



4. Experimental Techniques for Measuring Diffusion Parameters

General Remarks

Science

Let's start by finding out exactly what it is we want to measure experimentally. The headline says it all: Diffusion Parameters! OK, but what exactly? When we look at diffusion we have two basic cases:

- **Self diffusion.** Atoms of the crystal running about by a vacancy mechanism. (we won't go into the highly interesting but rare cases where other mechanisms might be found).
- **Impurity atom diffusion.** Either by a vacancy mechanism or by a direct interstitial mechanism.

If you need to refresh your memory - here is [the link](#).

In essence we need to determine the [diffusion coefficient](#) and that involves getting numbers for the migration energy E_M and the pre-exponential factor D_0 of the [basic equation](#) for the diffusion coefficient:

$$D = D_0 \cdot \exp(-E_M/kT)$$

True enough. But then we know (after looking up [this module](#)) that the migration energy E_M for all diffusion via vacancies contains the vacancy formation energy $E_F(V)$. For the case of [self-diffusion](#) $E_M(SD) = E_F(V) + E_M(V)$ obtains, with $E_M(V)$ = migration energy of the vacancy. We should know about this, too.

In total we want to measure four basic quantities. They cover essentially everything concerning the diffusion of **A** in **B**:

1. Migration energy E_M for all atoms **A** in host **B**.
2. Pre-exponential factor D_0 for all atoms **A** in host **B**.
3. Formation energy $E_F(V)$ for a vacancy in **B**.
4. Migration energy $E_M(V)$ for a vacancy in **B**.



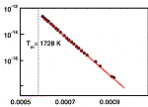
Getting a handle on the first two is not too difficult. The trouble starts with the vacancy properties, which are sometimes hard to get.

I will outline only a few basic techniques here. There are far more ways to measure some property of a material that relates to diffusion than I can cover here.

Self-Diffusion and Impurity Diffusion

The basic experiment for getting diffusion data is simple in principle. It involves the following steps

	1.	Get a high-purity specimen of B . Preferably a good single crystal. Definitely with a very good clean surface.
	2.	Put some A on the clean surface; make sure that there is no "dirt" or the typical oxide between A and B
	3.	Put your specimen in some furnace held at some temperature T_1 for a defined time. A will now diffuse into B . Make sure that there is no "dirt" around that would eagerly diffuse into A, too.
	4.	Back at low temperature, cut your specimen into a bunch of thin slices. Do that carefully and softly, without producing too much damage and saw dust.
	5.	Measure the concentration of A in each slice and plot the numbers obtained in a concentration - depth plot

$c(x,t) = c_0 - c_0 \cdot \text{erf}\left(\frac{x}{(D \cdot t)^{1/2}}\right)$	6.	Make a numerical fit to the proper standard solution of Fick's laws for your experiment. Extract the number for the diffusion coefficient $D(T_1)$ plus the error margin.
	7.	Repeat everything because very likely something went wrong.
	8.	Repeat the experiment at some other temperature T_2 , then at $T_3, 4., 5, \dots$
	9.	Plot your $D(T_i)$ values in an Arrhenius diagram. Discard everything and go back to start if they do not produce a straight line. If they do, extract D_0 and E_M . Tell your professor that she succeeded in her work and can now publish a paper. Have a beer, visit you girlfriend.

Obviously, this is a lot of tricky work. Far more tricky than you can imagine. It's a feast for [graduate students](#) (professors don't have time for things like that!).

Let's look at some of these steps in more detail to get an idea of what experiments like that involve

First step: So we want to measure self-diffusion in iron. We put some iron on the surface of an iron crystal and get to work. But how the hell do you measure the concentration of the iron atoms that diffused into the iron? All iron atoms are exactly equal, there is no way to tell one from the other. *Or is there?*

Yes there is. All iron atoms are *not* equal, after all. Iron atoms, as all atoms, come in variants called **isotopes**.

We need to take some iron isotope that is *not* part of natural iron. Somebody in possession of a nuclear reactor must make it, and it must and will be radioactive. That means it will not come cheap and that I need to do my experiments in a secure environment (not cheap either). Moreover, often I must do my experiments rather quickly before most of my isotope has decayed. Of course, for elements where there is no suitable or affordable isotope, I will have major problems in getting self-diffusion data.

