2.1.5 Essentials to Chapter 2.1: Point Defect Equilibrium

In global equilibrium all crystals contain point defects with a concentration c_{PD} given by an Arrhenius expression of the form:

$$c_{PD} = A \cdot \exp - \frac{G_F}{kT} = A \cdot \exp \frac{S_F}{k} \cdot \exp - \frac{H_F}{kT}$$

- A is a constant around (**1 ....10**), reflecting the geometric possibilities to introduce **1 PD** in the crystal (**A = 1** for a simple vacancy).
- G_F, H_F, S_F are the free energy of formation, enthalpy (or colloquial "energy") of formation, and entropy of formation, respectively, of **1 PD**
- The entropy of formation reflects the disorder introduced by **1 PD**; it is tied to the change in lattice vibrations (circle frequency ω) around a **PD** and is a measure of the extension of the **PD**. It must not be confused with the entropy of mixing for many **PDs**!
- Formation enthalpies are roughly around **1 eV** for common crystals ("normal" metals); formation entropies around **1 k**.

$$S_F = k \cdot \sum_i \ln \frac{\omega_i}{\omega'_i}$$

Small **PD** clusters (e.g. di-vacancies) are still seen as **PDs**, their concentration follows from the same considerations as for single **PDs** to:

$$c_{2V} = \frac{z}{2} \cdot \exp \frac{S_{2V}}{k} \cdot \exp - \frac{H_{F(2V)}}{kT}$$

$$c_{2V} = \frac{z}{2} \cdot c_{1V}^2 \cdot \exp \frac{\Delta S_{2V}}{k} \cdot \exp - \frac{E_{2V}}{kT}$$

- The constant A for di-vacancies is half the coordination number z (= number of possibilities to arrange the axis of a di-vacancy ***dumbbell)***
- The formation enthalpy and entropy of a **PD** cluster can always be expressed as the sum of these parameters for single **PDs** minus a binding enthalpy E and a binding entropy ΔS
- The term c_{1V}^2 or c_{1V}^n for a cluster of n vacancies makes sure that the concentration of clusters is always far smaller than the concentration of single **PDs**.

The same relations can be obtained by "making" di-vacancies (or any cluster) by a "chemical" reaction between the **PDs** and employing the mass action law:

$$1V + 1V \Leftrightarrow V_{2V} + E_{2V}$$

$$\frac{(c_{1V})^2}{c_{2V}} = K(T) = \text{const} \cdot \exp - \frac{\Delta E}{kT}$$

- There are, however, some pitfalls in using the mass action law; we also loose any information about the factor A
- Most important in doing "defect chemistry" with mass action, is a proper definition of the "ingredients" to chemical reaction equations. A vacancy, after all, is not an entity like an atom that can exist on its own. More to that in chapter 2.4.

- Note: All of the above is generally valid for *all independent* **PD**s: "**A**" and "**B**" vacancies, interstitials, antisite defects,. ... .
  - *However:* If there are *additional restraints* (like charge neutrality), we may have to consider pairs of (atomic) **PDs** as one point defect; e.g. Frenkel or Schottky defects.
  - First principle" calculation show that charge neutrality can only be locally violated on length scales given by the *Debye length* of the crystal.

$$c_V = A_V \cdot \exp \frac{S_F^V}{k} \cdot \exp - \frac{H_F^V}{kT}$$

$$c_i = A_i \cdot \exp \frac{S_F^i}{k} \cdot \exp - \frac{H_F^i}{kT}$$

- Frenkel and Schottky defects are vacancy-interstitial or vacancy$^-$- vacancy$^+$ pairs in ionic crystals.
  - They are extreme cases of the general "mixed defect case" containing all possible **PDs** (e.g. **V^-, V^-, i^+, i^+**) while maintaining charge neutrality.
  - Usually, one finds either Frenkel defects or Schottky defects - if the respective formation enthalpies H_{Fre} or H_{Scho} differ by some **0.1 eV**, one defect type will dominate.
  - It is, however, hard to predict the dominating defect type from "scratch".

Frenkel defect:	**$V^- + i^+$**
Anti-Frenkel defect:	**$V^+ + i^-$**
Schottky defect:	**$V^- + V^+$**

Frenkel disorder in:	**AgCl, AgBr, CaF_2, BaF_2, PbF_2, ZrO_2, UO_2, ...**
Schottky disorder in:	**LiF, LiCl, LiBr, NaCl, KCL, KBr, CsI, MgO, CaO, ...**