

2.1.3 Schottky Defects

Schottky- defects use the second *simple* possibility to maintain charge equilibrium in ionic crystals with two atoms in the base; they consist of the *two possible types of vacancies* which automatically carry opposite charge.

- Look at the [illustrations in the link](#) for visualizations of Schottky defects as a well as other defects in ionic crystals.
- You may call the *single* vacancy in metals a Schottky defect, if you like (some do), but that somehow misses the point.
- As pointed out in the context of [Frenkel defects](#), the vacancy in ionic crystal [carries a net charge](#) the same way a hole - a missing electron - carries a charge.

We have postulated, that charge neutrality must be maintained, but we have not proved it. Moreover, even for equal numbers of oppositely charged vacancies (or Frenkel defects for that matter), charge neutrality can only be maintained *on average*; on a scale comparable to the average distance between the point defects, we must have electrical fields which only (on average) cancel each other for larger volumes.

- The total formation energy therefore *must* contain some electrostatic energy part because we do have electrical fields around single point defects. The same is true for the interstitials in Frenkel defects or in the general case of mixed defects, and the consideration we are going to make for vacancies applies in an analogous way to interstitials, too.
- Moreover, the electrical field of one vacancy will be felt by other charged point defects, which means that there is also some electrostatic interaction between vacancies, or vacancies and other charged point defects. This interaction is stronger and has a much larger range than the elastic interactions caused by the lattice deformation around a defect.

Let's look at a relatively simple example. Here we are only going through the physical argumentation, the [details](#) of the calculations are contained in the link.

Calling the formation energy of the **anion vacancy** (= missing anion = *positively* charged vacancy) H^+ , the formation energy of the **cation vacancy** H^- , and the binding energy between close pairs H^B , we obtain for ΔG , the change in free enthalpy, upon introducing n^+ , n^- , and n^B anion vacancies, cation vacancies, and vacancy pairs, resp., is

$$\Delta G = \int \int \int \left(H^+ \cdot n^+(r) + H^- \cdot n^-(r) + [H^+ + H^- - H^B] \cdot n^B(r) + 1/2 \rho(r) V(r) - T S_n \right) dx dy dz$$

With $\rho(r)$ = local charge concentration, $V(r)$ = electrical potential, S_n = entropy of mixing; r is the space vector. The usual sum is replaced by an integral because the electrical potential is a smooth function and not strongly localized.

The number of point defects is now dependent on r . The (non-compensated) electrical charge stems from the charged vacancies, the net electrical charge density at any point r is thus given by

$$\rho(r) = e \cdot (n^+(r) - n^-(r))$$

With e being the elementary charge.

The electrostatic potential follows from the charge density via the [Poisson equation](#), we have

$$\Delta V(r) = - \frac{1}{\epsilon \epsilon_0} \cdot \rho(r)$$

With ϵ = dielectric constant of the material and ϵ_0 = vacuum constant

For equilibrium condition, ΔG must be minimal, i.e. we have to solve the variation problem

$$\Delta G = 0$$

for variations of the n 's. Using the conventional approximations one obtains solutions being rather obvious on hindsight:

$$n^+(r) = N \cdot \exp \frac{H^+ - e \cdot V(r)}{kT}$$

$$n^-(r) = N \cdot \exp \frac{H^- + e \cdot V(r)}{kT}$$

$$n^B = N \cdot z \cdot \exp \frac{H^+ + H^- - H^B}{kT}$$

For uncharged vacancies (where the $-eV$ term would not apply), this is the old result, except that now the divacancy is included.

We still must find the electrostatic potential as a function of space. It may be obtained by expressing the charge density now with the formulas for the charged vacancy densities given above, and then solving [Poissons equation](#). We obtain

$$\Delta V(r) = - \frac{e \cdot N}{\epsilon \epsilon_0} \cdot \left(\exp \frac{H^- + e \cdot V(r)}{kT} - \exp \frac{H^+ - e \cdot V(r)}{kT} \right)$$

This is a differential equation for the electrostatic potential; the problem now is a purely mathematical one: Solving a tricky differential equation.

It is now useful to introduce a "normalized" potential v by shifting the zero point in a convenient manner, and by utilizing a useful abbreviation. We define

$$v := \frac{e \cdot V(r) - 0.5(H^+ + H^-)}{kT}$$

$$x^{-2} := \frac{2 \cdot N \cdot e^2}{\epsilon \epsilon_0 \cdot kT} \cdot \exp \frac{H^+ + H^-}{kT}$$

This gives us a simple looking differential equation for our new quantities

$$\Delta v(r) = x^2 \cdot \sinh \{v(r)\}$$

x^{-1} has the dimension of a length, it is nothing (as it will turn out) but the (hopefully) well known [Debye length](#) for our case.

