptions, that $\Delta \overline{H}_{fus} \approx$ constant and that $\Delta \overline{V} \approx$ constant. This means we can pull these two terms out of the integral, and obtain

$$p_2 = p_1 + \frac{\Delta\overline{H}_{fus}}{\Delta\overline{V}} \ln\frac{T_2}{T_1}$$

Over a sufficiently small range of temperatures this equation is very close to linear in temperature. To show this we note that for small values of x, ln (1+x) ≅ x. Using this result we can rewrite

$$\ln\frac{T_2}{T_1} = \ln(1 + \frac{T_2 - T_1}{T_1}) \cong \frac{T_2 - T_1}{T_1} = \frac{T_2}{T_1} - 1$$

If we insert this into our equation for the liquid-solid phase boundary we get

$$p_2 = p_1 + \frac{\Delta\overline{H}_{fus}}{\Delta\overline{V}} (\frac{T_2}{T_1} - 1)$$

which is an equation for a straight line.

If the range of temperatures is large enough that the assumption that $\Delta\overline{V}$ is constant is invalid, the best practice is to use the cubic expansion coefficient α to express the temperature dependence of the volume. If the range of temperatures is too great for the assumption that $\Delta\overline{H}_{fus}$ is constant to be valid, then we use Kirchoff's Law to calculate the temperature dependence of $\Delta\overline{H}_{fus}$, where in this case $\Delta C_p = C_p(l) - C_p(s)$.

Let's turn next to the liquid - vapor boundary. We begin again with the Clapeyron Equation, $\frac{dp}{dT} = \frac{\Delta\overline{S}}{\Delta\overline{V}}$. As in our previous case, since this is a phase transition, we can write $\Delta\overline{S} = \Delta\overline{H}_{vap} / T_{vap}$, which yields

$$\frac{dp}{dT} = \frac{\Delta\overline{H}_{vap}}{T\Delta\overline{V}_{vap}}.$$

In this equation, $\Delta\overline{H}_{vap}$ will always be positive, $\Delta\overline{H}_{vap} > 0$, and the volume of the gas is always much higher than that of a liquid, which implies that ΔV_{vap} will be large and positive, $\Delta V_{vap} \gg 0$.

Therefore the slope of the liquid - vapor coexistence line will be positive and small.

In order to calculate the equation for the liquid - vapor coexistence line, let's make a couple of useful approximations. First note that $\overline{V}_l$ « $\overline{V}_g$. For example, at STP, $\overline{V}_{H_2O(l)}$ = 0.018 L, while $\overline{V}_{H_2O(g)}$ = 22.4 L. Because of this we can make the approximation that $\Delta\overline{V} = \overline{V}_g$. IS THERE A PLACE ALONG THE LIQUID-VAPOR COEXISTENCE CURVE WHERE THIS APPROXIMATION FAILS? WHY? If we make the further assumption that our vapor behaves as an ideal gas, we get $\Delta\overline{V} = \frac{RT}{p}$. Substituting this into our equation yields

$$\frac{dp}{dT} = \frac{p\Delta\overline{H}_{vap}}{RT^2}$$

or

$$\frac{dp}{p} = \frac{\Delta\overline{H}_{vap}}{RT^2}dT$$

Since integrating dp/p yields ln p, dp/p is often written as d (ln p), which means that this equation is often written in the form

$$d(\ln p) = \frac{\Delta\overline{H}_{vap}}{RT^2}dT\ .$$

This result is known as the Clausius-Clapeyron equation. Collecting terms yields

$$d(\ln p) = \frac{\Delta\overline{H}_{vap}}{R}\frac{dT}{T^2}$$

If we limit our calculation to small temperature ranges, we can make the further approximation that $\Delta\underline{H}_{vap} \approx$ constant, and integrating yields

$$\ln\frac{p_2}{p_1} = -\frac{\Delta\overline{H}_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

or

$$p_2 = p_1 e^{\frac{-\Delta\overline{H}_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

Note that this curve is only valid for $T<T_c$, since the liquid does not exist at $T>T_c$.

Notice that this derivation is limited to an ideal gas. Is there a way that we can retain the simplicity of this equation, but represent the behavior of real gases? Notice that after our approximation that $\Delta\overline{V} \approx \overline{V}_g$ our equation became

$$\frac{dp}{dT} = \frac{\Delta\overline{H}_{vap}}{T\overline{V}_g}.$$

For the ideal gas we wrote, $\overline{V}_g = \frac{RT}{p}$. This is because for an ideal gas, $1 = \frac{RT}{p\overline{V}}$. However for a real gas, $\frac{RT}{p\overline{V}} = \frac{1}{Z}$, where Z is the compressibility factor, which implies in turn that $\overline{V} = \frac{RTZ}{p}$. Substituting this into our equation yields

$$\frac{dp}{dT} = \frac{p\Delta\overline{H}}{RT^2Z}$$

or

$$\frac{dp}{p} = \frac{\Delta\overline{H}}{RT^2Z}dT.$$

Integrating over a sufficiently small temperature range (why is it necessary to specify this?) yields

$$\ln\frac{p_2}{p_1} = \frac{-\Delta\overline{H}}{RZ}\left(\frac{1}{T_2}-\frac{1}{T_1}\right).$$