[Basic Link](#)

Isotopes

Second step: This involves all kinds of tricks since you cannot simply put some **A** down on **B** with a trowel. You might put your **B** specimen into a vacuum chamber, shoot of the oxide or whatever with an energetic argon ion beam, and then deposit some **A** by evaporation or one of the many thin film deposition techniques developed for micro electronics. Mostly this is not so simple and never really cheap.

Third step: This is easy. Regular furnaces are standard equipment and rather cheap. Except if material **B** is, for example, tungsten (W) or something else with a very high melting point. Then you need a furnace that goes up to very high temperatures (not cheap). Of course, if **A** should melt long before **B**, you have a problem, too.

Fourth step: If you consider that it takes quite some time at high temperatures to drive some carbon just half a millimeter into you iron, your slices must be very thin. In many cases they actually need to be ultra-thin, far thinner than a hair. Best is to just have a few atomic layers. So forget about cutting off those slices with your trusty old hack saw. Your best bet is to take of one atomic layer after the other, e.g. by some ion beams in vacuum. I won't say more, except that whatever technique you use will most likely be neither easy nor cheap.

Fifth step: Now you have your ultra-thin slices (most likely on some substrate) - but how do you measure the concentration of **A** in there? Well, that's rather easy if you worked with radioactive isotopes for whatever **A** you used, not just for self-diffusion. You just measure how many decays you have, correct for the decays that happened before you got around to do the measurement, and here you are.

If that doesn't work, you may have to resort to using a mass spectrometer (not cheap) or other sophisticated gear (not cheap either). Forget about chemical analysis, it is never sensitive enough.

Sixth - ninth step: Trivial.

The message is clear: *Send us some money!* At least pay your taxes, they are needed for my salary (and for running our labs and paying the people who do the work).

All in all, getting self-diffusion data by experiments is possible but not all that easy. There are other techniques than the one described above but they are just as involved or even more so.

Getting "regular" diffusion data about some **A** diffusing in **B** with **A** being different from **B** is typically easier than getting "**A** in **A**" data, but of course it depends very much on which one of the about **80 · 80** combinations you are after.

● For iron by the way, we are in luck. There are three usable isotopes and that's why we have good self-diffusion data:

1. ^{59}Fe , half-life 45 days
2. ^{55}Fe , half-life 2.7 years
3. ^{52}Fe , half-life 8.3 hours

▶ Now that we have some idea about how to get data for diffusion coefficients, let's turn to the *difficult* part: getting *data for the vacancies* in B.

Measuring Vacancy Data

▶ We know that the activation energy in the exponent for self-diffusion is the sum of the vacancy formation and migration energy; $E_{SD} = E_F + E_M$. This implies that we only have to determine one of the two basic vacancy energies, the other one we get from subtracting it from E_{SD} . Typically we are after the formation energy E_F , and we get that if we succeed in measuring the vacancy concentration c_V because we have the simple relation $c_V = c_0 \cdot \exp(-E_F/kT)$.

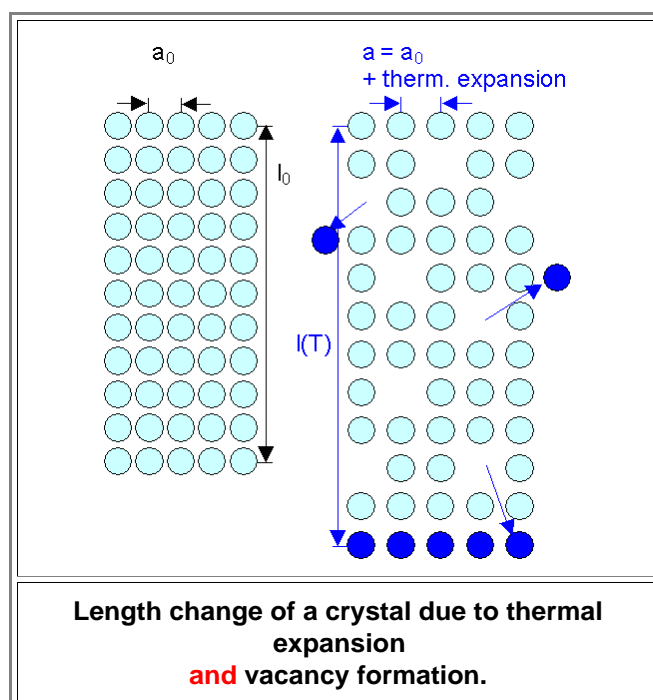
● The c_0 term above is new; I haven't bothered you with that so far. Well, c_0 is roughly about 1 so we need not be overly concerned about it. If one likes to wallow in unimportant details one might get rewarded sometimes because c_0 does hide tricky and interesting stuff about the inner structure of the vacancy. Don't believe for a second that missing things have no structure. Ask you wife about that vacancy in your account that appeared after her recreational shopping, and you will learn that there is a sophisticated structure to it. Anyway, when we measure vacancy properties, we absolutely want to have a good number for E_F and if we get c_0 too, we are happy. If we don't get it, we cannot calculate *precise* concentrations, unfortunately.

