

The Direction of a Reaction

Suppose we have a reaction such as



which has come to equilibrium at some temperature τ . Now we raise the temperature. Does the equilibrium shift to the left (more A and B) or to the right (more C)?

The heat of reaction at constant pressure, Q_p , is the heat that must be supplied to the system if the reaction goes from left to right. If $Q_p > 0$, heat is absorbed and the reaction is called *endothermic*. If $Q_p < 0$, heat is released and the reaction is called *exothermic*.

For a reaction at constant pressure, the heat is the change in the enthalpy of the system, $Q_p = \Delta H$. We have

$$H = G + \tau \sigma ,$$

and

$$\sigma = - \left(\frac{\partial G}{\partial \tau} \right)_{p, N_i} ,$$

so

$$H = G - \tau \left(\frac{\partial G}{\partial \tau} \right)_{p, N_i} = -\tau^2 \left(\frac{\partial}{\partial \tau} \left(\frac{G}{\tau} \right) \right)_{p, N_i} .$$

What we actually want to do is to change the temperature slightly. Then the system is no longer in equilibrium and the reaction (in the forward or reverse direction) will have to occur in order to restore equilibrium. When the reaction occurs from left to right, the change in particle number is $\Delta N_i = -\nu_i$ and the change in G is

$$\Delta G = - \sum_i \mu_i \nu_i .$$

If this is 0, we have the equilibrium condition (but we've taken it out of equilibrium by changing the temperature). The change in H is

$$Q_p = \Delta H = -\tau^2 \left(\frac{\partial}{\partial \tau} \left(\frac{\Delta G}{\tau} \right) \right)_{p, N_i} = +\tau^2 \left(\frac{\partial}{\partial \tau} \left(\sum_i \frac{\mu_i \nu_i}{\tau} \right) \right)_{p, N_i} .$$

The chemical potential is

$$\mu_i = \tau \log \left(\frac{x_i p / \tau}{n_{i,Q} Z_{i,int}} \right) .$$

We substitute into our expression for Q_p and obtain,

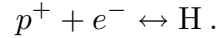
$$\begin{aligned}
 Q_p &= \tau^2 \frac{\partial}{\partial \tau} \sum_i (\nu_i \log(x_i p) - \nu_i \log(\tau n_{i,Q} Z_{i,\text{int}})) , \\
 &= -\tau^2 \frac{\partial}{\partial \tau} \sum_i (\nu_i \log(\tau n_{i,Q} Z_{i,\text{int}})) , \\
 &= -\tau^2 \frac{\partial}{\partial \tau} \sum_i (\log(\tau n_{i,Q} Z_{i,\text{int}})^{\nu_i}) , \\
 &= -\tau^2 \frac{\partial}{\partial \tau} \log \left(\prod_i (\tau n_{i,Q} Z_{i,\text{int}})^{\nu_i} \right) , \\
 &= -\tau^2 \frac{\partial}{\partial \tau} \log K_p(\tau) .
 \end{aligned}$$

We've related the heat of reaction to the equilibrium constant! This is called *van't Hoff's equation*. A note on signs: I've assumed that the ν_i are positive on the left hand side of the reaction and negative for the right hand side of the reaction. Mandl (who provides the basis for this section) assumes the opposite, so we wind up with our equilibrium constants being inverses of each other and opposite signs in the van't Hoff equation.

In any case, our law of mass action has the concentrations of the left hand side reactants in the numerator and the right hand side reactants in the denominator. So an increase in the equilibrium constant means the reaction goes to the left and a decrease means the reaction goes to the right. We see that if Q_p is positive (we have to add heat to go from left to right, an endothermic reaction), then our equilibrium constant decreases with temperature. This means increasing the temperature moves the reaction to the right. Rule of thumb: increasing the temperature causes the reaction to go towards whatever direction it can absorb energy. We've just shown that increasing the temperature drives an endothermic reaction to the right. It will drive an exothermic reaction to the left.

Application: the Saha Equation

This section is related to K&K, chapter 9, problem 2. Consider the ionization of atomic hydrogen,



Ionizing hydrogen from its ground state requires an energy of 13.6 eV, and as the above reaction is written, it's exothermic from left to right. If we are considering low density gases, we can treat them as classical ideal gases and apply our law of mass action:

$$\frac{[p^+][e^-]}{[\text{H}]} = \frac{(n_{p,Q} Z_{p,\text{int}})(n_{e,Q} Z_{e,\text{int}})}{n_{\text{H},Q} Z_{\text{H},\text{int}} \exp(I/\tau)},$$

where the partition function for the hydrogen atom is to be computed with the ground state at the zero of energy, as we've taken explicit account of the binding energy $I = 13.6$ eV. This (or more properly, some of the forms we will derive below) is called the *Saha equation*.