Finally let’s turn to the solid-vapor boundary. Let’s do this derivation together. Again we begin with the Clapeyron Equation, $\frac{dp}{dT} = \frac{\Delta \overline{S}}{\Delta \overline{V}}$. Q: WHAT IS ANOTHER WAY TO EXPRESS $\Delta \overline{S}$ FOR SUBLIMATION? This yields $\frac{dp}{dT} = \frac{\Delta \overline{H}_{sub}}{T \Delta \overline{V}}$. Q: WHAT APPROXIMATION CAN WE MAKE ABOUT THE CHANGE IN MOLAR VOLUME? [$\Delta \underline{V} \approx \underline{V}g \approx RT/p$]. Combining these yields

$$\frac{dp}{p} = \frac{\Delta \overline{H}_{sub}}{RT^2} dT .$$

Integrating this equation and solving for p yields

$$p_2 = p_1 e^{\frac{-\Delta H_{sub}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Note that for the solid-vapor curve, both the differential and integral equations are identical with those for the liquid-gas curve. The only differences are that $\Delta \overline{H}_{sub} > \Delta \overline{H}_{vap}$ and $T_{sub} < T_{vap}$. Taken together, these tell us that the shape of the solid-vapor coexistence curve will be similar to that of the liquid-vapor curve, but with a greater slope.

Let’s summarize our results. The general equation describing phase boundaries is the Clapeyron Equation, $\frac{dp}{dT} = \frac{\Delta \overline{S}}{\Delta \overline{V}}$. A completely equivalent expression of the Clapeyron equation is $\frac{dp}{dT} = \frac{\Delta \overline{H}}{T \Delta \overline{V}}$. Both of these equations are exact equations and involve no approximations. The three equations that we obtained for the integral form of the phase boundaries are all approximate equations. The solid-liquid equation is

$$p_2 = p_1 + \frac{\Delta \overline{H}_{fus}}{\Delta \overline{V}} \left(\frac{T_2}{T_1} - 1\right)$$

The liquid-vapor equation is

$$p_2 = p_1 e^{\frac{-\Delta \overline{H}_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

The solid-vapor equation is

$$p_2 = p_1 e^{\frac{-\Delta \overline{H}_{sub}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

Once again all of these involve approximations. More accurate versions of these latter two equations, which treat gases as non-ideal are

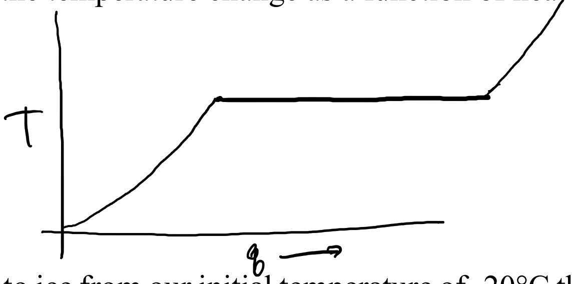
$$p_2 = p_1 e^{\frac{-\Delta \overline{H}_{vap}}{RZ}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

And

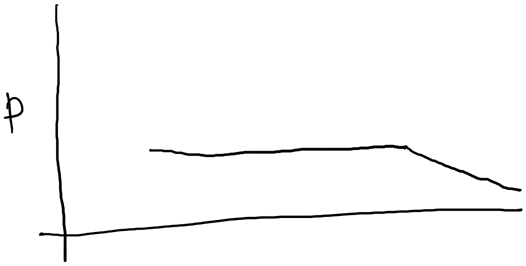
$$p_2 = p_1 e^{\frac{-\Delta \overline{H}_{sub}}{RZ}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

where Z is the compressibility factor. I expect you to be able to understand the derivations of these equations enough that you can both reproduce them and be able to identify each of the approximations involved.

Research into the microscopic mechanisms of phase transitions is an active field in physical chemistry. One reason for this is that phase transitions are intrinsically discontinuous processes. To see this let's look at the temperature change as a function of heat added to H_2O.

