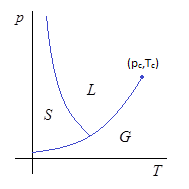
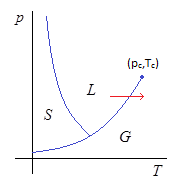
**Liquid-Gas Transition**

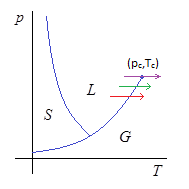
Consider the Gibbs potential G(T,p) and its differential dG = -SdT – Vdp. If we were so fortunate as to have an expression for this potential valid over all phases of a substance: solid, liquid, gas, we’d notice some things. Suppose we were to start with a substance in gas phase, at some low pressure and high temperature. Then suppose we slowly remove heat at constant pressure. This would make both the temperature and volume drop in proportion. But we would notice a time the temperature did not drop, while the volume did, even as we removed heat. The amount of heat, ΔQ, we’d remove w/o T changing would be called the latent heat, L. This generally doesn’t depend on T. And so the entropy change associated with this would be ΔS = L/T, as previously discussed. Thus we’d find a discontinuity in G’s derivative w/r to T. And this would herald a 1st order phase transition. We could infer that the internal structure of the substance is indeed changing because it would be evident that while T is not changing (and therefore KE isn’t changing), the overall U is definitely changing since we’re taking out heat. So that must mean that only the PE is changing, and since PE is a measure of the spatial relations of particles, we can infer that a change in phase is taking place. Additionally, a change in entropy is generally indicative of changing disorder, and so implicative of a change in phase. If we map these places on a p-T diagram then we would have a phase diagram. Below is the phase diagram for water.



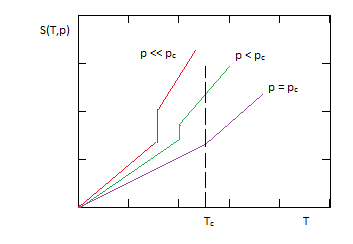
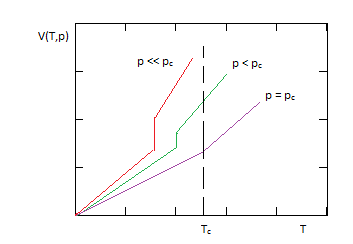
We can classify phase transitions according to what happens when we cross the coexistence curve.



First, we would expect the Gibbs potential G(T,p) to be continuous across the phase boundaries, and that *any* potential should be continuous, as a function of its natural variables. But its derivatives may not be [are we *guaranteed* they won’t be?]. 1st order phase transitions are characterized by a discontinuity in some of the first derivatives of G (i.e. S = ∂G/∂T, V = ∂G/∂p, (μ is constant as we cross the coexistence curve). 2nd order phase transitions are characterized by continuity in the first derivatives, but discontinuities in the 2nd derivatives of G, i.e. ∂2G/∂T2 = ∂S/∂T = Cp/T, and ∂2G/∂p2 = ∂V/∂p = -VκT. For first order, S is discontinuous because of the heat required to change phase, whereas for second order there is no entropy difference and so there is no discontinuity in S. The volume has a discontinuity as we said since during the phase transition we were compressing the gas into the liquid. Generally these discontinuities get smoothed out as we approach the critical point, which is where the first order transition becomes a second order transition,



as illustrated below:

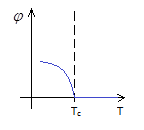
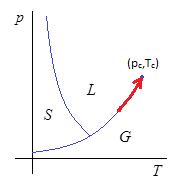
 

The infinities in the second derivatives presumably get less severe as we approach the critical point too. Nonetheless, at the critical point the second derivatives are still usually discontinuous, and look like this:

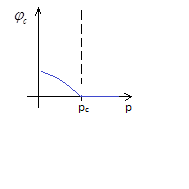
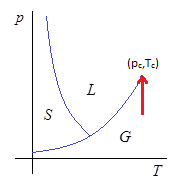


Note there is no critical temperature for solid-liquid transitions because a solid possesses definite symmetry which a liquid doesn’t, so the transition must be discrete – b/c there is a discrete entropy change. Accordingly, phase changes are usually heralded by an abrupt change in organization, therefore entropy. One can usually define an *order parameter*, Δφ, that quantifies the spatial structure of the substance, and which discretely changes as the phase shifts. For a liquid-gas phase transition for instance, the order parameter could be the difference in molar volume between the gas and liquid phases at identical temperature and pressure, i.e. φ = Vg – VL.

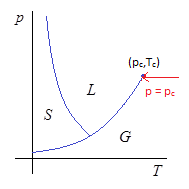
There are many characteristics of a substance that are of interest to calculate. One is a formula p(T) for the curves in the diagram that delineate the different phases. It is also of interest to know how the potentials and their 1st, 2nd derivatives and order parameter behave close to the critical point. Often times we’re interested in how the order parameter varies as we go up the coexistence curve (path illustrated below):

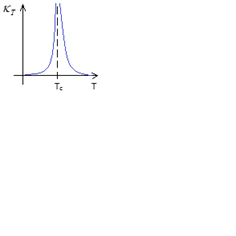
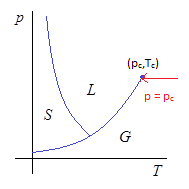
 

Or we might simply be interested how φc = Vg – Vc (where c refers to the critical point) varies with pressure as we keep T = Tc (path illustrated below):

And then we’re also usually interested in the aforementioned 2nd derivatives, along the illustrated constant volume paths:

For the last three, I don’t think it especially matters how you approach the critical point. Of special interest (just because it’s easier) is their behavior near the critical point. The so-called critical exponents define precisely how these quantities behave near the critical point.



