

Physics 3700

Free Energy. Thermodynamic Identities. Phase Transitions.

Relevant sections in text: §5.1–5.3

Helmholtz Free Energy

Thus far we have studied two observables which characterize energy aspects of a system. There is, of course, the internal energy U which is just the total energy of the system. The internal energy is of principal importance because it is conserved; more precisely its change is controlled by the first law. A second energy type of quantity is the enthalpy $H = U + PV$ which is the energy needed/yielded upon creation/destruction of the system with volume V in an environment at a fixed pressure P . The PV term represents the work done on/by the environment. The enthalpy also is the observable whose change corresponds to heat transfer during an isobaric process.*

There are other energy observables which have specialized utility like the enthalpy and can be analyzed in a similar fashion. Here we introduce two: the *Helmholtz free energy* and the *Gibbs free energy*. Just as the enthalpy can be used to characterize heat, the free energies can be used to characterize aspects of work. For appropriate processes, the free energy observables also have the virtue of serving as a sort of proxy for the entropy with regard to the second law, but for *open systems*. Just as the entropy gets maximized for closed systems by relaxation processes, so the free energies get *minimized* for appropriate types of processes. We begin with the Helmholtz free energy.

The Helmholtz free energy is the observable

$$F = U - TS.$$

We can get an interpretation of F analogous to that of H as follows. Imagine creating a system in a state with entropy S and energy U in equilibrium with an environment at fixed temperature T . How much energy must be provided? Some of the energy U can be obtained as heat from the environment – this heat is TS , where S is the entropy of the created system. The rest of the energy must be provided as work – this is F . Conversely, if you destroy the system at constant temperature T you need to reduce the entropy to zero via heat transfer TS to the environment, the remaining energy — work which can be extracted (for “free”) — is then F . You can think of F as the energy available to do work for a system at temperature T , with energy U , and with entropy S .

* With H as we’ve defined it, this statement assumes that only compressional work is done during the isobaric process. To maintain the relationship between change in enthalpy and heat when other kinds of work are done, one must generalize the definition of H to handle other kinds of work.

A more practical interpretation of F comes when we monitor its change due to an isothermal process. *For an isothermal process* we have

$$\Delta F = \Delta U - T\Delta S.$$

If the process is also quasi-static, then $T\Delta S = Q$ and we have (using the first law)

$$\Delta F = W.$$

Thus, F can be used to measure the work done in a quasi-static isothermal process. F is the observable used to determine work for an isothermal process just as H is used to measure heat for an isobaric process. Note that the work in the above formula is *all* work of any kind, not just compressional.

Note: if the isothermal process is not quasi-static (*e.g.*, free expansion), then

$$T\Delta S \geq Q,$$

and we have

$$\Delta F \leq W.$$

Here W is all work of any kind done on the system.* Keep in mind that all these deductions are valid for isothermal processes.

There are a number of important differential relations involving Helmholtz free energy, pressure, entropy, and chemical potential which constitute an alternative form of the thermodynamic identity. Infinitesimally, we have simply from the definition of the Helmholtz free energy”

$$dF = dU - SdT - TdS.$$

Using our original thermodynamic identity built from internal energy, we get a new form of the thermodynamic identity in terms of F :

$$dF = -PdV - SdT + \mu dN.$$

Evidently we have

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N},$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N},$$

and

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}.$$

* Including work done by a collapsing/expanding atmosphere in the case where the process is destruction/creation of the system.

Mathematically, if we express $F = F(V, T, N)$ we can just take partial derivatives to get P , S and μ (expressed as functions of (V, T, N)).

Gibbs Free Energy

Closely related to the Helmholtz free energy is the Gibbs free energy. This is defined as

$$G = U + PV - TS = H - TS = F + PV.$$

Based upon our interpretations of H and F you can probably figure out the corresponding interpretation of G . Imagine creating a system from nothing in a state which has volume V , entropy S and is in equilibrium with the environment at temperature T and pressure P . G is the extra energy which must be supplied beyond that obtainable from the environment. Let us add up the energy costs. There is the energy of the system itself, U . There is the work done *on* the environment PV , and there is the energy obtainable via heat *from* the environment TS .

Conversely, G is the (“free”) energy you can extract (by destroying the system at constant temperature and pressure) as *non-compressional work* from the system taking account of the work supplied by the collapsing atmosphere and the heat which must be dumped into the environment to remove the entropy of the system.

