Illustration

Solution to Exercise 2.1-6 "Enthalpy difference for the limiting cases of Schottky or Frenkel Defects"

- Calculate the ratio of the concentration of Schottky to Frenkel defect as a funtion of the enthalpy difference

- The equations for the concentrations of the point defects in the "mixed" case are

$$c_V(C) = c_S = \exp -\frac{H_S}{2kT} \cdot \left(1 + \frac{N'}{N} \cdot \exp \frac{H_S - H_{FP}}{kT}\right)^{1/2} = \exp -\frac{H_S}{2kT} \cdot K$$

$$c_V(A) = \exp -\frac{H_S}{2kT} \cdot \left(1 + \frac{N'}{N} \cdot \exp \frac{H_S - H_{FP}}{kT}\right)^{-1/2} = \exp -\frac{H_S}{2kT} \cdot K^{-1}$$

$$c_i(C) = c_{FP} = \frac{N'}{N} \cdot \exp \frac{H_S}{2kT} \cdot \exp -\frac{H_{FP}}{kT} \cdot \left(1 + \frac{N'}{N} \cdot \exp \frac{H_S - H_{FP}}{kT}\right)^{-1/2} = \frac{N'}{N} \cdot \exp \frac{H_S}{2kT} \cdot \exp -\frac{H_{FP}}{kT} \cdot K^{-1}$$

  - Note that $c_V(C)$ or $c_i(C)$ is, by definition, identical to the concentration c_S or c_{FP} of Schottky or Frenkel defects, respectively. If you have problems with this, refer to the link.
  - We abbreviated the root of the expression in square brackets by K for writing efficiency.

- The ratio c_S / c_{FP} is easy to obtain. The **K's** cancel, we are left with

$$\frac{c_S}{c_{FP}} = \frac{N}{N'} \cdot \exp -\frac{(H_S - H_{FP})}{kT} = \frac{N}{N'} \cdot \exp -\frac{\Delta H}{kT}$$

  - That is - of course - what we should have expected. The concentrations of Schottky and Frenkel defects are independent of each other and their relation could have been derived straight from the basic equations defining their equilibrium concentrations.

- Show in in particular, how large the difference must be if **90%** or **99%** of the defects are to be of one kind.

- We want to evaluate the equation for c_S/c_{FP} **= 0,011** or **= 0,001** (prevalence of Frenkel defects) and c_S/c_{FP} **= 90** or **= 99** (prevalence of Schottky defects).
  - For the difference ΔH of the formation enthalpies as defined above we obtain

$$\Delta H = -kT \cdot \left(\ln \frac{N'}{N} + \ln \frac{c_S}{c_{FP}}\right)$$

  - We have to define a value for N/N' ; we simply take this relation to be **1** or **0,1** as limiting cases.

- Values are easily obtained, we arrange them in a little table

$\frac{c_S}{c_{FP}}$		99	90	10	0,1	0,011	0,010
ΔH [eV]	$\frac{N}{N'} = 1$	–0,115	–0,112	–0,058	0,058	0,112	0,115
	$\frac{N'}{N} = 10$	–0,172	–0,169	–0,115	–0,0004	0,054	0,057

Discuss the result.

We have two interesting results:

- If the formation enthalpies of the two defect kinds differ by just about **1/10** of an **eV**, we are fully justified to consider that only one defect kind is present.
- The pre-exponential factor ***N'/ N***, which describes the differences in the basic geometry for interstitials relative to vacancies, accounts at most for about **1/20** of an **eV** if expressed in enthalpy differences.