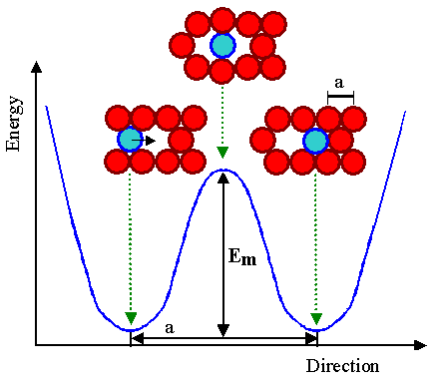
Science

1. Atomic Mechanisms of Diffusion

Jumping Atoms and Self-Diffusion

- Self-diffusion means the movement of the atoms that constitute the crystal in question. That is iron in our case but what follows applies to any crystal.
  In *ismple* crystals like iron self-diffusion can happen by two basic mechanisms:
  - Self-diffusion via vacancies
  - Self-diffusion via self interstitials.
- It is important to realize that concerning the atoms in a crystal, everything that *can* happen *will* happen. However, some things happen more often than others. In our case the movement of iron atoms via vacancies happens far more frequently than via self-interstitials. We will therefore simply ignore the self-interstitial mechanism in what follows.
  How do I know this? Well, there is ample evidence from experimental results and theoretical calculations. Compared to the concentrations of vacancies, the equilibrium concentration of self-interstitials in pretty much all metals is just too small to matter. Interestingly, in semiconductors like silicon (Si), this is not the case.
- Now let's look in some detail at what happens in any crystal if an atom jumps into an neighboring vacancy



Elementary jump of an atom into a vacancy.

- A simple hexagonal two-dimensional crystal has been drawn on the top of the figure and the red circles and the blue one denote atoms. It is clear, I hope, that the situation in a real three-dimensional crystals is the same *in principle*.
  a is the distance between the atoms. In simple crystals it is not much different from the lattice constant usually called ***a***.
  The blue atom with a vacancy as neighbor "wants" to jump into the vacancy. For doing this we might imagine that it must squeeze some of the other (red) atoms apart, so it has room for the jump. All this squeezing needs a certain amount of energy.
  In a slightly more abstract way we imagine the blue atom as vibrating in its potential well (blue line). Next to a vacancy the potential well is different from the potential well the atom usually occupies and looks more or less as drawn above. After the jump it vibrates again in its binding potential and since the situation is exactly the same as before the jump, just mirrored, the potential well looks the same, too. It follows that the potential across the vacancy must be symmetric as shown, and that the atom considered must have at least the energy $\boldsymbol{E_m}$ to be able to jump across the energy barrier that separates it from the vacancy.
  The energy $\boldsymbol{E_m}$ that needs to be overcome for a jump is called "**migration energy**" and will be - very roughly - around **1 eV** for typical metals.
- The essential question now is: How many atoms in a given crystal jump into a vacancy per second?
  Let's tackle this step by step. First we ask: how often does *one* atom, sitting next to a vacancy, manage to jump into that vacancy?
  - How often does a high jumper manage to get across a hurdle? Easy. Multiply the number of tries with the probability that he or she is successful on a try, which you also can call the probability that he or she can muster enough energy to make it.

Our atom vibrates with a frequency $\nu \approx 10^{13}$ Hz or, in other words, it tries $10^{13} = 10$ (US) trillion times per second to run up against the hurdle. The probability of success is simply the probability that it "has" at least the energy E_m when it makes a try. The probability that one atom out of many has a certain energy E is given by the Boltzmann factor $\exp -E/kT$, and that gives us for the **jumping rate** r_{1V} of a single atom the simple equation:

$$r_{1V} = \nu \cdot \exp - \frac{E_M}{kT}$$

- Let's get an idea about numbers. If we take $\nu = 10^{13}$ Hz and $E_M = 1$ eV, we get $r_{1V} = 4.25 \cdot 10^{-5}\ s^{-1}$ at room temperature, or about four jumps per day. At $T = 1.000\ ^oC$ (1.832 ^oF) we have $r_{1V} = 8 \cdot 10^{8}\ s^{-1}$ or almost a billion jumps per second. That's what exponentials do to you.
- Of course, one *specific* atom does not jump billions of time per second. After it has made its jump, some other atoms time has come. A billion jumps of *atoms* per second also means that the *vacancy* has jumped a billion times, too. This involves a billion neighbors but leaves open exactly which ones.
  So let's shift attention from atoms to vacancies. It is simply far easier to follow one and the same jumping vacancy instead of looking individually at all the zillions of atoms involved in the process.

We know now how often *one* vacancy jumps per second. So what is the total number r_{cryst} of vacancy jumps = total number of atoms jumping in a given crystal that consists of N_0 atoms?

- Easy. Just multiply r_{1V}, the number of jumps per second for *one* vacancy with the number N_V of vacancies that will be present in the crystal.
  We know how many vacancies N_V we have for nirvana, excuse me, thermal equilibrium conditions (we are in a science module here). It is given by $N_V = N_0 \cdot \exp -(E_F/kT)$; E_F was the *formation* energy for one vacancy. That gives us a grand total of

$$r_{cryst} = N_0 \cdot \nu \cdot \exp - \frac{(E_F + E_M)}{kT}$$

- Dividing by N_0 gives the more meaningful fraction of atoms (or the concentration) that jumps per second in any given crystal, irrespective of its size.

The two important numbers essentially describing the process are

- Vacancy formation energy E_F.
- Vacancy migration energy E_M.