▶ How do you measure a *vacancy concentration*? The first thing to realize is that we can forget about all kinds of microscopy. Yes, some microscopes actually can "see" a vacancy on the *surface* of a sample - [here is an example](#) - but they can never give you reliable *numbers* for a *volume* concentration. In essence, we have two major methods and a bunch of special ones. Here I will only look at the two major methods.

"Delta / minus delta a" Method

▶ The *first* method is conceptually simple. Imagine that you have a crystal full of vacancies. Now ask yourself a question: where are all the atoms that now are missing? They must still be part of the sample because they could not just disappear into nothingness. What happens is that the atoms that made room for a vacancy are now at some internal or external surface, [this link](#) gives an idea of how that works. But details don't matter, what happens is that our sample gets bigger if there are vacancies, see the figure below.

● All we have to do is to measure how the length $l(T)$ of a sample changes with increasing temperature T . The problem, of course, is that the length also changes because of thermal expansion, simply because the average distance between the atoms gets larger as schematically shown below



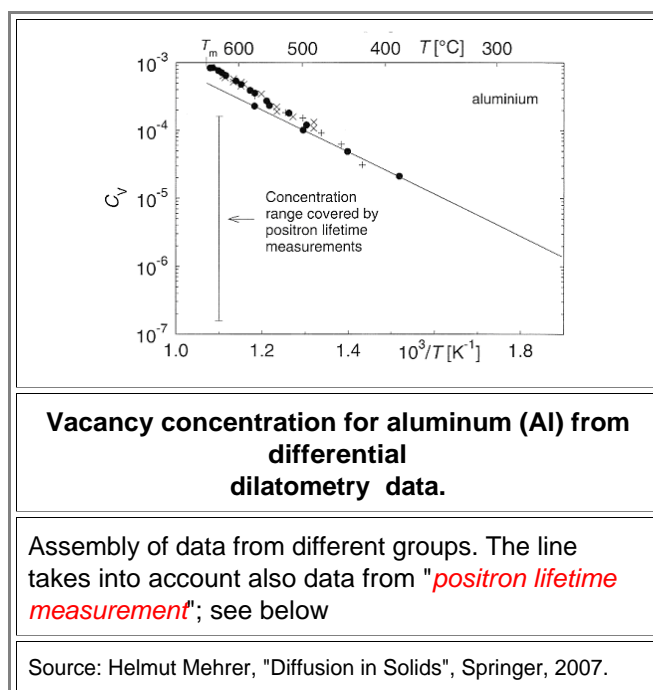
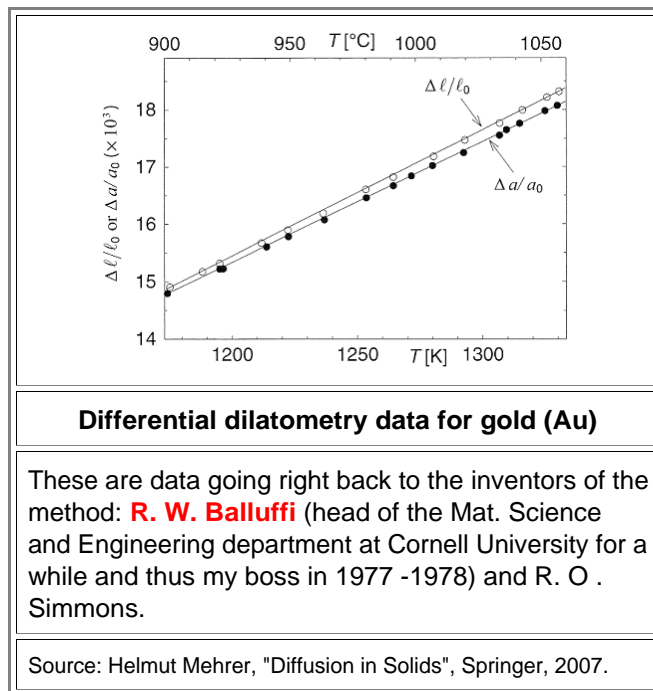
▶ Can we measure just the effect of thermal expansion somehow, and then subtract it from the *total* length change? The difference then must be due to vacancies.