Some of the factors in the equilibrium constant are easy to calculate and others are hard to calculate! Let's do the easy ones. First of all, the mass of a proton and the mass of a hydrogen atom are almost the same, so the quantum concentrations of the proton and the hydrogen are almost the same and we can cancel them out. The quantum concentration of the electron is

$$n_{e,Q} = \left(\frac{m_e \tau}{2\pi \hbar^2} \right)^{3/2}.$$

The internal partition functions for the electron and proton are both just 2, since each has spin 1/2. This leaves us with the internal partition function of the hydrogen atom. This is complicated. First of all, the electron and proton each have two spin states, so whatever else is going on there is a factor of four due to the spins.

Aside: in fact the spins can combine with the orbital angular momentum to give a total angular momentum. In the ground state, the orbital angular momentum is zero and the spins can be parallel to give a total angular momentum of $1\hbar$ with 3 states or anti-parallel to give a total angular momentum of 0 with 1 state. The parallel states are slightly higher in energy than the anti-parallel state. Transitions between these states are called hyperfine transitions and result in the 21 cm line which is radiated and absorbed by neutral hydrogen throughout our galaxy and others. In any case, the energy difference between these states is small enough to be ignored in computing the internal partition function for the purposes of the Saha equation.

When all is said and done, we have

$$\frac{[p^+][e^-]}{[\text{H}]} = 4 \left(\frac{m_e \tau}{2\pi \hbar^2} \right)^{3/2} e^{-I/\tau} \frac{1}{Z_{\text{H},\text{int}}},$$

where the factor of four accounts for the two spin states of the proton and the two spin states of the electron (there is a factor of four in the hydrogen partition function as well). If the temperature is small compared to the binding energy of hydrogen (which means it's small compared to the difference between the first excited state and the ground state), then we might as well approximate the partition function as 4. This gives,

$$\frac{[p^+][e^-]}{[H]} \approx \left(\frac{m_e \tau}{2\pi \hbar^2} \right)^{3/2} e^{-I/\tau}.$$

If we have only hydrogen and ionized hydrogen, $[p^+] = [e^-]$ and

$$[e^-] \approx \sqrt{[H]} \left(\frac{m_e \tau}{2\pi \hbar^2} \right)^{3/4} e^{-I/2\tau}.$$

Some points to note: the fact that the exponential has $-I/2\tau$ indicates that this is a mass action effect, not a Boltzmann factor effect. If there is another source of electrons (for example, heavier elements whose outer electrons are loosely bound), the reaction would shift to favor more hydrogen and fewer protons. The Saha equation applies to gases in space or stars as well as donor atoms in semi-conductors (modified for the appropriate physical characteristics of the atom and the medium).

In fact, we can do a little more with the Saha equation. Let's consider an atom which has several electrons, and ask about the ionization equilibrium between the ions that have been ionized i times and those that have been ionized $i + 1$ times,

$$\frac{n_{i+1}[e^-]}{n_i} = \frac{(n_{i+1,Q} Z_{i+1,\text{int}})(n_{e,Q} Z_{e,\text{int}})}{n_{i,Q} Z_{i,\text{int}} \exp(I_{i+1,i}/\tau)},$$

where n_{i+1} and n_i are the concentrations of the two ions, $n_{i+1,Q}$ and $n_{i,Q}$ are the quantum concentrations of the two ions which are essentially the same, so we cancel them out, $Z_{i+1,\text{int}}$ and $Z_{i,\text{int}}$ are the internal partition functions of the two ions, and $I_{i+1,i}$ is the difference in binding energy between the two ions. That is, $I_{i+1,i}$ is the energy required to remove an electron from ion i and produce ion $i + 1$. Now, each ion will have some internal structure and energy levels. We let $\epsilon_{i+1,j}$ be the energy (relative to 0 for the ion ground state) of the j^{th} state of ion $i + 1$. This state has multiplicity $g_{i+1,j}$. (If there is more than one state at a given energy we say that energy is degenerate and the multiplicity is the number of such states. Sometimes the multiplicity is called the degeneracy or the statistical weight.) Similarly, $\epsilon_{i,k}$ and $g_{i,k}$ are the energy and multiplicity of the k^{th} state of ion i . The fraction of ions $i + 1$ which are in state j is given by a Boltzmann factor,

$$\frac{n_{i+1,j}}{n_{i+1}} = \frac{g_{i+1,j} e^{-\epsilon_{i+1,j}/\tau}}{Z_{i+1,\text{int}}}.$$

If we substitute this expression into the Saha equation, and also substitute the quantum concentration of the electrons and the internal partition function of the electrons (2), we get

$$\frac{n_{i+1,j}[e^-]}{n_{i,k}} = \frac{2g_{i+1,j}}{g_{i,k}} \left(\frac{m_e \tau}{2\pi \hbar^2} \right)^{3/2} e^{-(I_{i+1,i} + \epsilon_{i+1,j} - \epsilon_{i,k})/\tau}.$$

This form of the Saha equation connects the concentration of ions in various energy levels to the electron concentration and the temperature. Note that we managed to get rid of the internal partition functions. Of course, now we have a relation connecting concentrations of states of a given energy level rather than concentrations of ions of a given ionization.

