

2. Properties of Point Defects

2.1 Intrinsic Point Defects and Equilibrium

2.1.1 Simple Vacancies and Interstitials

Basic Equilibrium Considerations

- We start with the most simple point defects imaginable and consider an **uncharged vacancy** in a simple **crystal** with a **base** consisting of only one atomic species - that means mostly metals and semiconductors.
- Some call this kind of defect "**Schottky Defect**", although the original **Schottky** defects were introduced for **ionic** crystals containing at least **two** different atoms in the base.
 - We call vacancies and their "opposites", the self-interstitials, **intrinsic point defects** for starters. **Intrinsic** simple means that these point defects can be generated in the ideal world of the ideal crystal. No external or **extrinsic** help or stuff is needed.
- To form **one** vacancy at constant pressure (the usual situation), we have to add some **free enthalpy** G_F to the crystal, or, to use the name commonly employed by the chemical community, **Gibbs energy**.
- G_F , the free enthalpy of vacancy formation, is defined as

$$G_F = H_F - T \cdot S_F$$

- The index **F** always means "**formation**"; H_F thus is the **formation enthalpy** of **one** vacancy, S_F the **formation entropy** of **one** vacancy, and **T** is always the absolute temperature.
- The formation **enthalpy** H_F in solids is practically indistinguishable from the formation **energy** E_F (sometimes written U_F) which has to be used if the volume and not the pressure is kept constant.
- The **formation entropy**, which in elementary considerations of point defects usually is omitted, must not be confused with the **entropy of mixing** or configurational entropy; the entropy originating from the many possibilities of arranging **many** vacancies, but is a property of a **single** vacancy resulting from the disorder introduced into the crystal by changing the vibrational properties of the neighboring atoms (**see ahead**).
- The next step consists of minimizing the free enthalpy **G** of the complete crystal with respect to the number n_V of the vacancies, or the concentration $c_V = n_V / N$, if the number of vacancies is referred to the number of atoms **N** comprising the crystal. We will drop the index "**V**" from now on because this consideration is valid for all kinds of point defects, not just vacancies.
- The number or concentration of vacancies in **thermal equilibrium** (which is not necessarily identical to **chemical equilibrium**!) then follows from finding the minimum of **G** with respect to **n** (or **c**), i.e.

$$\frac{\partial G}{\partial n} = \frac{\partial}{\partial n} (G_0 + G_1 + G_2) = 0$$

- with G_0 = Gibbs energy of the perfect crystal, G_1 = Work (or energy) needed to generate **n** vacancies = $n \cdot G_F$, and $G_2 = -T \cdot S_{\text{conf}}$ with S_{conf} = **configurational entropy** of **n** vacancies, or, to use another expression for the same quantity, the **entropy of mixing** **n** vacancies.
- We note that the partial derivative of **G** with respect to **n**, which should be written as $[\partial G / \partial n]_{\text{everything else} = \text{const.}}$ is, **by definition**, the **chemical potential** μ of the defects under consideration. This will become important if we consider chemical equilibrium of defects in, e.g., **ionic crystals**.
- The partial derivatives are easily done, we obtain

$$\frac{\partial G_0}{\partial n} = 0$$

$$\frac{\partial G_1}{\partial n} = G_F$$

- which finally leads to

$$\frac{\partial G}{\partial n} = G_F - T \cdot \frac{\partial S_{\text{conf}}}{\partial n} = 0$$

= chemical potential μ_V in equilibrium

▶ We now need to calculate the *entropy of mixing* or configurational entropy S_{conf} by using **Boltzmann's** famous formula

$$S = k_B \cdot \ln P$$

● With $k_B = k$ = Boltzmanns constant and P = number of different configurations (= [microstates](#)) for the same **macrostate**.

● The exact meaning of P is sometimes a bit confusing; activate [the link](#) to see why.

▶ A *macrostate* for our case is any possible combination of the number n of vacancies and the number N of atoms of the crystal. We obtain $P(n)$ thus by looking at the number of possibilities to arrange n vacancies on N sites.

● This is a standard situation in combinatorics; the number we need is given by the [binomial coefficient](#); we have

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

● If you have problems with that, look at [exercise 2.1-1](#) below.