● Yes, we can! Thermal expansion changes the distance between *all* atoms in the lattice, and thus the lattice constant a . Lattice constants are easy to measure with high precision if you have some good X-ray equipment. I won't go into how it is done but in essence you use interference effects due to the periodic arrangement of atoms.

- What one does is to measure the relative change in length, $(l(T) - l_0)/l_0 = \Delta l/l_0$ with a "ruler" (I won't go into how it is really done) and then subtract the relative change in lattice constant. The vacancy concentration obtained by this "Delta l minus delta a" method (more fancily we call it "**differential dilatometry**" method) is simply given by

$$c_v = \frac{\Delta l}{l} - \frac{\Delta a}{a_0}$$

- Nice, straightforward, and and rather simple. But not without problems, which become apparent by looking at some "classical" examples



- The basic problem of differential dilatometry is that you need to measure rather small effects with high precision. That limits the method to "large" vacancy concentrations as shown above; it should not be much below **10⁻⁵ (10 ppm or 0.001 %)**. Since the largest vacancy concentrations close to the melting point are in the **10⁻⁴** range, the method is restricted to high temperatures. Even then it does not work for crystals with a generally low vacancy concentration like silicon (Si).

● That's why we invented a truly far-out technique for measuring vacancy concentrations called:

Determining Vacancy Concentrations via Positron Lifetime Measurements

▶ If you ever read some science fiction or watched some Star Trek episode, you are familiar with antimatter. All [elementary particles](#) like protons, neutrons, electrons, and so on, always come with a kind of mirror image particle called "**anti particle**".

● We have anti-protons, anti-neutrons and anti-electrons - but for historical reasons we call the latter **positrons**. If a particle happens to meet its *anti*-particle, they engage in violent activities that invariably destroy both of them, producing some (typically two) high-energy photons or light "particles" that we call γ -rays. When the universe made itself, there were about equal amounts of particles and antiparticles. All couples have long since disappeared, the matter that is left are just the few survivors resulting from a small imbalance in the original numbers. That's the present wisdom.

[Advanced Link](#)
Elementary particles

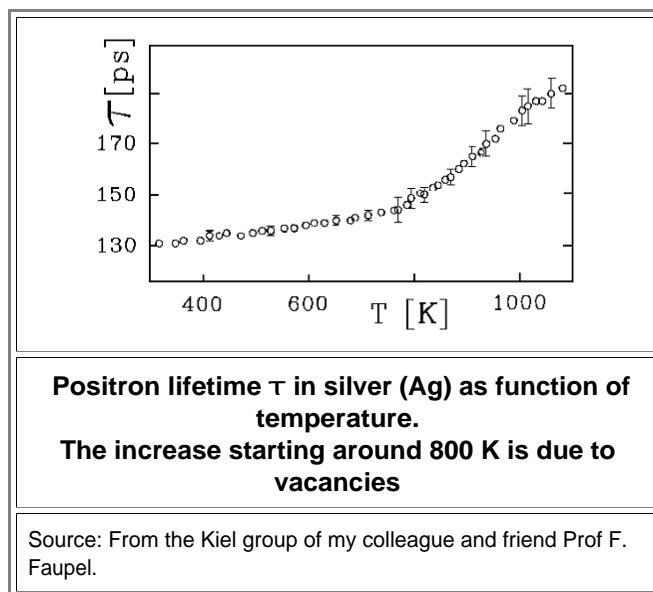
So if you need some *positrons* for an experiment that is supposed to measure the vacancy concentration, you must make your positrons right where you need them. This is typically right at the surface of your specimen, from where they are "shot" into the bulk of the sample. Inside the sample they do a [random walk](#) until they find a partner for self-destruction, and off they go.