So, just as the Helmholtz free energy is designed to give you the total work available in a system with energy U and entropy S in equilibrium with an environment at temperature T . The Gibbs free energy is designed to give you the non-compressional work available in a system in equilibrium with an environment at constant temperature T and constant pressure P .

Again, we can interpret G in a more practical way by considering a process occurring at constant pressure P and constant temperature T . For an isothermal, isobaric process we have:

$$\Delta G = \Delta U + P\Delta V - T\Delta S.$$

For a quasi-static process* (with N held fixed) the first law tells us

$$\Delta U = Q - P\Delta V + W_{other},$$

where W_{other} is any work besides compressional work. Since (for this quasi-static, isothermal process)

$$Q = T\Delta S,$$

we have

$$\Delta G = W_{other}.$$

* Or for states which can be connected by a quasi-static process.

So, for states which can be connected by a quasi-static, isothermal, isobaric process the change in the Gibbs free energy represents the non-compressional work done.

For states which cannot be connected by a quasi-static process, (but assuming the process is isobaric and isothermal) we have

$$T\Delta S \geq Q \implies \Delta G \leq W_{other}.$$

So, in this case the change in Gibbs energy is bounded from above the the non-compressional work.

As with F , there is a version of the thermodynamic identity expressed in terms of the Gibbs free energy. Infinitesimally, we have

$$dG = dU - SdT - TdS + PdV + VdP.$$

Using the original thermodynamic identity built from the internal energy, we have

$$dG = -SdT + VdP + \mu dN.$$

You see that we have

$$V = \left(\frac{\partial G}{\partial P} \right)_{T,N},$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P,N},$$

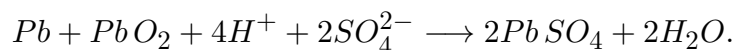
and

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}.$$

If we express $G = G(T, P, N)$ we can just take partial derivatives to get V , S and μ (expressed as functions of (T, P, N)).

Example: Thermodynamics of a battery

The battery in your car produces energy via the chemical reaction



Note that this energy corresponds to electrical work, so the work is of the non-compressional variety. By using the Gibbs free energy, we are going to see how much electrical work is produced. This is feasible because (i) the work of interest is non-compressional, (ii) the battery can be modeled as operating isothermally and isobarically.

As we did some time ago with the enthalpy, we can compute the change in the Gibbs free energy by taking the difference of the formation values for the initial and final states

of the system. These values can be found in tables, as in the back of your text. To do this, we imagine breaking the various initial reactants into their stable constituents and then combining them to make the final reactants. We have then for each mole (remembering the change is final minus initial)

$$\Delta G = 2(-813.0) + 2(-237.1) - 0 - (-217.3) - 4(0) - 2(-744.5) = -393.9 \text{ kJ}.$$

From the minus sign we see that the electrical work for this process represents energy transferred to the environment (as it should) and is about 394 kJ per mole.

Since the process is isobaric and (approximately) isochoric, we have that $\Delta H = \Delta U$.* Looking up values for enthalpy in the table we get for the change in internal energy of the battery:

$$\Delta U = \Delta H = 2(-920.0) + 2(-285.8) - 0 - (-277.4) - 4(0) - 2(-909.3 \text{ kJ}) = -315.6 \text{ kJ}.$$

Note: the magnitude of ΔU is *less* than the magnitude of ΔG . Somehow the battery has actually put out more energy as electrical work than was available from the chemical reaction! How did this happen? Well, from the first law we have (for each mole)

$$Q = \Delta U - W = -316 \text{ kJ} + 394 \text{ kJ} = 78 \text{ kJ}.$$

So, for each mole reacting there is a transfer of 78 kJ via heat *from* the environment *into* the system, which adds to the energy output. The battery uses energy from the environment!

When you charge the battery you run this reaction in reverse. To put the battery back into its initial state you must add 394 kJ per mole via electrical work. Of this 394 kJ, 316 kJ gets stored in the reactants, 78 kJ goes into the environment as heat. You may have noticed some of this heat when you've encountered a charging battery that is getting warm.

Observables – extensive and intensive.