▶ The calculation of $\partial S / \partial n$ now is straight forward in principle, but analytically only possible with two approximations:

● 1. *Mathematical Approximation*: Use the **Stirling formula** in its simplest version for the **factorials**, i.e.

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

● 2. *Physical Approximation*: There are always far fewer vacancies than atoms; this means

$$N - n \approx N$$

▶ As a first result we obtain "approximately"

$$T \cdot \frac{\partial S}{\partial n} \approx kT \cdot \ln \frac{N}{n}$$

▶ If you have any doubts about this point, you should do the following exercise.

Exercise 2.1-1

Derive the Formula for c_V

With $n/N = c_V$ = concentration of vacancies as defined before, we obtain the familiar formula

$$c_V = \exp \frac{G_F}{kT}$$

or, using $G_F = H_F - T S_F$

$$c_V = \exp \frac{S_F}{k} \cdot \exp - \frac{H_F}{kT}$$

For **self-interstitials**, exactly the same formula applies if we take the formation energy to be now the formation energy of a self-interstitial.

However, the formation enthalpy of self-interstitials is usually (but not necessarily) considerably larger than that of a vacancy. This means that their equilibrium concentration is usually substantially smaller than that of vacancies and is mostly simply neglected.

Some numbers are given in this [link](#); far more details are found [here](#). The one number to remember is:

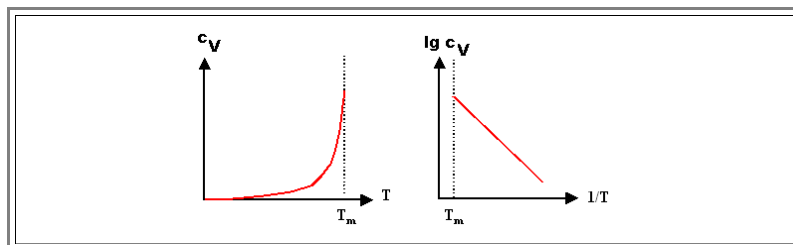
$$H_F(\text{vacancy}) \approx 1 \text{ eV}$$

in simple metals

It goes without saying (I hope) that the way you look at equations like this is via an **Arrhenius plot**. In the [link](#) you can play with that and refresh your memory

Instead of plotting $c_V(T)$ vs. T directly as in the left part of the illustration below, you plot the logarithm $\lg[c_V(T)]$ vs. $1/T$ as shown on the right.

In the resulting "Arrhenius plot" or "Arrhenius diagram" you will get a straight line. The (negative) slope of this straight line is then "**activation**" **energy** of the process you are looking at (in our case the formation energy of the vacancy), the y -axis intercept gives directly the pre-exponential factor.



Compared to simple formulas in elementary courses, the factor $\exp(S_F/k)$ might be new. It will be justified below.

Obtaining this formula by shuffling all the factorials and so on is not quite as easy as it looks - let's do a little fun exercise

Exercise 2.1-2

Find the mistake!

Like always, one can second-guess the assumptions and approximations: Are they really justified? When do they break down?

The reference enthalpy G_0 of the perfect crystal may not be constant, but dependent on the chemical environment of the crystal since it is in fact a sum over chemical potentials including all constituents that may undergo reactions (including defects) of the system under consideration. The concentration of oxygen vacancies in oxide crystals may, e.g., depend on the partial pressure of O_2 in the atmosphere the crystal experiences. This is one of the working principles of **ionics** as used for **sensors**. [Chapter 2.4](#) has more to say to that.

The simple equilibrium consideration does not concern itself with the kinetics of the generation and annihilation of vacancies and thus makes no statement about the **time required to reach equilibrium**. We also must keep in mind that the addition of the surplus atoms to external or internal surfaces, dislocations, or other defects while generating vacancies, may introduce additional energy terms.

- There may be more than one possibility [for a vacancy](#) to occupy a lattice site (for [interstitials](#) this is more obvious). This can be seen as a degeneracy of the energy state, or as additional degrees of freedom for the combinatorics needed to calculate the entropy. In general, an additional entropy term has to be introduced. Most generally we obtain

$$c = \frac{Z_d}{Z_0} \cdot \exp - \frac{G_F}{kT}$$

- with Z_d or Z_0 = [partition functions](#) of the system with and without defects, respectively. The link (in German) gets you to a short review of statistical thermodynamics including the partition function.