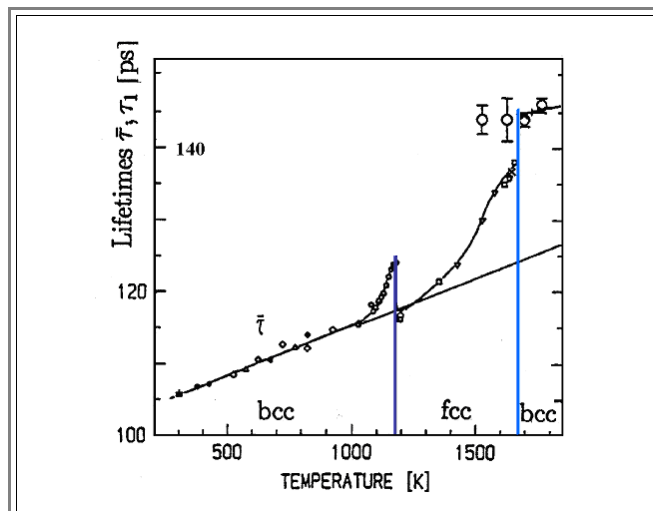
● Fortunately, making positrons is not a difficult thing to do. Buy yourself a suitable sodium [isotope](#), typically Na 22. This isotope is radioactive and decays with a life time of **2.6 years** into something else by emitting a positron and, at *exactly* the same time, a γ photon with a high energy of **1,28 MeV**.

● The great thing about those positrons is that they announce their birth *and* their death with a flash of (γ) light that we can easily measure. Since there are plenty of electrons inside normal matter, a positron let loose in there doesn't need very long to find an innocent electron who has no choice but to become a partner for self-destruction. Typically, it's all over after 100 ps (10^{-10} s). Fortunately once more, the stop watches we use in modern science have no problem in measuring elapsed time with picosecond precision. To start an experiment we shoot positrons into the crystal at room temperature, sort of one-by-one, and measure their life time with high precision in the picosecond region.

If that works we start to heat up our sample in order to create an appreciable concentration of vacancies. Inside a vacancy there are no electrons. If a positron on its arandom walk happens to come close to a vacancy, it likes it there and hangs around inside the vacancy for a little while (it is "trapped" in science lingo). Since there are no electrons, it cannot commit suicide quite that easily, and the net effect is that it lives a little longer.

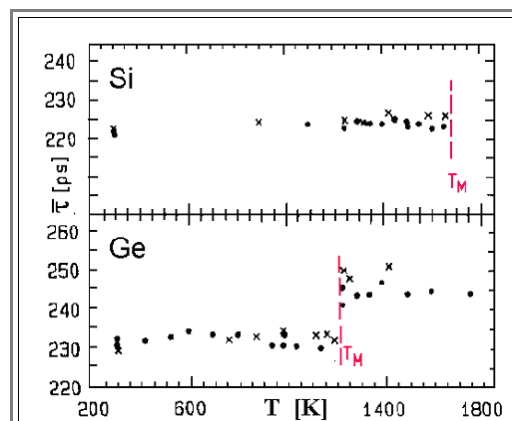
In other words, the average positron lifetime increases a bit if a lot of vacancies are around. That we can measure. We also can (with some little difficulty) calculate the vacancy concentration from the positron lifetime data. Here are some results:





Positron lifetime in iron (Fe) as function of temperature.

Source: From a 1998 review paper about "Lattice vacancies in high-purity iron" of A. Seeger, phys. stat. sol. (a) 289 (1998). Prof Alfred Seeger was my Boss when I did my PhD work in his large group in Stuttgart, Germany, way back around 1975.



Positron lifetime in silicon (Si) and germanium (Ge) as function of temperature.

There is no measurable effect

Source: Sorry - don't know anymore

The major strength of the method is that it can detect vacancies at lower concentrations than differential dilatometry; [see the figure above](#). Sadly, however, it is not sensitive enough to detect anything in silicon, germanium or other important semiconductors as you can see.

- Positron lifetime measurements (and some other things you can do with positrons) have advantages and problems, but I won't go into that. I will also not go into what one can learn about diffusion and vacancies by using other exotic elementary particles like *muons*. I'll stop right here about methods. The message is clear:

Getting experimental diffusion data is possible but neither easy nor cheap. In some cases a full set of data is almost impossible to obtain.