We can apply the above expression to hydrogen (again!). There are only two ionization states. We let $i = 0$ and $k = 0$, so $n_{i,k}$ is the concentration of hydrogen atoms in the ground state (which has multiplicity $g_{0,0} = 4$ and energy $\epsilon_{0,0} = 0$). The ionized state is just a proton which has a multiplicity of 2, and no excited states. So

$$\frac{[p^+][e^-]}{n_{0,0}} = \left(\frac{m_e \tau}{2\pi \hbar^2} \right)^{3/2} e^{-I/\tau},$$

which is essentially the same equation we had before except that now it includes only hydrogen atoms in the ground state and it is “exact.”

Phase Transitions

Phase transitions occur throughout physics. We are all familiar with melting ice and boiling water. But other kinds of phase transitions occur as well. Some solids, when heated through certain temperatures, change their crystal structure. For example, sulfur can exist in monoclinic or rhombic forms.

When iron is cooled below the Curie point, it spontaneously magnetizes. The Curie point of iron is $T_c = 1043$ K. A typical chunk of iron has no net magnetization because it magnetizes in small domains with the direction of the magnetic field oriented at random. The magnetization, even in the small domains, disappears above the Curie temperature.

The transition between the normal and superfluid states of ^4He is a phase transition as are the transitions between normal and superconducting states in superconductors.

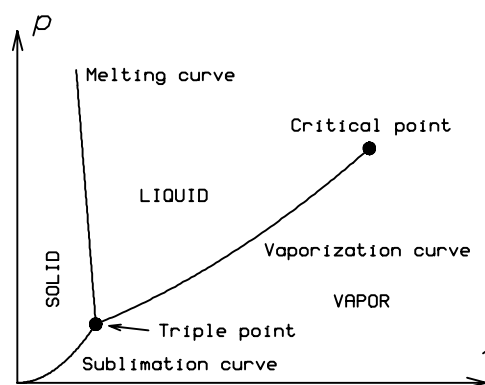
You’ve probably heard about the “symmetry breaking phase transitions” that might have occurred in the very early universe, as the universe cooled from its extremely hot “initial” state. Such transitions “broke” the symmetry of the fundamental forces causing there to be different couplings for the strong, weak, electromagnetic, and gravitational force. The latent heat released in such a transition might have driven the universe into a state of very rapid expansion (inflation).

The spontaneous magnetization of iron as it's cooled below the Curie temperature is an example of a symmetry breaking transition. Above the Curie point, the atomic magnets (spins) are oriented at random (by thermal fluctuations). So any direction is the same as any other direction and there is rotational symmetry. Below the Curie point (and within a single domain) all the atomic magnets are lined up, so a single direction is picked out and the rotational symmetry is broken.

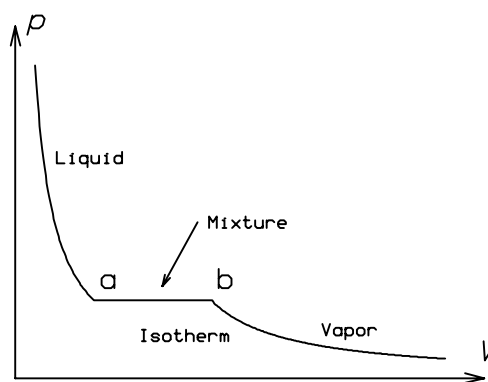
This is not an exhaustive list of phase transitions! Even so, we will not have time to discuss all these kinds of phase transitions. We will start with something "simple" like the liquid to gas transition.

Phase Diagrams

Suppose we do some very simple experiments. We place pure water inside a container which keeps the amount of water constant and doesn't allow any other kinds of molecules to enter. The container is in contact with adjustable temperature and pressure reservoirs. We dial in a temperature and a pressure, wait for equilibrium to be established, and then see what we have. For most pressures and temperatures we will find that the water is all solid (ice), all liquid, or all vapor (steam). For some temperatures and pressures we will find mixtures of solid and vapor, or solid and liquid, or liquid and vapor. The figure shows a schematic plot of a phase diagram for water. I didn't put any numbers on the axes—which is why it's schematic. (Also, there are several kinds of ice which we're ignoring!) K&K give a diagram, but it doesn't have any resolution at the triple point.