We have now introduced a lot of thermodynamic observables. Let us list the most basic ones:

$$T, P, V, N, \mu, U, H, S, F, G.$$

There are many formulas involving/relating these quantities, not to mention using these observables to define still more observables (*e.g.*, heat capacities). When making formulas using these variables we have to make the units match of course, but there is another

* Note that you can't interpret this ΔH as heat transferred since the relation $\Delta H = Q$ for isobaric processes requires that the only work is compressional, and here we have electrical work.

important constraint on these formulas. This constraint arises because we have intensive observables and extensive observables. From the list above, the intensive ones are (T, P, μ) . The extensive observables are (V, N, U, S, H, F, G) . Note that the product of an extensive quantity with an intensive quantity is again extensive. The ratio of extensive quantities is intensive. The sum of two quantities of a given type is of the same type, *etc.* The key new constraint is that formulas can only equate quantities of the same type. As an example, consider the original thermodynamic identity

$$dU = TdS - PdV + \mu dN.$$

U is extensive, and each term on the right hand side is the produce of an intensive with an extensive quantity - hence an extensive quantity, as is their sum.* As another example, consider the thermodynamic energy expressed in terms of the Gibbs free energy:

$$dG = -SdT + VdP + \mu dN.$$

You can easily check the consistency of the intensive/extensive variables here.

We shall see next how considerations of extensive versus intensive can lead to useful new information.

Free energy and chemical potential

Knowing whether an observable is extensive or intensive can be very useful. As an important example, we know that G is extensive and we have

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}.$$

This formula means that the chemical potential is the change of Gibbs free energy as you add a particle holding temperature and pressure fixed. As you add a particle N goes up, of course. But, since $G = G(N, T, P)$ is extensive, and the only extensive variable used to build G is N , then G must be proportional to N ! Think about it: if you double N (holding T and P fixed) then G , being extensive, must double. This implies that (assuming $G = G(N, T, P)$ and, for simplicity, that there is only one kind of particle) G is proportional to N , and hence from the above relationship between G and μ :

$$G = \mu N.$$

* Note also, by the way, that the thermodynamic identity – in conjunction with the first law and the quasi-static idealization – gives a nice presentation of heat and work in terms of thermodynamic observables. Additional types of work (e.g., magnetic work) would appear as additional terms of the form XdY where X is intensive and Y is extensive.

So we can interpret the chemical potential as the Gibbs free energy per particle! Note also that this reasoning indicates we can express

$$\mu = \mu(T, P).$$

More generally, if there are several species of particles each with a μ_i and an N_i , $i = 1, 2, \dots$, we have

$$G = \sum_i \mu_i N_i.$$

Note that μ is intensive and N is extensive, so this formula yields an extensive quantity as it should.

Chemical Potential of an Ideal Gas

We can use our key result on the relation of the chemical potential to G to obtain a nice formula for the chemical potential of an ideal gas. First of all, since we view $G = G(N, T, P)$ it is clear that $\mu = \mu(T, P)$. Keeping in mind we are viewing everything as a function of the independent variables (N, T, P) , we have

$$\frac{\partial \mu}{\partial P} = \frac{\partial}{\partial P} \left(\frac{G}{N} \right) = \frac{1}{N} \frac{\partial G}{\partial P}.$$

But we found in a previous lecture that

$$\left(\frac{\partial G}{\partial P} \right)_{T, N} = V.$$

Using this and the ideal gas law to get the right hand side in terms of N, T, P , we conclude that

$$\frac{\partial \mu}{\partial P} = \frac{V}{N} = \frac{kT}{P}.$$

We can integrate this little differential equation:

$$\mu(T, P) = \alpha(T) + kT \ln P,$$

where α is an arbitrary function of temperature. If we fix a reference pressure P° and define $\mu^\circ(T)$ to be the chemical potential at that pressure (as a function of temperature) then we must have

$$\alpha(T) = \mu^\circ - kT \ln P^\circ,$$

so that we can write

$$\mu(T, P) = \mu^\circ(T) + kT \ln \left(\frac{P}{P^\circ} \right).$$

Traditionally P° is taken to be 1 atmosphere. Since $\mu = \frac{G}{N}$, you can find μ° from tables of G as in the back of your text. The key feature of the formula for μ is that it shows the (logarithmic) dependence of chemical potential on pressure.