Let's look at two examples where this may be important:

- The energy state of a vacancy might be "degenerate", because it is charged and has trapped an electron that has a spin which could be either up or down - we have two, energetically identical "versions" of the vacancy and $Z_d/Z_0 = 2$ in this case.
- A double vacancy in a **bcc** crystals has more than one way of sitting at one lattice position. There is a preferred orientation along $\langle 111 \rangle$, and $Z_d/Z_0 = 4$ in this case.

Calculation and Physical Meaning of the Formation Entropy

The formation entropy is associated with a single defect, *it must not be mixed up with the entropy of mixing* resulting from many defects.

- It can be seen as the *additional* entropy or disorder added to the crystal with every additional vacancy. There is disorder associated with every single vacancy because the *vibration modes* of the atoms are disturbed by defects.
- Atoms with a vacancy as a neighbour tend to vibrate with lower frequencies because some bonds, acting as "springs", are missing. These atoms are therefore less well localized than the others and thus more "unorderly" than regular atoms.

Entropy residing in lattice vibrations is nothing new, but quite important outside of defect considerations, too:

- Several **bcc** element crystals are stable *only* because of the entropy inherent in their lattice vibrations. The $-TS$ term in the [free enthalpy](#) then tends to overcompensate the higher enthalpy associated with non close-packed lattice structures. At high temperatures we therefore find a tendency for a phase change converting **fcc** lattices to **bcc** lattices which have "softer springs", lower vibration frequencies and higher entropies. For details compare Chapter 6 of [Haasens book](#).

The *calculation* of the formation entropy, however, is a bit complicated. But the *result* of this calculation is quite simple. Here we give only the essential steps and approximations.

- First we describe the crystal as a sum of **harmonic oscillators** - i.e. we use the well-known harmonic approximation. From quantum mechanics we know the energy E of an harmonic oscillator; for an oscillator number i and the necessary quantum number n we have

$$E_{i,n} = \frac{h \omega_i}{2\pi} \cdot (n + 1/2)$$

We are going to derive the entropy from the all-encompassing **partition function** of the system and thus have to find the correct expression.

- The partition function Z_i of *one* harmonic oscillator as defined in statistical mechanics is given by

$$Z_i = \sum_n \exp - \frac{h \omega_i \cdot (n + 1/2)}{2\pi \cdot kT}$$

- The partition function of the *crystal* then is given by the *product* of all individual partition function of the $p = 3N$ oscillators forming a crystal with N atoms, each of which has three degrees of freedom for oscillations. We have

$$Z = \prod_{i=1}^p Z_i$$

From statistical thermodynamics we know that the free energy F (or, for solids, in a very good approximation also the free enthalpy G) of our oscillator ensemble which we take for the crystal is given by

$$F = -kT \cdot \ln Z = kT \cdot \sum_i \left(\frac{h\omega_i}{4\pi kT} + \ln \left(1 - \exp - \frac{h\omega_i}{2\pi kT} \right) \right)$$

Likewise, the entropy of the ensemble (for const. volume) is

$$S = - \frac{\partial F}{\partial T}$$

Differentiating with respect to T yields for the entropy of our - so far - ideal crystal without defects:

$$S = k \cdot \sum_i \left(- \ln \left(1 - \exp - \frac{h\omega_i}{2\pi \cdot kT} \right) + \frac{\frac{h\omega_i}{2\pi \cdot kT}}{\exp \left(\frac{h\omega_i}{2\pi \cdot kT} \right) - 1} \right)$$

Now we consider a crystal with just **one** vacancy. All **eigenfrequencies** of all oscillators change from ω_i to a new as yet undefined value ω'_i . The entropy of vibration now is S' .

The formation entropy S_F of our single vacancy now can be defined, it is

$$S_F = S' - S$$

i.e. the difference in entropy between the perfect crystal and a crystal with **one** vacancy.

