4.3 The Second Law

4.3.1 Nirvana for Crystals

- **Peter W. Atkins**, a well-known textbook and public science writer, has put it this way: "When you first encounter the **SECOND LAW**, you ought to kneel down and worship".
- He is right, up to a point. Since I'm a cool and tolerant guy, I let you keep worshiping whatever deity or deities you presently like best. I *only* request that you should now ponder the essential **"why" question**:

> **WHY do metals come in**
> **three lattice types,**
> **and why do some change their type**
> **if you make them hot, while others don't?**

- You may ask your deity of choice for an answer, or go for my answer, which is: it's all in the **second law of thermodynamics** or *second law*, for short.
  - Now, if there is a second law, there ought to be a first one. There is a **first law of thermodynamics**, indeed. I've already covered it.
    The first law simply states that **energy is conserved**, and that **heat** is a form of energy.
    It's nothing but the good old energy conservation law, just including heat as a form of energy.
- For example, the first law states that you can't get more mechanical energy out of your car engine than you put chemical energy in (in the form of the bonding energy of gasoline and oxygen).
  - In colloquial terms the first law states that you can't win forever, that somebody always looses if you win.
    This is depressing, especially if you are the loser; sometime also known as tax payer or believer of financial gurus.
    It is essentially the same as saying that there is no such thing as a free lunch, and we already know that as the first law of economics.
- The *second law* makes things even worse. It says that you can't even get all the energy contained in your gasoline transformed into mechanical energy; it will always be less.
  - Quite a lot less, in fact. For example, if your car engine transforms just 50 % of the energy contained in the fuel to forward motion, it's doing extremely well.
    In colloquial terms, while the first law says that you can't win on the long run; the second law states that you can't even break even.
    In other words: there is not only no free lunch, you don't even get ~~your~~ somebodies money's worth. Some of what you invest is always funneled off and dissipated. In physics we call it *entropy*, in normal life we call it taxes (or relatives, banks, governments, ...).
- The first and second law can be expressed in many smart quips but—far more important—also in precise equations.
  - With the first and second law you can calculate precisely what can be achieved with all kinds of machinery where energy is jiggled around—steam engines of old, your car engine, airplane turbines, an electric generator. Provided, of course, you know your calculus, including partial differential equations, and so on.

> **Science Link**
>
> **Second law**

- And what, you might ask a bit piqued, does all that have to do with our "*why*" question from above?
  - Well - everything! Let's formulate the second law in a way where we can use it—but still without equations. I promised.

Every system (like a large bunch of atoms), if left to its own devices, will strive to assume a most stable state that is a compromise between keeping the energy low and being disorderely

- If the system ever achieves this most stable and most preferred state, and most of the time it will not, it will not "*do*" anything anymore, it just "*is*".
  - This is very easy to understand. If you (the system or you, personally) actually *do* something, things must change. If they don't, you might as well have spared yourself the bother.
    So if you do something while you are already in the best possible state you can be in, you can only change it to a less desirable state, so you better stop doing altogether.
    If you are not in this best-of-all-state, then you do whatever it takes to get there.
- This *best-of-all-states* is known among connoisseurs as: "absolute minimum of the "**free enthalpy**", or "**thermodynamic equilibrium**".
  - I thought you should have seen those fancy words at least once. I will give this "absolute minimum and so on" state a better name here. I call this best-of-all states, where everything is peaceful and nothing changes anymore, by its true name:

Nirvana

- **Nirvana** will be obtained if you keep your energy as low as sensible at all *temperatures* while allowing for increasing disorder as the *temperature* rises.
  Now I have connected two magic words that make for real (as opposed to magical) swords:
  - *Niravana*, the best-of-all states or arrangements the atoms will want to assume, and
  - *Temperature*, the agent of change.
  - The rule is, and I want you to read that out loud:

The hotter the system, the more it needs to be disordered to achieve nirvana.

- If you are a male of our species, you recognize fun when you see it. Fun is often tied to disorder, here is an example:

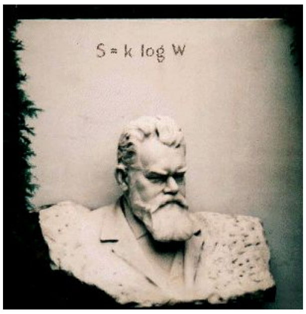
	Very *orderly* array of folks. Some fun to watch, very little fun to participate in (especially if you are not a North Korean).
	Rather *disorderly* array of folks. Good fun to watch, great fun to participate.

The general relations between fun and oderliness

- If you are a male of our species, you recognize fun when you see it, but not necessarily disorder—in contrast to your wife. However, since we want to be precise, we won't rely on your wife. We must now find a way to *measure* disorder, not just talk about it in so many words.
  - Measuring something always means to assign a *number* to whatever you measure. If you have numbers you can do calculations. If you have natural laws (like the second law) in the form of equations *and* some numbers, you can do science. If you can do science you need not consult crystal spheres or (worse) consultants if you want to find out what will happen.
    Being able to assess disorder by numbers is quite useful in other contexts, too. For example in computer science, not to mention in everyday life ("Paris, your room today is 4,7 time more disorderly than yesterday, when it was at a 16,3 level. Clean up at least to a disorder level of 5! That means you must cast out two used lovers and you must put your used underwear in the hamper").

- Measuring and calculating disorder is actually rather easy, provided you like to wallow in mathematical things like logarithms, factorials, combinatorics and some calculus. Just look up the science module or ask your friendly physicist down the block to see how it is done.
  - She will tell you to use one of the famous fundamental equations of **statistical thermodynamics** that goes back to one of the big if unknown heroes of physics: **Ludwig Boltzmann** (1844 - 1906). We will get back to him later again, but here is his grave stone for starters:

Science Link **2nd Law**



Boltzmann's grave stone in the famous Vienna "Zentralfriedhof"
(central cemetery)
S, by the way, is short-hand for entropy, **k** for Boltzmann's constant
and ***w*** for the probability of a state.