It is worth verifying this relationship explicitly. Recall that we derived a formula for the chemical potential of a monatomic ideal gas — we used the S-T formula for the entropy and took a derivative with respect to N :

$$\mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right].$$

To compare with our new formula for μ (which is valid for any ideal gas, not just monatomic, by the way) we need to express μ in terms of P and T , which we do with the ideal gas law:

$$\mu = -kT \ln \left[\frac{kT}{P} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right].$$

We need to introduce the ratio P/P° , which we can do by multiplying and dividing by P° in the kT/P factor. We get

$$\mu = -kT \ln \left[\frac{P^\circ}{P} \frac{kT}{P^\circ} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] = -kT \ln \left[\frac{kT}{P^\circ} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + kT \ln \left(\frac{P}{P^\circ} \right).$$

Evidently,

$$\mu^\circ(T) = -kT \ln \left[\frac{kT}{P^\circ} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right].$$

Maxwell Relations

The thermodynamics identities give relations which must exist between various thermodynamic observables, *e.g.*, we can express T in terms of S , V , and N , via $T = \frac{\partial U(S,V,N)}{\partial S}$. There are many other relationships which are implied by the thermodynamic identities. In particular, there are a large number of relations between derivatives of thermodynamic observables, called *Maxwell relations*. You will derive and apply some of these in the homework problems. Here is how they arise.

First, pick an observable, say, the internal energy. Next, consider the appropriate thermodynamic identity (we have just derived some new ones, above). For internal energy we have

$$dU = TdS - PdV + \mu dN.$$

As we have seen, U can be viewed as a function $U = U(S, V, N)$. Assuming the function is sufficiently well-behaved (the second partial derivatives are continuous), we have that

$$\frac{\partial}{\partial V} \frac{\partial U}{\partial S} = \frac{\partial}{\partial S} \frac{\partial U}{\partial V}.$$

This is just a simple math fact. Next, still viewing $U = U(S, V, N)$ the thermodynamic identity tells us

$$\frac{\partial U}{\partial S} = T, \quad \frac{\partial U}{\partial V} = -P.$$

We conclude from the second partial derivative relation above that

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}.$$

This is a Maxwell relation.

You can see how this Maxwell equation works, say, by considering an ideal gas using the Sackur-Tetrode equation, which is an expression of the entropy of the form

$$S = S(U, V, N).$$

In this formula use $U = \frac{3}{2}NkT$, then solve for T to get

$$T = T(S, V, N).$$

Explicitly, we have*

$$T = \frac{1}{2} \left(\frac{N}{V}\right)^{2/3} \frac{h^2}{\pi m k} e^{-\frac{5Nk+2S}{3Nk}}.$$

Now you can compute $\partial T/\partial V$, with S and N held fixed. We get

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\frac{1}{3} \left(\frac{N}{V^{5/2}}\right)^{2/3} \frac{h^2}{\pi m k} e^{-\frac{5Nk+2S}{3Nk}}.$$

Next, write $U = \frac{3}{2}PV$ and solve the S-T formula for P :

$$P = P(S, V, N).$$

We get

$$P = \frac{1}{2} \left(\frac{N}{V}\right)^{5/3} \frac{h^2}{\pi m} e^{-\frac{5Nk+2S}{3Nk}}.$$

Now you can compute $\partial P/\partial S$ with V and N held fixed and verify the Maxwell relation, *i.e.*,

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}.$$

If you try this calculation, you can see that it is bit of work, and the Maxwell relationship would be virtually impossible to guess. As we shall see a bit later, one can often

* All the following computations are algebraically a little tedious, but very doable. I did them using the symbolic software *Maple*.

times use a Maxwell relation to express important observables in terms of more easily measurable/accessible observables.

Free Energy and Equilibrium

We have seen that two (macroscopic) systems in thermal contact but isolated from the rest of the universe will share energy until they have the same temperature. This sharing of energy corresponds to an increase in entropy of the total system. Put differently, *if the volume and energy of the total system are kept constant, entropy increases until equilibrium is obtained at the maximum entropy.* On the other hand, when the thermodynamic system of interest is not a closed system (*i.e.*, it can exchange energy, volume, particles, *etc.* with some “environment”) the entropy of the system can decrease – it is only the total entropy of the system + environment which is maximized in equilibrium. One useful feature of the free energies is that, for appropriate processes, one can use them to characterize the equilibrium of an open system, without worrying about the environment. Let us see how this works.