It is now time to get more precise about the ω_i , the frequencies of vibrations. Fortunately, we know some good approximations:

At temperatures higher than the **Debye temperature**, which is the interesting temperature region if one wants to consider vacancies in reasonable concentrations, we have

$$\frac{h\omega_i}{2\pi} \ll kT$$

$$\frac{h\omega'_i}{2\pi} \ll kT$$

which means that we can expand $h\omega_i/2\pi$ into a series of which we (as usual) consider only the first term.

Running through the arithmetic, we obtain as final result, summing over all eigenfrequencies of the crystal

$$S_F = k \cdot \sum_i \ln \frac{\omega_i}{\omega_i^*}$$

This now calls for a little exercise:

Exercise 2.1-3

Do the Math for the formula for the formation entropy

For analytical calculations we only consider next neighbors of a vacancy as contributors to the sum; i.e. we assume $\omega = \omega^*$ everywhere else. In a linear approximation, we consider bonds as linear springs; missing bonds change the frequency in an easily calculated way. As a result we obtain (for all cases where our approximations are sound):

- S_F (single vacancy) $\approx 0.5 k$ (Cu) to $1.3 k$ (Au).
- S_F (double vacancy) $\approx 1.8 k$ (Cu) to $2.2 k$ (Au).

These values, obtained by assuming that only nearest neighbors of a vacancy contribute to the formation entropy, are quite close to the measured ones. (How formation entropies are measured, will be covered in [chapter 4](#)). *Reversing the argumentation*, we come to a major conclusion:

The formation entropy measures the spatial extension of a vacancy, or, more generally, of a zero-dimensional defect. The larger S_F , the more extended the defect will be because than more atoms must have changed their vibrations frequencies.

- As a rule of thumb (that we justify with a little exercise below) we have:
- $S_F \approx 1k$ corresponds to a truly atomic defect, $S_F \approx 10k$ corresponds to *extended defects* disturbing a volume of about 5 - 10 atoms.
- This is more easily visualized for interstitials than for vacancies. An "atomic" interstitials can be "constructed" by taking out *one* atom and filling in *two* atoms without changing all the other atoms appreciably. An interstitial extended over the volume of e.g. 10 atoms is formed by taking out 10 atoms and filling in 11 atoms without giving preference in any way to one of the 11 atoms - you cannot identify a given atom with the interstitial.

Vacancies or interstitials in elemental crystal mostly have formation entropies around 1k, i.e. they are "point like". There is a big exception, however: *Si does not fit this picture*.

- While the precise values of formation enthalpies and entropies of vacancies and interstitials in **Si** are still [not known with any precision](#), the formation entropies are definitely large and probably temperature dependent; values around 6k - 15k at high temperatures are considered. Historically, this led **Seeger** and **Chik** in 1968 to propose that in **Si** the self-interstitial is the dominating point defect and not the vacancy as in all other (known) elemental crystals. This proposal kicked off a major scientific storm; the dust has not yet settled.

Exercise 2.1-4

Calculate formation entropies

Multi Vacancies (and Multi - Interstitials by Analogy)

So far, we assumed that there is no interaction between point defects, or that their density is so low that they "never" meet. But interactions are the rule, for vacancies they are usually attractive. This is relatively easy to see from basic considerations.

Let's first look at **metals**:

- A vacancy introduces a disturbance in the otherwise perfectly periodic potential which will be screened by the free electrons, i.e. by a rearrangement of the electron density around a vacancy. The formation enthalpy of a vacancy is mostly the energy needed for this rearrangement; the elastic energy contained in the somewhat changed atom positions is comparatively small.
- If you now introduce a second vacancy next to the first one, part of the screening is already in place; the free enthalpy needed to remove the second atom is smaller.
- In other word: There is a certain **binding enthalpy** (but from now on we will call it energy, like everybody else) between vacancies in metals (order of magnitude: **(0,1 - 0,2) eV**).

Covalently bonded crystals

- The formation energy of a vacancy is mostly determined by the energy needed to "break" the bonds. Taking away a second atom means that fewer bonds need to be broken - again there is a positive binding energy.