- The importance of the vibration frequency ν pales by comparison. First of all, we know it pretty well, and secondly, any imprecision in that number changes the result computed by the same percentage. If the real vibration frequency would be 50 % larger than the one used for the computation, we have 50 % more jumps than calculated. In contrast, even small changes in the values of the energies change the computed numbers dramatically.
- How do we get precise numbers for E_F and E_M for our most important crystals, including iron? There are, as always, the two basic ways:

  1. Calculate it.
  2. Measure it.

  Calculations with the required precision are extremely involved. In a few years, we hope, available computer power will be up to the job. Right now calculated values start to look good but there is still a lot of work to do.

  Science module

  Experimental Diffusion

  Measurements involve rather special experiments that are notoriously difficult to do, in particular for iron crystals. Even in your wildest dreams you could not imagine what kind of strange (and expensive) experiments Materials Scientists designed and performed to get numbers for those two parameters. This link will deal with this.
- As a general rule, it is not too difficult to measure $E_{SD} = E_F + E_M$, the sum of the two basic energies that we also call the **self-diffusion energy** E_{SD}. The problems start when you have the sum but want individual values. You need to know at least one of the two basic energies and that is not so easy to come by.

Vacancy Mechanism for Impurity Diffusion

- This will be a short paragraph. Just imagine that the diffusing blue atom in the figure above is an impurity atom instead of an atom of the crystal. For example, it might be a manganese (Mn) or nickel (Ni) atom in iron. Everything discussed for self-diffusion can be taken over, we just need to make some minor adjustments:
  - **1.** The energy barrier E_M is different. We need to have the precise number number for all possible combinations of **A** diffusing (via a vacancy mechanism) in **B**.

    2. The vibration frequency is somewhat different. Big heavy atoms will vibrate less vigorously then light and small ones.

    3. Instead of N_0, the number of atoms in the crystal, we now must take A_0, the number of impurity atoms in the crystal.

    Looking very closely, we may have to make a few more very minor (but hard to calculate) adjustments but in the end we get a simple equation for the jumping rates that contains essentially the Boltzmann factor $\exp-[E_M(A)/kT]$ with $E_M(A)$ = migration energy of the impurity **A** jumping around in the crystal considered and some not-so-important pre-exponential factor.
- That's it. We are done.
  Just note in passing that for covering diffusion of about **80** eligible elements A_i; **i = 1 - 80** in *iron*, we now need to know all the individual $E_M(A_i)$ (including **A** in **A** or self-diffusion), plus the vacancy formation energy E_F and the pre-exponential factors There is work to do!
  Then all that work has to be done once more for some *steel*, e.g. iron with 0.4 % carbon. We don't expect very different numbers but some difference will be found. Then we do the other 2.000 or so kinds of steels.....

Interstitial Mechanism for Impurity Diffusion

- This will be an extremely short paragraph. Interstitial diffusion doesn't need vacancies. The diffusion atom just jumps over some energy barrier E^i_M into a neighboring interstitial place.
  - I won't even write down the equations for that. You can do it yourself by now.

What have We Learned?

- What have we learned? A lot about the deep-down stuff of diffusion. But is all of that really useful for a practitioner, e.g. a sword smith?
  - Not really. Except, perhaps for one deep insight that is hidden in all of the above:

    - The number of jumps that the atoms we look at make per time unit determines how much the material can change. Remember: if atoms don't move, nothing changes.
    - The number of jumps and thus the "speed" for things to happen *increases exponentially* with temperature! Temperature matters very much!
  - In other words: Doubling the *time* (= *100 %* increase) that you hold a piece of steel in the fire on your hearth at best *might* double an effect that depends on atoms running around. Increasing or decreasing the temperature by just a *few* percent may have a far larger effect!
- Why do I say "*might* double an effect" and not "*will* double the effect"? Could it be that I have a lot of atoms running around and there is *no* effect on the properties of my crystal?
  Time to get philosophical. Let's do a little exercise.
  - With all the equations given here, one could answer an interesting little question:
    Let's assume I have some (perfect) crystal consisting of N_0 atoms. I keep it at some high temperature T where the atoms can jump around merrily. How long do I have to wait until every damned atom in the crystal has made at least one jump and thus is somewhere else?
  - The answer is: Not all that long at sufficiently high temperatures. That is weird. All the atoms in the crystal are now somewhere else - but my crystal has not really changed. It is the same crystal, same properties, no measurable difference. Weird - but easy to top.
  - Take a close look at your personal brain. Use your brain microscope for this. See the phosphorous atoms in there, being part of some molecules? See that those atoms occasionally jump to a different place?
    You do? That's good - because that is what really happens, as proved beyond doubts by experiments. So here comes the question:
    How long does it take (around room temperature where you feel comfortable) until all phosphorous atoms presently in your brain have left your body and were replaced by other ones?
    The answer is: just a few weeks! Phosphorous atoms come into your body from the food you eat and leave your body - well. I won't detail this. Some of those atoms make it to your brain, do a weird kind of dance in there, and leave after a few weeks to be replaced by new ones.
    Does this make you different? Have you changed?
    Pondering these kind of questions opens a huge barrel of worms. Since at the time being I'm not in need of worms, I won't say anything more to that issue.

- Before your mind now boggles, proceed to the next module

- Back to **Diffusion**
- On to
  - **2. Random Walk**
  - **3. Phenomenological Modelling of Diffusion**
  - **4. Experimental Techniques for Measuring Diffusion Parameters**.
  - **5. Diffusion in Iron**