Note that the first figure (which we'll talk about some more in a minute) is something like a map: it says here we have vapor, there we have solid, etc. The second figure is a schematic of a pV diagram showing an isotherm. For an ideal gas, we would have a hyperbola. For the isotherm as shown, we have pure liquid on the branch to the left of point a , pure vapor to the right of point b and along the segment from a to b we have a mixture of liquid and vapor. If we move along this isotherm from left to right, we are essentially moving down a vertical line in the pT diagram. To the left of point a we are moving to lower pressures, with liquid water. from a to b we are stuck at the line in the pT diagram that divides the liquid from the vapor region, and to the right of b we are moving down in the vapor region. So the



entire transition from all liquid to all vapor which is a to b in the pV diagram happens in a single point in the $p\tau$ diagram. At this point, the water has a fixed temperature and pressure, and what adjusts to match the volume is the relative amounts of liquid and vapor.

Now, at each location in the $p\tau$ diagram, we fix the temperature and pressure and let the system come to equilibrium. The equilibrium condition is that the Gibbs free energy is minimized. Ignoring for the moment the fact that the water can be a solid, the Gibbs free energy is

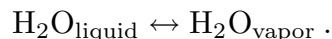
$$G(p, \tau, N_l, N_v) = N_l \mu_l(p, \tau) + N_v \mu_v(p, \tau) ,$$

where the subscripts l and v refer to the liquid and vapor and we've made use of the fact that for a single component substance the chemical potential can be written as a function of p and τ only. There are several ways we might minimize G . First of all, if $\mu_l(p, \tau) < \mu_v(p, \tau)$, then we minimize G by setting $N_l = N$ and $N_v = 0$ where N is the total number of water molecules. In other words, the system is entirely liquid. If $\mu_v(p, \tau) < \mu_l(p, \tau)$, we minimize the free energy by making the system entirely vapor. Finally, if $\mu_l(p, \tau) = \mu_v(p, \tau)$, we can't change the free energy by changing the amount of vapor and liquid, so we can have a mixture with the exact amounts of liquid and vapor determined by other constraints (such as the volume to be occupied).

So, what we've just shown is that where liquid and vapor coexist in equilibrium, we must have

$$\mu_l(p, \tau) = \mu_v(p, \tau) ,$$

which is exactly the same condition we would have come up with had we considered the "reaction"



This is a relation between p and τ and it describes a curve on the $p\tau$ diagram. It's called the vapor pressure curve.

With similar arguments, we deduce that solid and vapor coexist along the curve defined by

$$\mu_s(p, \tau) = \mu_v(p, \tau) ,$$

which is called the sublimation curve, and solid and liquid coexist along the curve

$$\mu_s(p, \tau) = \mu_l(p, \tau) ,$$

which is the melting curve.

If we have all three chemical potentials equal simultaneously,

$$\mu_s(p, \tau) = \mu_l(p, \tau) = \mu_v(p, \tau) ,$$

we have two conditions on p and τ and this defines a point. This unique (for each substance) point where solid, liquid, and vapor all coexist is called the triple point. For water,

$$T_t = 273.16 \text{ K} , \quad p_t = 4.58 \text{ mm Hg} .$$

Actually, this is now used to define the Kelvin scale.

If a substance has more than three phases, it can have more than one triple point. For example, the two crystalline phases of sulfur give it four phases, and it has three triple points.

The vapor pressure curve eventually ends at a point called the critical point. At this point, one can't tell the difference between the liquid phase and the vapor phase. We'll say more about this later, but for now, consider that as you go up in temperature, you get sufficiently violent motions that binding to neighboring molecules (a liquid) becomes a negligible contribution to the energy. As one goes up in temperature, the heat of vaporization decreases. At the critical point it is zero. The critical point for water occurs at

$$T_c = 647.30 \text{ K} , \quad p_c = 219.1 \text{ atm} .$$

Another way to think of the phase diagram and the coexistence curves is to imagine a 3D plot. Pressure and temperature are measured in a horizontal plane, while $\mu(p, \tau)$ is plotted as height above the plane. This defines a surface. In fact we have several surfaces, one for μ_s , μ_l , and μ_v . We take the overall surface to be the lowest of all the surfaces—remember we're trying to minimize G . Where μ_v is the lowest, we have pure vapor, etc. Where two surfaces intersect, we have a coexistence curve.

Of course, the phase diagram corresponds to equilibrium. It is possible to have liquid in the vapor region (superheated), or solid region (supercooled), etc., but these situations are unstable and the system will try to get to equilibrium. Whether this happens rapidly or slowly depends on the details of the particular situation.