  - You must admit that I kept my promise of "no equations" here. Boltzmann never promised anything like that.

- For the special kind of disorder that we find in crystals and that we can calculate and measure precisely, we will now use a different word, and that word is

Entropy=measure (in numbers) of disorder.

- If that sounds Greek to you, that's because it is: "*Tropae*" means "metamorphism" or "transformation", and that is what entropy does: it forces things to change, sometimes rather suddenly.
  - *Entropy*, for reasons even I don't know, is *always* abbreviated with the capital letter "**S**" in equations or otherwise, and I will use that abbreviation every now and then in what comes up. Like right now, because we need to be a bit more precise about that compromise between low energy and high disorder, the way you must balance the two for achieving nirvana. Without using equations, here is what you do: multiply the number that tells you how disorderly things are (the entropy **S**) by the absolute temperature ***T*** as measured in degrees Kelvin (K).
    What you get is the product **TS**, a number, and that's the quantity you **balance** against the energy (another number).

    Science Link

    Entropy

    Balancing is simple: You subtract the number **TS** from the number giving the energy. The resulting number is your comfort account (measured in terms of energy). In contrast to your investment account (measured in terms of in Dollars), you want your comfort account to be small. If it is *as small as possible* under the prevailing circumstances you have achieved nirvana. See it like your tax account. The smaller the better.
- By the way, it's easy to **convert Centigrade to Kelvin**: just add 273 to whatever ^{o}C temperature you have in order to obtain the absolute temperature. **Room temperature** is about 21 ^{o}C; on the absolute scale we thus have 21 + 273=294 Kelvin (K).
  - Being magnanimous about details, we take 300 K to give **room temperature**.
  - If you like Fahrenheit best, you figure out the conversion to Kelvin yourself. That's the proper punishment for weird tastes. This link may help.
- So once more: **T** times **S** is the number that you balance against whatever number describes the energy of your system.
  - While that looks easy it is, in fact, a bit tricky. If the energy would be constant, all you have to do is to create as much disorder as possible to achieve nirvana. However, generating disorder and thus a large **S** may cost you in terms of energy.
    Your problem thus is to figure out just how much investment in some *additional* energy will give you the best return in terms of **TS**. If you do it right (don't let investment bankers help you), you will achieve nirvana.
    Let's look at a simple example. If your present state is described by having an energy of 12 and a TS of 4, your balance is 12 - 4=8. If an investment of 3 in terms of additional energy buys an additional TS of 5, your balance is now (12 + 3) - (4 + 5)=6. You are then better off to raise your energy because the return on that investment gets you closer to nirvana.
- For iron and steel crystals, the only systems we are interested in here, low energy means *perfect* order. Then you have the maximum energy *gain* by bonding to as many neighbors as possible. Energy *gain* means that the energy goes *out of the system* (think about the bonding of hydrogen and oxygen described before), and that's why the system energy goes down and becomes smaller.
  - Perfect order means that the entropy **S** is *zero* and therefore **TS** is also zero.
    For an iron crystal or better, for *any* crystal, you simply can't have low energy and a lot of disorder at the same time. We need to compromise. Invest some additional energy and reap the benefits in a sizeable **TS**. If a certain investment in energy (say 3 units) buys a certain **S** (say 5 units), then the best return on investment obviously occurs at high temperature **T**.
- Congratulations! Now you suddenly understand *why* things melt at high temperature. And you understand *why* the melting point always goes down when you alloy a pure element with something else, as already claimed in chapter 2.3.1.
  Or do you?
  - Well, things **melt** because at the melting point it "pays" to invest heavily into entropy, to make things far more disordered. Atoms milling around in a liquid are certainly far less orderly than being nicely kept at fixed crystal positions.
    It always takes a *lot* of energy (the **melting energy** or **heat of melting**) to turn a crystal into a liquid; it is a big investment. You must, after all, take all the atoms apart. At the melting point the product of temperature **T** and entropy **S** exactly balances the melting energy; for temperatures higher than the melting point it thus *pays* to be liquid. **TS** is then larger than the energy investment.
    If you go the other way around, it works the other way around. Upon freezing or solidification, things get far more orderly and you loose out on the **TS** term. For that you *gain* energy, the **heat of solidification**.

- So when you melt something, you must *invest* energy. That's everyday experience. You *know* that because things don't melt all of a sudden. You have to keep heating (investing energy) your frozen dinner quite a while before it is no longer solid.
  Contrariwise, when you freeze something, you *release* energy—exactly the same amount it took to liquefy it. That's why it takes a while to make ice cubes from water. The energy released when the first part freezes heats up the water again and you need to take that energy away. That's all your refrigerator / freezer does: sucking out the energy released when things cool down or freeze.

Why does the melting point always come down if we **alloy** our material with something else? Put some salt into water and it is still liquid somewhat below 0 ^oC (32 ^oF).

- Easy. If the crystal is alloyed with something, it is automatically *more* disorderly than in its pure state (all these foreign atoms not fitting in properly, loitering around at random). **S** is always larger for a dirty crystal than for the pure state. So the product **TS** now balances the not much changed melting energy already at *lower* temperatures.

The melting point of any mix of atoms with a little bit of B in A always comes down because the entropy is always larger for the mix.

That is important! Adding a little bit of something (like carbon to iron) makes the system *always* more disorderly and thus increases the entropy.

- Now we start to get somewhere. This is the precise moment where we can start to look seriously into the big "*why*" question:

Why does adding a little bit of something to iron produces a material with radically changed properties called "steel"?