The Second Law

Science

The *first*, *second*, and *third* law, (not to mention the *zeroth* law) of thermodynamics are rather complex in detail and not so easy to grasp in full generality. Small wonder. These laws don't just describe thermodynamics (whatever that might be) but essentially *everything* there is, including life, the universe, and whatever else you can come up with.

- I'm now going to drop the "full generality". In other words, I won't attempt to describe something really complex like my wife with a bunch of equations but something much *simpler*, for example a piece of iron or silicon that is virtually isolated from the rest of the universe. Then only the first and second law are of essence, and the task is not too difficult.
- This module is about the *second* law. Having a second law implies that there is a first law. Yes there is - and you know it:

First Law:
Energy is conserved.

The first law simply states that the **total energy** contained in the isolated systems (= bunches of atoms) that we are now considering is *constant*. If we take as system a *perfect* iron crystal containing N_{Fe} iron atoms, the total energy of this crystal is the sum of the individual energies of the N_{Fe} atoms that constitute the crystal. Note that if the crystal is large enough so you can just see it without a microscope, N_{Fe} is a huge number - something like the US public debt in cents (presently around $1.6 \cdot 10^{15}$ Cents)

- Any atom in an iron crystal at any given point in time has energy because it *vibrates*. Look at the spring model of a crystal to get an idea of what is going on, and at this module to see how we can calculate some stuff.
  Vibrations are pretty much the *only* way to have some **energy in a crystal** that is independent of the choice of a coordinate system and thus relevant. The iron of you car body has some additional kinetic energy when the car moves in a coordinate system that is painted on the road, but not in a coordinate system that is inside the car. We don't count that external stuff.
  It is easy enough to write down exactly how much energy is contained in the vibrations. I won't do it, however, because for our purpose here it suffices to note that larger vibration amplitudes mean more energy.
  If some atoms start to vibrate more wildly in our isolated crystal, other atoms must vibrate less vigorously says the first law. **Energy is conserved**.
- Since the energy contained in the *random* vibrations of the atoms is also called temperature, the first law states:

The temperature in an isolated system is constant.

- Well - big deal. The first law, however, goes on. It also implies that if you want to increase or decrease the temperature, you need to put energy into, or take some out of your system, respectively.
  When you do that your system is no longer isolated, of course.

The first law, however, does not specify exactly how the energy is distributed among the atoms of your system. What could happen in principle is:

- Just a few atoms might have a lot of energy and the rest has none.
- The upper part of the crystal has all the energy and the lower part has none.
- The left part has a lot of energy and the right part only a little.

All these, and an infinite number of other scenarios like these, are not forbidden by the first law. So with the first law alone you cannot know or predict what your system (a crystal) would actually look like.

- To get on, one needs to realize that many of those scenarios, while not forbidden by the first law, are just *extremely unlikely*.
  A piece of iron just lying there (in splendid isolation from the environment) with a temperature of 300 K (= room temperature) could, in principle, suddenly get very hot on top and very cold below so that the average temperature (= total energy) hasn't changed - but nobody has ever observed this or similar effects like that.

Logic then dictates that there must be an universal principle that sees to it that weird things don't happen. This universal principle should be able to tell what's likely to occur and what's unlikely to occur. This universal principle is called the **second law**.

- The second law comes in many disguises and wordings. We will look at it in just one formulation, invoking the concept of "**free energy**" (old-fashioned "**Helmholtz** energy") or "**free enthalpy**" (old-fashioned "**Gibbs'** energy").
  - The differences are kind of technical. We use "free energy" when we look at systems where the *volume* doesn't change with temperature (typically a gas in a *solid* container that defines a fixed volume).
    "Free enthalpy" is used for system where the *pressure* doesn't change with temperature. That's you, me, a piece of iron, anything under normal conditions. That's why for our purposes *enthalpy* and not *energy* would be the proper word.
    No, don't stop reading. While enthalpy is one of those deep-physics words that tend to send people scrambling for cover, it is not only just another word for energy, it is pretty much the *same thing* in our case.
    If you heat up a piece of iron the pressure stays constant. The volume does change by thermal expansion - but only slightly. That means that the free energy and the free enthalpy are about the same for any solid, so we don't have to worry about it.
    To keep things easy, I will henceforth use the term *free energy*, even so purists would insist that it should be "free enthalpy".
- So what is free energy? It is simply the **total energy *H*** of the system (here the energy in the vibrations of the atoms) *minus disorder energy* ***TS***.
  I use the letter "***H***" as abbreviation for the total energy because that's what one usually does, simply because the letter "***E***" is an abbreviation for many other things already in serious physics (e.g. for (general) "energy" or "electrical field strength").
  - "Disorder energy" is not an acknowledged term in physics but my term for the *product* of the absolute temperature ***T*** (measured in Kelvin (K)) and the *entropy* ***S***. Now the magic word has come up. So what is entropy?

Entropy is another word for "degree of disorder".

- We all know disorder when we see it and have some feeling about degrees of disorder. Entropy, however, is not just *felt* disorder but *measured* disorder. It assigns a *number* to the degree of disorder it describes.
  We won't worry here how one *measures* the degree of disorder (that's done in another science module) but just accept that it can be done.
  - We now can write down the defining equation for the free energy, abbreviated ***G***:

$$G = H - T \cdot S$$

- That's one of the most powerful general equations physics has to offer, but it is not yet the second law. The second law actually states:

Second Law:
A system has reached nirvana
(= thermodynamic equilibrium)
if its free energy is at an absolute minimum.