● That is the reason that we still know far less than we ought to about the details of diffusion in semiconductors. In particular, the data about vacancies (and [self-interstitials](#), which happen to be important in these materials) are not known very well and still cause a lot of controversies in Materials Scientist circles.

▣ In the last part of this module I will give you some exemplary data about diffusion and vacancies, which provide a kind of background for the *iron data* in the [main module](#).

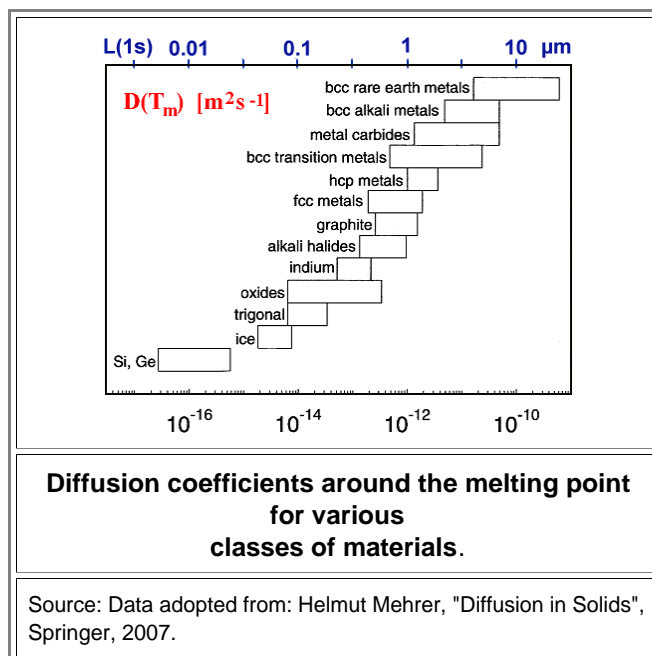
Some Diffusion and Vacancy Data

▣ First a few vacancy data. Below is a table from the "[vacancy](#)" module, augmented by the maximum vacancy concentration as far as it is known.

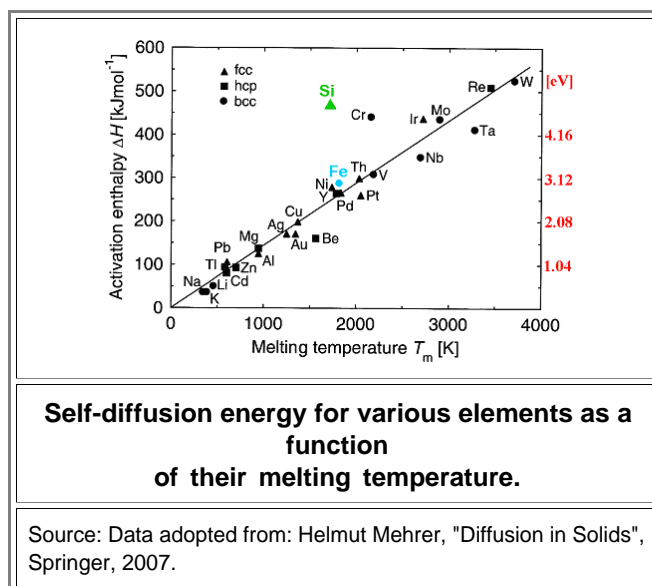
Crystal	$H^F(V)$ [eV]	Concentration around T_M ($\cdot 10^{-4}$)
Ag	1,09	1.7
Al	0,66	9.4
Au	0,94	7.2
Cu	1,17	2
Ni	1.7	?
Mo	3.0	?
Pb	0.49	1.7
Pt	1.49	?
W	4.0	1
Vacancy data in some metals. ? indicates that the c₀ data are missing.		
Data adopted from: Helmut Mehrer, "Diffusion in Solids", Springer, 2007.		

▣ Now let's look at self-diffusion coefficients $D(T_m)$ close to the melting point where the maximum value will be found.