Ionic crystals

- Vacancies are charged, this leads to Coulomb attraction between vacancies in the cation or anion sublattice, resp., and to repulsion between vacancies of the same nature. We may have positive and negative binding energies, and in contrast to the other cases *the interaction can be long-range*.

The decisive new parameter is the **binding energy E_{2V}** between two vacancies. It can be defined as above, but we also can write down a kind of "chemical" **reaction equation** involving the binding energy E_{2V} (the sign is positive for attraction):



- V in this case is *more* than an abbreviation, it is the "*chemical symbol*" for a vacancy.
 - If you have some doubts about writing down chemical reaction equation for "things" that are not atoms, you are quite right - this needs some [special considerations](#). But rest assured, the above equation is correct, and you can work with it exactly as with any reaction equation, i.e. apply reaction kinetics, the [mass action law](#), etc.
- Now we can do a calculation of the equilibrium concentration of **Divacancies**. We will do this in two ways.

First Approach: Minimize the total free enthalpy (as before):

- First we define a few convenient quantities

$$G_F(2V) = H_F(2V) - TS_F(2V)$$

$$H_F(2V) = 2H_F(1V) - E_{2V}$$

$$S_F(2V) = 2S_F(1V) + \Delta S_{2V}$$

- With ΔS_{2V} = **entropy of association** (it is in the order of $1k - 2k$ in metals), and E_{2V} = binding energy between two vacancies.

We obtain in complete analogy to single vacancies

$$c_{2V} = \frac{z}{2} \cdot \exp \frac{S_{2V}}{k} \cdot \exp - \frac{H_F(2V)}{kT}$$

$$c_{2V} = c_{1V}^2 \cdot \frac{z}{2} \cdot \exp \frac{\Delta S_{2V}}{k} \cdot \exp \frac{E_{2V}}{kT}$$

- The factor $z/2$ (z = coordination number = number of (symmetrically identical) next neighbors) takes into account the different ways of aligning a divacancy on one point in the lattice as already [noticed above](#). We have $z = 12$ for **fcc**, **8** for **bcc** and **4** for diamond lattices.

The formula tells us that the concentration of divacancies in *thermal equilibrium* is always *much* smaller than the concentration of single vacancies since $c_V \ll 1$. "Thermal equilibrium" has been emphasized, because in *non-equilibrium things are totally different!*

- Some typical values for metals close to their melting point are

$$c_{1V} = 10^{-4} - 10^{-3}$$

$$c_{2V} = 10^{-6} - 10^{-5}$$

In the *second approach*, we use the **mass action law**.

- With the reversible reaction $1V + 1V \rightleftharpoons V_2 + E_{2V}$ and by using the [mass action law](#) we obtain

$$\frac{(c_{1V})^2}{c_{2V}} = K(T) = \text{const} \cdot \exp - \frac{\Delta E}{kT}$$

- With ΔE = energy of the *forward reaction* (you have to be [extremely careful with sign conventions](#) whenever invoking mass action laws!). This leads to

$$c_{2V} = (c_{1V})^2 \cdot \text{const}^{-1} \cdot \exp - \frac{\Delta E}{kT}$$

- In other words: Besides the "**const.**⁻¹" we get the same result, but in an "easier" way.
- The only (small) problem is: You have to know something additional for the determination of reaction constants if you just use the mass action law. And that it is not necessarily easy - it involves the concept of the [chemical potential](#) and does not easily account for factors coming from additional freedoms of orientation. e.g. the factor **z/2** in the equation above.
- The important point in this context is that the reaction equation formalism also holds for **non-equilibrium**, e.g. during the cooling of a crystal when there are too many vacancies compared to equilibrium conditions. In this case we must consider **local** instead of **global** equilibrium, see [chapter 2.2.3](#).
- There would be much more to discuss for single vacancies in simple mono-atomic crystals, e.g. how one could calculate the formation enthalpy, but we will now progress to the more complicated case of point defects in crystals with *two* different kinds of atoms in the base.
- That is not only in keeping with the historical context (where this case came first), but will provide much food for thought.

Questionnaire

Multiple Choice questions to 2.1.1

Exercise 2.1-7

Quick Questions to 2.1.1