

Solution to [Exercise 2.1-5](#) "Do the Math for Mixed Point Defects"

For obvious reasons some of the symbols deviate a little from the symbols used in the text; e.g. we have h_{FP} instead of H_{FP} .

We start with the system of equations that came from [the mass action law](#)

$$\begin{aligned}c_V(C) \cdot c_i(C) &= \frac{N}{N} \cdot \exp\left(-\frac{h_{FP}}{kT}\right) \\c_V(A) \cdot c_V(C) &= \exp\left(-\frac{h_S}{kT}\right) \\c_V(C) &= c_V(A) + c_i(C)\end{aligned}$$

We start with the calculation of $c_V(C)$:

Inserting the first and the second equation into the third equation yields:

$$\begin{aligned}c_V(C) &= \frac{\exp\left(-\frac{h_S}{kT}\right)}{c_V(C)} + \frac{N}{N} \cdot \exp\left(-\frac{h_{FP}}{kT}\right) \\c_V^2(C) &= \exp\left(-\frac{h_S}{kT}\right) + \frac{N}{N} \cdot \exp\left(-\frac{h_{FP}}{kT}\right) \\c_V(C) &= \sqrt{\exp\left(-\frac{h_S}{kT}\right) + \frac{N}{N} \cdot \exp\left(-\frac{h_{FP}}{kT}\right)} \\c_V(C) &= \sqrt{\exp\left(-\frac{h_S}{kT}\right) + \frac{N}{N} \cdot \exp\left(-\frac{h_{FP}}{kT}\right) \cdot \exp\left(-\frac{h_S}{kT}\right) \cdot \exp\left(+\frac{h_S}{kT}\right)} \\c_V(C) &= \exp\left(-\frac{h_S}{2kT}\right) \cdot \sqrt{1 + \frac{N}{N} \cdot \exp\left(\frac{h_S - h_{FP}}{kT}\right)}\end{aligned}$$

That was the [first equation](#) for $c_V(C)$. Next we calculate $c_i(C)$.

Start with the third equation and eliminate $c_V(A)$ using the second. We have the final result after a series of mathematical manipulations:

$$\begin{aligned}c_i(C) &= c_V(C) - c_V(A) \\c_i(C) &= c_V(C) - \frac{\exp\left(-\frac{h_S}{kT}\right)}{c_V(C)} \\c_i(C) &= \frac{c_V^2(C) - \exp\left(-\frac{h_S}{kT}\right)}{c_V(C)} \\c_i(C) &= \frac{1}{c_V(C)} \cdot \left\{ \exp\left(-\frac{h_S}{kT}\right) + \frac{N}{N} \cdot \exp\left(-\frac{h_{FP}}{kT}\right) - \exp\left(-\frac{h_S}{kT}\right) \right\} \\c_i(C) &= \frac{1}{c_V(C)} \cdot \frac{N}{N} \cdot \exp\left(-\frac{h_{FP}}{kT}\right) \\c_i(C) &= \frac{\frac{N}{N} \cdot \exp\left(\frac{h_S}{2kT}\right) \cdot \exp\left(-\frac{h_{FP}}{kT}\right)}{\sqrt{1 + \frac{N}{N} \cdot \exp\left(\frac{h_S - h_{FP}}{kT}\right)}}\end{aligned}$$

That was the [third equation](#). Next we calculate $c_V(A)$.

Start with the third equation and eliminate $c_i(C)$ using the first, we obtain

$$c_V(A) = c_V(C) - c_i(C)$$

$$c_V(A) = c_V(C) - \frac{N}{N} \cdot \frac{\exp\left(-\frac{h_{FP}}{kT}\right)}{c_V(C)}$$

$$c_V(A) = \frac{c_V^2(C) - \frac{N}{N} \cdot \exp\left(-\frac{h_{FP}}{kT}\right)}{c_V(C)}$$

$$c_V(A) = \frac{1}{c_V(C)} \cdot \left\{ \exp\left(-\frac{h_S}{kT}\right) + \frac{N}{N} \cdot \exp\left(-\frac{h_{FP}}{kT}\right) - \frac{N}{N} \cdot \exp\left(-\frac{h_{FP}}{kT}\right) \right\}$$

$$c_V(A) = \frac{1}{c_V(C)} \cdot \exp\left(-\frac{h_S}{kT}\right)$$

$$c_V(A) = \frac{\exp\left(-\frac{h_S}{2kT}\right)}{\sqrt{1 + \frac{N}{N} \cdot \exp\left(\frac{h_S - h_{FP}}{kT}\right)}}$$

That's it. Nothing to it. ;-)

- Well, not exactly. I myself certainly cannot solve problems like this without making some dumb mistakes in breaking down the math. Almost everybody does.
- However, I usually notice that I made a stupid mistake because the result just can't be true. And I can, if I really employ myself, get the right result eventually - because I did some exercises like this before. *And that is why you should do it, too!*

As a last comment we may note that solving equations coming from the mass action law can become rather tedious very quickly - compare the [example in the link](#), which is about as simple as it could be.

Now we look at the limiting cases of pure Schottky or pure Frenkel disorder.

- For pure Frenkel disorder we must have $h_{FP} \ll h_S$, and $c_V(A) = 0$.
- For pure Schottky disorder we must have $h_{FP} \gg h_S$, and $c_i(C) = 0$.

For the first case - pure Frenkel disorder - just look at the expression

$$\left(1 + \frac{N}{N} \cdot \exp \frac{h_S - h_{FP}}{kT} \right)^{1/2}$$

- For $h_S \gg h_{FP}$, the exponential in this case is positive which means

$$\frac{N}{N} \cdot \exp \frac{h_S - h_{FP}}{kT} \gg 1$$

- So you may neglect the 1 in the above expression and replace the whole square root by

$$\frac{N}{N} \cdot \exp \frac{h_S - h_{FP}}{2kT}$$

- This gives for $c_i(C)$

$$c_i(C) = \frac{N}{N} \cdot \frac{\left(\exp \frac{h_S - 2h_{FP}}{kT} \right)^{1/2}}{\left(\exp \frac{h_S - h_{FP}}{kT} \right)^{1/2}} = \frac{N}{N} \cdot \exp - \frac{h_{FP}}{kT}$$

● This is the result as as it should be.

▮ With this we immediately obtain

$$c_V(C) = \frac{N}{N} \cdot \exp - \frac{h_{FP}}{2kT}$$
$$c_V(A) = 0$$

● This is so because

$$\frac{N}{N} \cdot \exp \frac{h_S - h_{FP}}{kT} \gg 1$$

▮ Contrariwise, if $h_S \ll h_{FP}$, $1 + \frac{N}{N} \cdot \exp[(h_S - h_{FP})/kT] \approx 1$ obtains.

● Because $h_S - 2h_{FP}$ is a large negative number we get

$$c_V(C) = \frac{N}{N} \cdot \exp \frac{h_S - 2h_{FP}}{2kT} \approx 0$$

● The expressions for $c_V(C)$ and $c_V(A)$ immediately reduce to the proper equation

$$c_V(C) = c_V(A) = \exp - \frac{h_S}{2kT}$$