Recall that, when T and N are held fixed for a given system, the change in Helmholtz free energy for a process satisfies

$$\Delta F \leq W.$$

Suppose we have a system undergoing processes where T and N are held fixed and no work is done. After such a process, when equilibrium occurs, we have

$$\Delta F \leq 0$$

So, the Helmholtz free energy of the system *decreases* as it relaxes to equilibrium, irrespective of the environment. During an isothermal process with N fixed, if F reaches a minimum then equilibrium must occur.

Next, recall that when T , P and N are held fixed we have

$$\Delta G \leq W_{other}.$$

So, if we have a process where T, P, N are fixed, and nothing but compressional work is done, then

$$\Delta G \leq 0.$$

So, under the conditions described above, the Gibbs free energy of the system *decreases* as equilibrium is obtained, irrespective of the environment. If G decreases to a local minimum equilibrium must occur.

These ideas give a hand-waving way of thinking about some very basic “intuition” we have about systems coupled to an environment. The relaxation of a system to equilibrium

occurs in such a way as to maximize the entropy of the system + environment. For constant temperature processes involving no work, the approach to equilibrium minimizes the Helmholtz free energy $U - TS$. Evidently, relaxation under these conditions tends to reduce the energy of the system and/or add entropy to the system. Similarly, relaxation under the assumption of constant temperature and pressure minimizes the Gibbs energy $U + PV - TS$, we see that under these conditions relaxation corresponds to a tendency of U and/or V to decrease and/or S tends to increase.

As a simple example of this sort of hand-waving. Consider the processes of freezing and melting. This happens at constant T (and P) and no work need be done. So, both of these processes should somehow correspond to reducing F (to its minimum).

First consider freezing. On the one hand, this corresponds to energy leaving the system via heat, so the entropy of the system goes down – this tends to increase F ! The only way F can decrease (toward a minimum) is if the energy decreases to undo the increase caused by the change in entropy. Of course, a liquid to solid transition will reduce the energy of the system by the first law.

Next consider melting. Energy enters the system as heat. This raises the energy and tends to raise F , but it also raises the entropy sufficiently to decrease F . Thus, both of these phase transitions correspond to a decrease in the free energy.

Phase Transitions and the Gibbs Free Energy

One can use the Gibbs free energy to analyze important features of systems when phase transitions (*e.g.*, liquid-gas) are taken into account. You *must* read the discussion in section 5.3 of your text to learn/review the phenomenology and terminology of phase transitions.

The first order of business is to understand that, all other things being equal, the phase with the lowest value of G will be the most stable. This follows from our discussion of equilibrium and minimization of G : for processes at a fixed temperature and pressure with only compressional work the Gibbs free energy is minimized at equilibrium. As an illustration, consider the example of carbon given in your text. Two solid phases of carbon are graphite and diamond (which have different arrangements of the atoms). As you can see from the table in the back of your book, the Gibbs energy of graphite is 2900 J/mole lower than that for diamond at STP. Thus, at STP diamond tends to turn into graphite (although this happens very, very slowly). Diamonds are hard to come by!

It is interesting to see how this situation varies as we change the values of P and T . The rate of change of G with respect to pressure is given by one of those formulas we

derived:

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V.$$

Now, as it happens, for a fixed number of carbon atoms the crystalline structure of the two phases is such that graphite has a larger volume than diamond. Thus as you increase the pressure (holding N and T fixed), the free energy for graphite will increase more rapidly than that for diamond. Eventually, the free energy for graphite must exceed that for diamond, which becomes the stable form of carbon. At sufficiently high pressures, diamonds are formed!

A similar analysis works for changes in temperature. Now the relevant relation is

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S.$$

Because the entropy is positive, raising the temperature decreases the free energy. But, all other observables being equal, graphite should have a bigger entropy than diamond (since entropy grows with volume and graphite has a larger volume). Thus the free energy for graphite ought to decrease more rapidly with increasing temperature than that of diamond. So, if the pressure and temperature are such that diamond is the stable phase, raising the temperature high enough will make graphite the stable phase again. High temperatures tend to destroy diamonds!

Here is another key set of results in this regard. As you know, it is possible to have two (or even three) phases coexist, *e.g.*, water and water vapor, or water and ice. For example, liquid water and water vapor are in equilibrium at $100^\circ C$ and 1 atmosphere of pressure.* As it happens, there exists a continuous family of equilibria of mixtures of the two phases for appropriate values of pressure and temperature.. Put differently, there are equilibrium states of the system – the system being the substance – in which either of the phases can occur, and these equilibrium states are characterized by combinations of pressure and temperature. Evidently, these pressure-temperature combinations denote the conditions under which a phase transition can occur. We can understand all of these empirical observations using the Gibbs free energy.