One can also derive relationships between the critical exponents. For instance,



And it seems that these must follow from the mere fact that they all are derivable from a single function G(T,p), no?

**Clausius - Clapeyron equation**

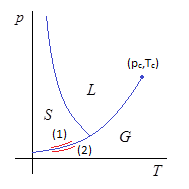
If one knows the exact equation S(U,V,N) for a substance, valid through all of its phases, then of course we could precisely determine all of these quantities of interest. Same if we know G(T,p,N). Supposing so, let’s determine an equation for the coexistence curves. I guess the easiest way, in principle, would be to simply say:



which says that Cp = ∞. This would give us an equation of the form f(T,p) = 0, which one could then solve to get p(T). Of course there would be multiple solutions to this equation corresponding to the multiple curves. An easier way to relate this to physical quantities that can be readily measured would be this. First we’ll assume that we have a homogeneous substance so that the Gibbs – Duhem equation applies. Note that even if the two phases have different densities, we can still say that the substance is homogeneous as all this depends on is that if we double the number of particles we would double the energy, etc., so can still say that:



Or even if we don’t concede this, certainly it is true on either side of the phase transition. So let’s us draw on either side of the, say, solid-gas coexistence curve, a path in T-p space closely tracking the coexistence curve.



And let’s consider the change in chemical potential along either side of the curve:



Now the chemical potential, like T and p, is continuous across the transition. How do we know? Well

G(T,p,N) is continuous across the transition, and μ(T,p) = ∂G/∂N, so it must also be continuous across the transition? Notice how similar this diagram is to branch cuts in complex analysis. We can equate the two changes dμ1 and dμ2, and thereby obtain the equation:



and so we have the Clausius equation:



So the slope is just equal to the ratio of the change of the two first order quantities. Another way to write this is as follows. When we convert 1 into 2 by applying heat dQ at constant pressure (the ΔS and ΔV in Clausius equation are those we get when we cross the phase boundary at constant pressure). According to the first law, we have dU = dQ + dW → dU = dQ – pdV → dQ = d(U + pV) = dH (H enthalpy). Moreover then, dS = dQ/T = dH/T. So we can write this as:



Now if we’re considering a solid or liquid in phase with a gas, the volume of the gas will by far dominate the other and so we can say ΔV = Vg – Vs/ℓ ≈ Vg = NkT/p. So then we have:



We have assumed that L is indeed temperature-independent. And so we have:



Note that L would be a material-dependent quantity, independent of the *amount* of the material.



**Example**

Benzene (with formula mass 78.1134 g/mol) melts at 5.5°C at a pressure of 1 atm and the latent heat for this phase transition ΔH is 10.59 kJ/mol. Under these conditions, the density of liquid benzene is 0.879 g/cm3 and the density of solid benzene is 0.891 g/cm3. Calculate the freezing temperature of benzene at 1000 atm.

We’ll use the Clausius-Clapeyron equation.



For solid-liquid transitions, the enthalpy/heat of fusion doesn’t change much with pressure, as one might imagine. And importantly, the volume of the respective phases won’t change much either. So we can take ΔH and ΔV as constants. So integrating and solving for T, we find:



We can get the volumes from:



Filling in the numbers,



**Appendix**

Some comments/questions…

Note when place liquid in container at volume V and pressure p = 0, and temperature T, it will not be in an equilibrium state. And so it will maximize its entropy to obtain equilibrium, and this will involve partially vaporizing or whatever, to expand volume, etc.

Let’s consider a liquid in equilibrium with its vapor phase, in a closed container of volume V. The pressure of this vapor phase is called the saturated vapor pressure. Note that when you place a liquid at temperature T in an empty, evacuated container, basically at pressure p = 0, the liquid will evaporate until its vapor reaches this saturated vapor pressure. I guess the liquid and gas would at this point occupy a point on the liquid-gas coexistence curve.

This equation gives us p(T), in terms of an initial p and T, and so it gives us the formula for the coexistence curve. So if you put a liquid under pressure p, it will not begin to boil until you heat it to temperature T. At lower temperatures, the vapor bubbles that randomly form will be crushed by the external pressure, p (should consider this state with vapor bubbles a sort of non-equilibrium state, or meta-stable state?). But at temperature T, when the vapor bubble pressure equals the external pressure, the liquid will start to boil. When pressure is atmospheric, this is called the boiling point. Equilibrium will never be set up in an open container however since the liquid will just evaporate away. Even if had a large closed evacuated container with some liquid on the bottom, the liquid would evaporate until pressure equaled the vapor bubble pressure. But this never happens, I presume, and so it completely evaporates – because it will maximize its volume to maximize entropy. Thus at that given temperature, and volume, and pressure, the phase must be gaseous.