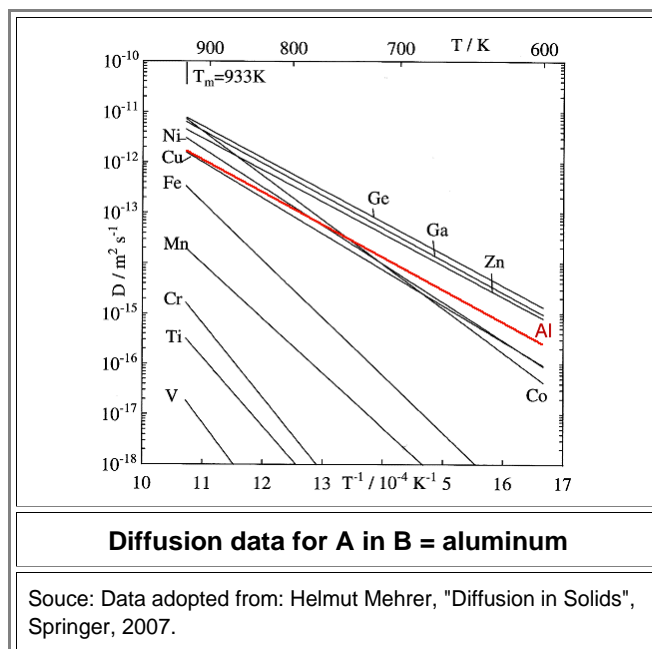
● The lower scale gives $D(T_m)$ in the usual units of m^2s^{-1} .
 The upper scale uses the important relation $L = (Dt)^{1/2}$ for the [diffusion length](#) L and give this average [penetration depth](#) for a diffusion time of 1 second. Multiply by 10 for 100 seconds, 100 for 10 000 seconds or close to 3 hours, and so on.



Now let's look at some numbers for the exponents E_D of the [exponential expression](#) for the self-diffusion coefficient. We called that [diffusion energy](#) or "activation energy for self-diffusion". In addition we also know that for self-diffusion running by a vacancy mechanism, we have $E_D = E_F + E_M$, with E_F and E_M = formation energy and migration energy of the vacancy, respectively. The graph here calls the diffusion energy by its proper name "activation *enthalpy*" but never mind. In some rare cases like silicon (Si), self-diffusion is believed to be carried mostly by self-interstitials, so the equation above might not apply to all elements in the figure below.



- As one could expect, the self-diffusion energy scales with the melting point. That allows to guess that number for materials where measurements have not yet been made. You might be off quite a bit, however, as chromium (Cr) and silicon (Si) nicely demonstrate
- Now I only need to supply millions of data for **A** diffusing in **B**. Or **A** diffusing in any *compound* or alloy **B** can make with all other elements of the periodic table. For example we might look at the diffusion of carbon in iron, all iron oxides, iron silicides, ..., you get the point.
- One example must suffice. In order to get the maximum amount of data in as little space as possible, it is best to use an [Arrhenius plot](#). Here are the data for some elements diffusing in aluminum (Al). A similar diagram for all kinds of elements diffusing in silicon (Si) can be found in [the link](#).



Some elements diffuse faster than aluminum (red line), some diffuse slower. Some like cobalt (Co) diffuse slower at lower temperature but faster at higher temperature. There are no obvious rules. If you want to know the diffusion coefficient, you must measure it.

What remains to look at are the migration energies E_M for vacancies but I gave you some numbers for those [already before](#).

What also remains to consider, for example, is

- Diffusion in *amorphous* materials like glass or polymers.
- Diffusion in *quasi crystals*, whatever that might be. Hint: use the link or look up the Nobel price winners in 2012.
- Diffusion inside grain boundaries or down a dislocation line.
- Diffusion when charged atoms (= ions) are around, e.g. in ionic crystals like rock salt or the solid electrolyte in batteries and fuel cells.
- Diffusion in *magnetic* crystals like iron (Fe), nickel (Ni) or cobalt (Co)
-

You get the point once more:

Diffusion is fundamental to many devices. Studying it will keep Materials Scientists and Engineers busy for some time to come.



You also appreciate the importance of the first law of applied science. A lot of time and effort could be saved if there were a good theory that allows to *calculate* all those numbers we are after with sufficient precision.

This, however, is a notoriously difficult enterprise. But there is hope. To quote *B. Grabowski* et al. who published the presently last word on this topic in "physica status solidi B, 248, 2011":

"The situation (*of not being able to do precise calculations*) is likely to change in the near future."

More power to our theoreticians (and the guys who make more powerful computers)!

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