Science

Making Vacancies

Calculating the Equilibrium Vacancy Concentration from Scratch

- How many **vacancies** does a real crystal need for achieving ~~nirvana~~?— excuse me, here in the science section we call it **thermodynamic equilibrium**. It is about the most simple thing one can calculate "from scratch" by using the second law.
  - First we need to determine the free ~~energy~~—excuse me once more. Among purists it's called **free enthalpy** but that is just a different word for the same thing. What matters is the mathematical definition:
    ***G*(*N*, *n*, *T*)** is the free enthalpy of a crystal with the variables
    N = number of atoms forming the crystal.
    n = number of vacancies in the crystal.
    T = (absolute, of course) temperature of the crystal.
    I will give you the full function **G(*N*, *n*, *T*)** first and then discuss it. What we have is

$$\boxed{G(N, n, T) \quad = \quad \underbrace{G(N, T)}_{1^{\text{st}}\text{term}} \quad + \quad \underbrace{n \cdot E_F}_{2^{\text{nd}}\text{term}} \quad - \quad \underbrace{TS(N, n)}_{3^{\text{rd}}\text{term}}}$$

  - The *first* term, **G(*N*, *T*)** , simply describes the total free enthalpy of a *perfect* crystal with ***N*** atoms at the temperature ***T*** and no vacancies. It contains the energy E_{cryst} of the crystal, essentially contained in the vibrations of the atoms, and the entropy S_{vib} resulting from that.
    If you like you can write it out as $G(N, T) = E_{cryst}(N, T) - TS_{vib}(N, T)$ but that will just make the equation longer. For any number of atoms ***N*** and temperature ***T***, the function **G(*N*, *T*)** would produce some number if we put our mind to it. We won't do that, however, since it will turn out that we don't really need **G(*N*, *T*)**
  - The *second* term acknowledges that we expect to have ***n*** vacancies in our crystal.
    Making a vacancy requires that we sever the bonds between the atoms an and rip out the cut-off atom *somehow*. That will take some effort or *energy*. The energy needed to make one vacancy in a given crystal is always the same, no matter how "we" make the vacancy. It is aptly named **formation energy of a vacancy** and abbreviated with E_F.
    We want to make ***n*** vacancies so we need to *add* $n \cdot E_F$ to the energy contained in the otherwise perfect crystal.
  - The *third* term acknowledges that having vacancies increases the disorder and thus the entropy ***S*** of the crystal. This is called the "**entropy of mixing**" since it comes exclusively from mixing up "things" and not from the "things" itself.
    We thus must subtract ***TS*** from the total energy of the situation. The entropy depends *only* on the number of atoms ***N*** and the number of vacancies ***n*** so we can write it **S(*N*, *n*)**.
- The third term with the entropy **S(*N*, *n*)** is the decisive term. Boltzmann's famous formula for the entropy, $S = k \cdot \ln P$, applies. We have

$$\boxed{S(N, n) \quad = \quad k \cdot \ln \{P(N, n)\}}$$

  - **P(*N*, *n*)** is the number of possibilities to arrange ***n*** vacancies in a crystal consisting of ***N*** atoms; **k** = Boltzmann's constant. And of course, you know what "**ln**", the symbol for a natural logarithm means
- How large is **P(*N*, *n*)**? You might also ask: In how many ways can I distribute **7** socks in my bedroom, assuming I have **42** places (in the actual sock drawer, in any of the **11** other drawers, under the bed, on the bed, ...).
  - Question like that are answered by **combinatorics**, a much-hated branch of **stochastic math**. Another combinatorial question (but not mathematically equivalent) could be "How many different car license plates can you make by using a combination of two letters and three numbers" or "How many ways to dress differently with two pairs of pants, three shirts, five pairs of socks", or "how many different hands are there at poker", or... You get the idea.
  - The answer to our question is so elementary (and simple) that the combinatoric folks came up with a special mathematical symbol, the **binomial coefficient**, to abbreviate equation writing. We have

$$P(N, n) = \binom{N}{n} = \frac{N!}{n! \cdot (N - n)!}$$

$$\binom{N}{n} = \textbf{Binomial coefficient of } N \textbf{ over } n$$

- In case you forgot: An exclamation mark behind a mathematical symbol or number means the **factorial** of that number.
  A factorial is an extremely simple thing: $n! = 1 \cdot 2 \cdot 3 \cdot 4 \cdot 5 \cdot ..... \cdot n$. Take **5!** as example. We have
  $5! = 1 \cdot 2 \cdot 3 \cdot 4 \cdot 5 = 96$. Nothing to it? Just wait.

