

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:

- 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.

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

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

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

- 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 $c_1 v^2$ or $c_1 v^n$ for a cluster of n vacancies makes sure that the concentration of clusters is always far smaller than the concentration of single PDs.

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

$$c_{2V} = \frac{z}{2} \cdot c_1 v^2 \cdot \exp \frac{\Delta S_{2V}}{k} \cdot \exp - \frac{E_{2V}}{kT}$$

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:

- There are, however, some pitfalls in using the mass action law; we also lose 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.



$$\frac{(c_1 v)^2}{c_{2V}} = K(T) = \text{const} \cdot \exp - \frac{\Delta E}{kT}$$

Note: All of the above is generally valid for *all independent* PDs: "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, CaF₂, BaF₂, PbF₂, ZrO₂, UO₂, ...
Schottky disorder in: LiF, LiCl, LiBr, NaCl, KCl, KBr, CsI, MgO, CaO, ...