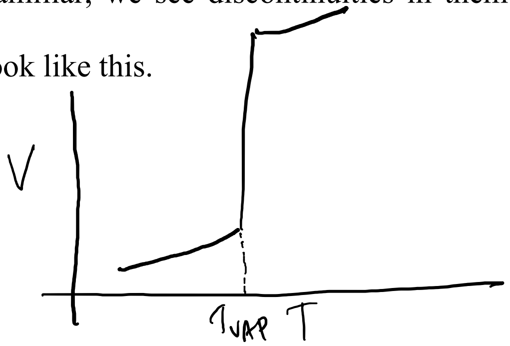


As we begin to add heat to ice from our initial temperature of -20°C the temperature increases with a slope equal to $C_p(s)$. When we reach the phase transition, the temperature stops changing until all the solid has melted and the phase transition is over. Then the temperature starts rising again with a new slope equal to the heat capacity of the liquid water. Notice that the slope of the temperature-heat curve does not change gradually, but switches abruptly from one stage to the next.



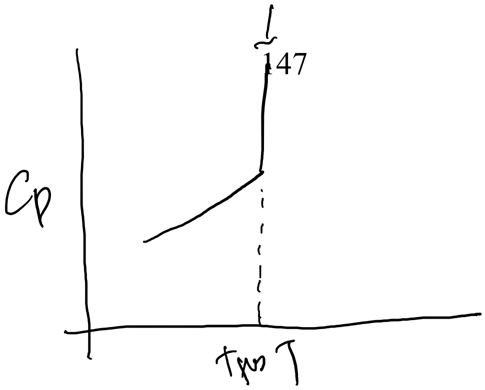
Another example is a p-V isotherm below the critical temperature. We begin at a large volume and low pressure. Now we slowly decrease the volume. As the volume decreases, the pressure increases until the phase transition occurs. At this point the volume decreases without an attendant change in pressure. When all of the vapor has been converted to liquid, the pressure increases rapidly as the volume is decreased. Notice again, that our isotherm is not a continuous curve.

If we plot thermodynamic variables like V, H, μ, S and C_p vs. T, for all the phase transitions with which we are familiar, we see discontinuities in them. For example, a V vs. T plot for vaporization would look like this.

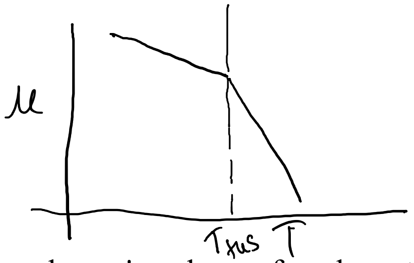


In this plot, T_{vap} is the vaporization temperature.

A plot of C_p vs T shows a different type of discontinuity, where the C_p becomes infinite at the transition temperature.

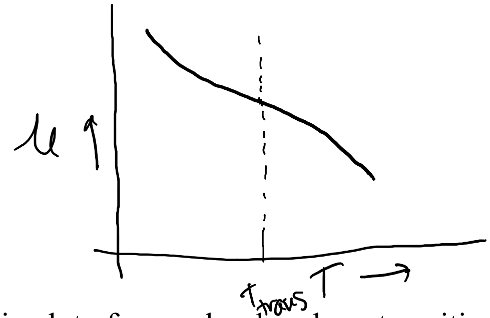


Finally, we note that the discontinuity in μ also shows a different type of behavior. In this case the discontinuity is in the slope of the μ vs T curve.

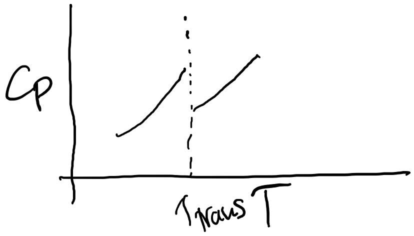


Notice that all of the graphs we've shown for phase transitions like melting, vaporization and sublimation show discontinuities in the slopes. Since slopes are first derivatives, all of these phase transitions are called first order phase transitions. All of the phase transitions with which we are most familiar are first order phase transitions.

There is also another group of phase transitions, most of which deal with phenomena of interest to physicists, like the fluid-superfluid transition of helium, or the onset of ferromagnetism, which are continuous in the first derivative of μ, but discontinuous in the second derivative. These transitions are called second-order phase transitions. A typical μ vs T curve for a second order phase transition is



A particularly characteristic plot of second order phase transitions is the plot of C_p vs T.



You can see that this curve takes on the general appearance of the letter λ (at least if you squint and use your imagination a lot). For this reason, second order phase transitions are often called lambda transitions.

The main thing that phenomenologically differentiates a first order phase transition from a second order phase transition is that during a first order phase transition there is a sudden change in the properties of the sample at the transition temperature. The sharpness of melting points of pure compounds that makes melting points so useful in identifying organic compounds is an example of the suddenness with which phase transitions take place. In contrast, second order phase transitions take place gradually, and are complete at the transition temperature.

So far no one has been able to come up with a theory of phase transitions which can explain the discontinuities, either the first or second order types.