- Now we are done. The full expression for the free enthalpy $G(N, n, T)$ of a crystal consisting of N atoms that contains n vacancies at the temperature T is

$$G(N, n, T) = E_{\text{cryst}}(N) - TS_{\text{vib}}(N) + n \cdot E_F - kT \cdot \ln \frac{N!}{n! \cdot (N - n)!}$$

- We are seeking nirvana for a crystal of given size (i.e. given and constant N) at some given and constant temperature T and that means we are seeking the minimum value of that function.
  The only variable left is n, the number of vacancies. We now need to determine the *minimum* of the function $G(N, n, T)$ with respect to the number of vacancies n.
  - Obviously we have to differentiate $G(N, n, T)$ with respect to n and set it to zero: $\mathrm{d}G(N, n, T)/\mathrm{d}n = 0$. The first constant term disappears if we do that (that's why we didn't need to worry about it) and we get

$$\frac{\mathrm{d}G(N, n, T)}{\mathrm{d}n} = E_F - kT \frac{\mathrm{d}}{\mathrm{d}n}\left(\ln \frac{N!}{n! \cdot (N - n)!}\right) = 0$$

- Oh Sh...!
  If you had an *extremely* good high school education in the US, or an *average* one in Germany, you know how to differentiate a natural logarithm:
  $y = \ln x$; $\mathrm{d}y/\mathrm{d}x = 1/x$.
  But only with an extremely good high school education in Germany you know how to differentiate a factorial function:
  $y = x!$; $\mathrm{d}y/\mathrm{d}x =$ **can't be done**!
  It can't be done! It's not a *smooth* function.
  - Thank God for **Stirling's formula** that makes an approximate smooth function out of factorials for large x:

$$\ln x! \approx x \cdot \ln x$$

Since we have a hell of a lot of atoms (if you can see a crystal it has more than about 10^{15} atoms) and therefore also a lot of vacancies, Stirling's formula is extremely precise for our undertaking.
We now replace all the factorials by Stirling's expression, do the differentiation (lengthy but simple), use the fact that $n << N$, i.e. we have way fewer vacancies than atoms, and and the extremely *simple final* result emerges:

$$\frac{n}{N} = \text{concentration of vacancies} = \exp -\frac{E_F}{kT}$$

- To be honest, it is a bit too simple. In full generality our **basic equation** for the **equilibrium** or **nirvana concentration c_{PD}** of all **point defects** we have:

$$c_{PD} = c_0 \cdot \exp -\frac{E_F}{kT}$$

  - The only difference is that we now have a **pre-exponential factor c_0** that takes into account that there is a bit more to the entropy than just the entropy of mixing atoms and vacancies. For example, a single vacancy, or just about any point defect, also carries some *direct* entropy around, since it disturbs the arrangement and in particular the vibration spectra of its neighbors and thus increases the local disorder.
    The pre-exponential factor c_0 carries a lot of information about what is going on in detail. However, its numerical value is typically around **1 - 5**, which means it doesn't matter much as long as we just look at the basics of what is going on.
- Puhhh! Quite a bit of work. And I didn't even run through the details.
  - The result, however, is of supreme beauty. We have derived the most important mathematical expression in sword making.
    No, it's not the vacancy concentration, it is the **exp–(E/kT)** term known as **Boltzmann factor**. The link takes you there. Here we look at bit more closely at what we can learn from our vacancy concentration formula.

Discussion and Generalization

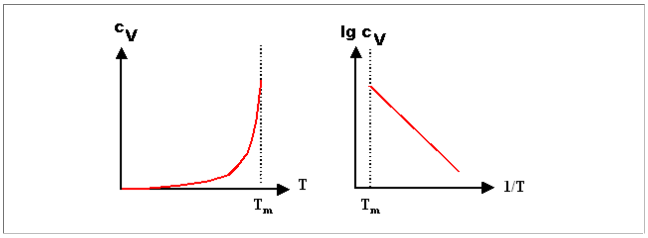
- The first thing to realize is that we calculated far more than just the vacancy equilibrium concentration. We can use this basic equation also to calculate, for example:
  - The self-interstitial concentration. Everything is pretty much the same, except that the quantity E_F now would be the formation energy of one self-interstitial. In most cases this energy is somewhat larger than the formation energy of vacancies, meaning that we have a lot less interstitials than vacancies in equilibrium. That's what exponential functions will do.
  - The **di-vacancy** concentration, i.e. the concentration of vacancy pairs. E_F is now the formation energy of a di-vacancy, which we can safely assume to be twice the formation energy of a single vacancy *minus* some binding energy.
  - The equilibrium concentration of foreign atoms - interstitial or substitutional. Same procedure once more (eschewing some details that really don't matter much). The energy in the exponent then is called "**solution energy**" and tells you how much a crystal likes or hates to have a foreign atom sitting around. If the solution energy would be zero, the crystal doesn't care - the foreign atom is just as good as one of the own kind. Positive values mean the crystal does not like the foreign atom, negative values (possible in this case) that it actually prefers a bit of change.
    You realize, of course, that the *equilibrium* concentration value of foreign atoms depends exponentially on the temperature, while the *real* value is more or less constant. You can't easily change a given concentration of foreign atoms, after all.
  - In essence the major difference between point defects is only how much energy E - formation energy, solution energy, whatever - they carry around with them.
- The basic equation for the equilibrium concentration of all those point defects always contains the "Boltzmann factor" **exp–(E/kt)**. The link will show that the vacancy concentration equation derived here is just a special case of a much more general principle around the Boltzmann factor.
- We now need a number for E_F so we can evaluate our basic equations for the concentration of point defects. So are we now going to calculate formation or solution energies for all kinds of point defects?