The "simple" differential equation obtained above, however, still cannot be solved easily. We must resort to the usual approximations and linearize, i.e. use the approximate relation $\sinh v \approx v$ for small v 's.

We also need some boundary conditions as always with differential equations. They must come from the physics of the problem.

The first guess is always to assume an infinite crystal with $v = 0$ for $x = \pm \infty$. The solutions for an infinite crystal are trivial, however, we therefore assume a crystal infinite in y - and z -direction, but with a surface in x -direction at $x = 0$; from there the crystal extends to infinity.

Now we have a one-dimensional problem with $r = x$. One general solution is (please appreciate that I didn't state "obvious solution")

$$v(x) = \frac{v_0^2 - \left(\frac{v_0'}{x}\right)^2 + \left(\frac{v_0' + v_0}{x}\right)^2 \cdot \exp[2x \cdot (x - x_0)]}{\left(v_0 + \frac{v_0'}{x}\right) \cdot \exp[x \cdot (x - x_0)]}$$

with $v_0 = v(x=0)$ and v_0' = integration constant which needs to be determined.

Cool, but we can do better yet:

If we do not want infinities, the divergent term $\exp[2x(x - x_0)]$ must disappear for x approaching infinity, this means

$$\lim_{x \rightarrow \infty} v(x) = 0 \Rightarrow v_0 = -\frac{v_0'}{x}$$

$$\Rightarrow v(x) = 2v_0 \cdot \exp -x \cdot x$$

x^{-1} obviously determines at which distance from a charged surface, or more generally, from *any* charge, the (normalized) potential (and therefore also the real potential) decreases to $1/e$ - this is akin to the definition of the [Debye length](#).

For a charged surface and $x \gg X$ (i.e. the bulk of the crystal) we obtain $v(x \gg X) = 0$, and therefore

$$V(r \gg X) = \frac{H^+ + H^-}{2e}$$

If we substitute $V(r)$ into the [equations for the equilibrium concentrations](#) above, we obtain the *final equations* for the vacancy concentrations in the case of Schottky defects

$$n^+ = n^- = N \cdot \exp - \frac{H^+ + H^-}{2kT}$$

i.e. both concentrations are identical, and *charge neutrality is maintained!*

The energy costs of not doing it would be very large! That is exactly what we expected all along, *except* that now we proved it.

More important, however, we now can calculate what happens if there are electrical fields that *do not have their origin in the vacancies themselves*, but may originate from fixed charges on e.g. surfaces and interfaces (including grain boundaries or precipitates), or from the outside world.

In this case the concentrations of the defects may be quite different from the equilibrium concentrations in a neighborhood "Debye Length" ($= X$) from the fixed charges.

We also see that we have (average) electrical neutrality in the bulk and a statistical distribution of vacancies there, *but this is not necessarily true in regions within one Debye length* X next to an external or internal surface.

Charged surfaces thus may change point defect concentrations within about one Debye length. And charged point defects, if they are mobile, may carry an electrical current or redistribute (and then changing potentials), if surface or interface charges change.

This is the basic principle of using ionic conductors (and, to some extent, semiconductors) for *sensor applications!*

The interaction between point defects, the electrical potential and the Debye length may be demonstrated nicely by plotting the relevant curves for different sets of parameters; this can be done with the following JAVA module.



We see that the [Debye length](#) as expressed in the formulas is strongly dependent on temperature. Only for high temperatures do we have enough charged vacancies so that their redistribution can screen a external potential on short distances. For **NaCl** we have, as an example, the following values

T [K]	χ^{-1} [cm]
1100	$1.45 \cdot 10^{-7}$
900	$4.55 \cdot 10^{-7}$
700	$2.83 \cdot 10^{-6}$
500	$8.21 \cdot 10^{-5}$
300	$2.20 \cdot 10^{-1}$

The large values, however, are unrealistic in real crystals, because grain boundaries, other charged defects, and especially impurities must also be considered in this region; they will always decrease the Debye length.

It's time for exercises!

[Questionnaire](#)

Multiple Choice questions to 2.1.3

[Exercise 2.1-8](#)

Quick Questions to 2.1.2 - 2.1.4