Take a fixed quantity of a substance, *e.g.*, H_2O , all of which is in one of two phases, denoted 1 and 2, at one of the P - T values which delineates the phase transition boundary. Consider its Gibbs free energy. For either of the phases, the Gibbs energies must be the same or else the *mixed* system would not be stable – it would relax into the phase with the lowest Gibbs energy (phase transition). We know $G = \mu N$, so for a fixed amount of the

* If you, say, add energy to the system via heat relaxation occurs via *phase transitions* (boiling, melting) until a new equilibrium state is established (with the same temperature and pressure).

substance (fixed N) the condition that the Gibbs free energies of the two phases are equal defines a relation between P and T , namely: $\mu_1(P, T) = \mu_2(P, T)$. This mathematical relation defines a curve in the P - T plane. This the origin of the phase coexistence curves in the P - T plane!

The Clausius-Clapeyron Relation

It is difficult to construct formulas for the chemical potential as a function of P and T except in very simple situations (*e.g.*, the ideal gas). Consequently, a direct assault on solving $\mu_1 = \mu_2$ to get the relation between P and T on the phase co-existence curve is usually not practical. Fortunately, there is a very nice differential equation characterizing the relation between pressure and temperature for phase transitions which can be obtained using the thermodynamic identity.

Let $P = P(T)$ be the relationship between pressure and temperature for which two phases are both stable, *i.e.*, $P = P(T)$ solves $\mu_1(P, T) = \mu_2(P, T)$. We will use liquid and gas, but any two phases will do. In the following, V_l and V_g refer to the volume of the liquid and gas phases, respectively. Let L be the latent heat (of vaporization). The formula we are after is the *Clausius-Clapeyron Relation*:

$$\frac{dP}{dT} = \frac{L}{T(V_g - V_l)},$$

This relation comes about as follows.

Imagine making a small (infinitesimal) change in the conditions for the two phases to be stable. Put differently, imagine a small displacement along the phase co-existence curve in the P - T plane. We know that, for the new equilibrium conditions, the Gibbs energies for a given quantity of substance – in either the gas or liquid phase – must still be the same. So we have

$$dG_l = dG_g.$$

Now, keeping the number of molecules fixed, the thermodynamic identity for G tells us that

$$dG = -SdT + VdP.$$

Hence

$$-S_l dT + V_l dP = -S_g dT + V_g dP.$$

Solving for $\frac{dP}{dT}$ we get

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l}.$$

As before, we assume that the phase transition turning all the material from liquid to gas is quasi-static,* and occurs at constant temperature and pressure. We then can identify

$$L = T(S_g - S_l)$$

and we get the Clausius-Clapeyron relation.

This formula works for any (quasi-static) phase transition. Because the temperature at which the two phases are stable corresponds to the temperature of the phase transition (boiling, melting), we can view the C-C relation as giving the dependence of pressure on temperature for the occurrence of the phase transition.

If we apply the C-C relation to the solid-liquid phases we get

$$\frac{dP}{dT} = \frac{L}{T(V_l - V_s)},$$

where V_s is the volume of the solid and L is the heat of fusion of the solid. As you may know, most substances contract upon freezing; this means $V_l > V_s$, and so the pressure needed to effect the phase transition grows with temperature. Thus, for example, CO_2 , has $V_l > V_s$ and you can raise the freezing point of liquid CO_2 by raising the pressure. A few substances, most notably H_2O , actually increase their volume upon freezing (this is why water pipes can burst if it gets too cold). In this case $V_l < V_s$ so the pressure needed to effect the phase transition actually decreases with temperature. Put differently, increasing/decreasing the pressure lowers/raises the freezing point. You can melt ice just by increasing the pressure! This fact is often used to explain the ability of ice skates to glide over the ice so well. You will explore how true this is in a homework problem. Reversing our point of view, we can use the empirically observed dependence of the melting point of ice on pressure to *infer* that H_2O must expand as it freezes!

* Or, as we discussed previously, even if the actual process is not quasi-static, we assume the initial and final states can be connected by a quasi-static process.