No, we won't. It simply can't be done with pencil and paper. Just about now, it might be possible to get reliable numbers with the biggest computers around. It's not that we don't know how to do it; it's just too much number crunching. Since E_F comes up in an exponent, we need a rather precise number in order to avoid big uncertainties.
So far we actually do experiments and *measure* those numbers, as far as possible (which is not very far). It's not easy and we don't have as many reliable numbers as we would like.
Here are some examples:

Crystal	**H^F(V) [eV]**	**H^F(i) [eV]**
Ag	1,09	Sufficiently larger than H^F to make concentrations negligible
Al	0,66	
Au	0,94	
Cu	1,17	
Fe	1.4	
Ni	1.7	
Mo	3.0	
Pb	0.49	
Pt	1.49	
W	4.0	
Si	? 2,0 - 4,5 Still debated	? Small enough to make concentrations count.
Data adopted from: Helmut Mehrer, "Diffusion in Solids", Springer, 2007.		

As a rule of thumb, "normal" metals have vacancy formation energies **H^F(V)** roughly around **1 eV**, and self-interstitial formation energies **H^F(i)** a bit larger, say **1,5 eV**. No reliable numbers are known for self-interstitials. However, if their formation energies are just a few tenth of an eV larger than those of vacancies, the interstitial concentrations will be far smaller (factor **100** or more) than the vacancy concentration. In this case some interstitials will be around but are neither of any importance for diffusion nor experimentally accessible.
Another rule of thumb asserts that the maximum vacancy concentration close to the melting point is around **10^{-4}**

Now let's look at some graphs, representing the point defect concentration.

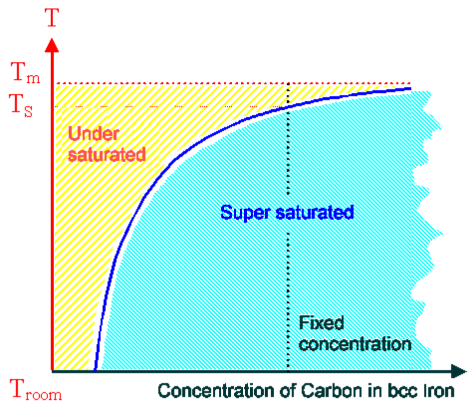


Direct representation
$c_V = \exp-(E_F/kT)$

Arrhenius representation
$\lg(c_V) = -(E_F/k) \cdot 1/T$

  - A direct plot is not very helpful. Except for temperatures close to the melting point, the curve is indistinguishable from the ***T***-axis. That's why we mostly plot equations with exponentials in a so-called **Arrhenius plot**. We simply take as new parameter the *logarithm* of the concentration, **$\lg(c_V)$**, and the reciprocal value of the absolute temperature, **$1/T$**. If we call them "***y***" and "***x***", respectively, the equation reads **$y = -(E_F/k) \cdot x$** and that is the equation of a straight line with slope **$-(E_F/k)$**.

- Now we interpret the equation as giving the equilibrium concentration for some foreign atom in some crystal, e.g. *carbon in bcc iron*. Then we typically plot it directly, but with the axes' switched as shown below:



Phase diagram plot of foreign atom concentration

  - The dotted line indicates some fixed concentration. Only concentrations *on* the blue line are the proper nirvana or equilibrium concentrations for the extrinsic point defect "carbon in iron" at the temperature ***T***. Since the concentration of foreign atoms typically can't change but has some fixed value, any point in the yellow region signifies that the crystal is *undersaturated*, i.e. has less foreign atoms dissolved than necessary for nirvana. There is absolutely nothing the crystal can do about undersaturations of extrinsic point defects, in contrast to the intrinsic point defects that it can make (or remove) "at will".
    In the blue region, the extrinsic point defect is *supersaturated*; there are too many. The crystal can and will do something about that: it can imprison the surplus atoms in a precipitate and thus remove them. What exactly a crystal does about supersaturations of extrinsic point defects is at the very core of steel technology (and about any other material-based technology).

- Hey, I'm just about to invent *phase diagrams* and thus get ahead of myself. So let's stop here. You might come back after you went through chapter 6.