# Solution to Exercise 2.1-5 "Do the Math for Mixed Point Defects"

Illustration

- *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

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

- We start with the calculation of ***c*$_V$(C)**:
  - Inserting the first and the second equation into the third equation yields:

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

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

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

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

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

- 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:

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

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

$$c_i(C) = \frac{c_V^2(C) - \exp\left(-\frac{h_S}{kT}\right)}{c_V(C)}$$

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

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

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

- 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

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

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

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

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

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

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

- 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 $\boldsymbol{h_{FP} << h_S}$, and $\mathbf{c_V(A) = 0}$.
    - For pure Schottky disorder we must have $\boldsymbol{h_{FP} >> h_S}$, **and** $\mathbf{c_i(C) = 0}$.
- 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 $h_S >> h_{FP}$, the exponential in this case is positive which means

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

- 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 $\mathbf{c_i(C)}$

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

- 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

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

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

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

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

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

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