This is clear enough. *Absolute* minimum means hat the value (a number) of the function ***G*** that depends on the variables describing the system, is the smallest you can ever get for any values of the variables. This leaves us with two problems:

1. What are the variables in ***H*** and ***S*** and therefore also in ***G***?
2. How do I compute the minimum of a function with many variables?

Let's look at each problem separately.

1. The variables.

If we look in full generality at *any* possible system made of atoms - a nanocrystal, a real crystal, you, the earth, the universe - figuring out the variables for the functions ***G*** is a tough and touchy job.
If we restrict ourselves once more to a simple system like an iron *crystal* with some carbon in it, we may describe its total energy ***H*** by variables like:

- The temperature ***T***. It is a measure of the average energy of the particles of the system.
- Pressure ***p***. We can forget about it because we know it is constant. That was our starting point.
- Volume ***V***. We can forget about that as well, since the small changes due to thermal expansion can be *neglected*.
- The number of iron atoms N_{Fe} found in the iron crystal, which - surprise! - will *not* be constant!
- The number of carbon atoms N_C dissolved in the iron crystal, which - next surprise - will *not* be constant either!
- The number n_1 of single vacancies. That number depends only on the temperature.
- The number n_2 of di-vacanies that could form from two single vacancies.
- The number n_3 of tri-vacancies - *and so on*. Thank God or something, the number of di-, tri-, and so on vacancies is very close to zero at all conditions and we will neglect them.
- The number N_{FeC} of Fe_3C molecules that might form by iron atoms *reacting* with carbon atoms. That's why `the number of iron and carbon atoms in the iron crystal is *not* constant. The ones now in the iron carbide crystal are missing from the (constant) total
- ....

Note that the entropy ***S*** is *not* a variable. It is a function in its own right, depending on the same set of variables as the total energy ***H***.

Good grief! Didn't I claim that things now are manageable? Well, yes, but only because we know a few more things about our system that we can use to our advantage. There are three helpful things to consider:

- **Approximations**. Some are already mentioned above. Some new ones are, for example: the number of self-interstitials can be neglected, the number of vacancies ***n*** is always very much smaller than the number of atoms ***N***, ...
- **Limits**. We need, for example, not consider temperatures higher than the melting point as long as we don't care for liquid iron. Neither do we have to worry much about extreme pressures, and so on.
- **Relations** between "variables". This is a bit more tricky. Some of the variables above actually are *not* true variables because there are unambiguous relations that allow to calculate these "variables" from others.

The latter points needs to be clarified a bit more. Let's write the equations first and then discuss them. We have the following relations between the numbers of iron and carbon atoms and iron carbide molecules, or single vacancies (1V) and double vacancies (2V):

$Fe_3C \Leftrightarrow 3\,Fe + C$	**Reaction equations**
$n_{2V} \Leftrightarrow n_{1V} + n_{1V}$	
$dN_{FeC} = -\,3\,dN_{Fe} = -\,dN_C$	**Differential concentration changes**
$dn_{2V} = -2dn_{1V}$	

It's obvious. If a Fe_3C or cementite molecule forms, we have to consider it to be something new. Fe_3C precipitates are phases in their own right, after all. So if a Fe_3C molecule forms, 3 iron atoms and 1 carbon atom must needs disappear. They are still there, of course, but are now counted in their new phase.
Same thing with di-vacancies and so on. If a di-vacancy forms, two single vacancies have disappeared.

The concentration of Fe_3C and the concentration of, e.g., the number N_{Fe} of iron atoms (in iron) are thus not independent variables.
We now can drop some "variables". If you know the change (expressed by the "**d**" = (differential) change) of the carbon number, you know the changes in the two other parameters, too.

- Taken all these points into account, the system becomes *manageable*, indeed. Note, I haven't said it becomes *easy*!

2. Finding the minimum of a function with many variables. Well, that's rather simple (advanced) math. Set the **total differential** of the function to zero. Here is the equation for our case:

$$\boxed{\mathrm{d}G(T, N_C, n_1) \;=\; \frac{\partial G}{\partial T}\cdot \mathrm{d}T \;+\; \frac{\partial G}{\partial N_C}\cdot \mathrm{d}N_C \;+\; \frac{\partial G}{\partial n_1}\cdot \mathrm{d}n_{1V} \;=\; 0}$$

- The "∂" symbols mean "partial derivation". There is nothing to it. The partial differential quotient $\partial G/ \partial T$, for example, is obtained by differentiating G with respect to T and treating all other variables as constants.
  Insert $G = H - TS$, differentiate it with respect to the variables and, and you get the conditions for nirvana.

Except you can't do it. We know the variables for **H** (and the also for **S**). But we need the precise functional relationship for both so we can do the differentiation.

- As far as the total energy H is concerned, we have some idea of what we need to do: look at those vibrations for whatever is there. This implies looking at all possible springs for all kinds of bonding we encounter inside the crystal. It's not particular easy because we need to know quite a bit about how the atoms of the system interact to find the proper relations. it can be done however.
  But what about the dependance of the entropy on our parameters? So far we don't even have an idea on what to do. It can and will be done, however, and as a result you get relations like the concentration of vacancies as a function of temperature and in particular **phase diagrams**.
- I will give you an idea of how it is done in this science module, where the concentration of vacancies is derived by following the recipe from above, and in the nucleation science "super" module.