Exercise 2.1-7

Quick Questions to

2.1. Intrinsic Point Defects and Equilibrium

2.1.1 Simple Vacancies and Interstitials

Here are some quick questions:

- The *answers* are sometimes (and possibly only indirectly) contained in the links.

- Write down the free enthalpy of a crystal with N atoms for
  - **1** vacancy
  - n vacancies
  in terms of the relevant quantities "G", "H", "S" for a single vacancy.
- The binomial coefficient as defined below gives the number of possibilities that one has in selecting n *different elements* from a given set of N elements with the condition that *different arrangements* of the same elements do *not* count ("Indistinguishable arrangements").
  Example: Set = **{1,2,3,4,5,6,7,8,9}**; i.e. **N = 9**, Selected elements = **{1,5,8}**, i.e. $n = 3$ = equivalent to **{5,1, 8}**; **{1,8,5}**, …
  How do you have to phrase the question for the vacancy arrangement so that the answer is immediately obvious?

$$\binom{N}{k} = \textbf{Binomial coefficient} = \frac{N!}{(N-k)! \cdot k!}$$

- Write the entropy of mixing with the binomial coefficient from above and then express it with the help of the Stirling equation.
- What is the chemical potential μ, and what must be valid for n vacancies *in equilibrium*?
- In the famous Boltzmann entropy equation $S = k_B \cdot \ln P$ the number P could be a probability for a state; i.e. a number between **0** and **1**, or the number of arrangements, i.e. a huge number. Explain why this doesn't matter.
- How is the formation entropy defined formally? Why and how is it connected to a single vacancy? What does it describe or measure in practical terms? How large is it (order of magnitude)?
- Give some numbers for formation enthalpies of vacancies in common crystals.
  Give some numbers for formation enthalpies of self-interstitials in common crystals.
  Draw some conclusion.
- What kind of difference $\Delta H = H_i - H_V$ of the formation enthalpy of vacancy and self interstitial produces a concentration ratio of $n_V/n_i > 10$? Do a quick and dirty estimation!
- Write down the basic equation for the concentration of single vacancies. Produce a graph of this equation with some numbers on the axes:
  - in a direct representation.
  - in an Arrhenius representation.
- Describe how you can tell from the n_V curves for *two* crystals in *one* Arrhenius plot which one has the larger H_V and S_V.
- What is the relation between the Boltzmann distribution (or Boltzmann factor) and the vacancy concentration? How does on have to pose the question for the vacancy concentration to obtain the result directly from this?
- Write down the free enthalpy n_{2V} and the resulting concentration c_{2V} for *divacancies* in a crystal with N atoms.
- Generalize for n_{xV} and c_{xV}, i.e. for *multiple vacancy clusters*. Use two different approaches for this.
- Discuss the relative concentration of c_{xV}/c_{1V} in *equilibrium.*
- Describe the use of the mass action law for obtaining vacancy concentrations.