

5. Defects

According to the third law of thermodynamics, only in 0[K] crystal's entropy can reach its minimum. As a consequence, if the temperature is higher than 0[K] there must be imperfections in the structure, which are called defects. There are several types of defects:

- **Thermal defects**
 - Phonons
- **Planar defects**
 - Outer surfaces of the crystal
 - Inner surfaces of the crystal (e.g. grain boundaries)
 - Stacking faults
- **Linear defects**
 - Dislocations
- **Point defects**
 - Vacancies
 - Interstitial defects
 - Impurities
 - Frenkel pairs
 - Electronic defects

During our classes we will focus on the point defects, since they are the most important in terms of mass transport in the system because they can easily move inside the crystal. Concentration of such defects depends on the temperature and pressure in the system, which is why we call these defects thermodynamically reversible.

In the **stoichiometric compounds** (let's assume MeX as a general form of a compound), we can distinguish 5 "boundary" types of defects:

- **Schottky defects** - the defect forms when oppositely charged ions leave their lattice sites, creating vacancies. These vacancies are formed in stoichiometric units, to maintain an overall neutral charge in the ionic solid. Ions after leaving their sites, travel to the crystal surface, what leads to the crystal expansion. Such type of defects leads to decrease in crystal density.
- **Anti-Schottky defects** - the defect forms when equivalent number of oppositely charged ions travel from the crystal surface inside and locates in interstitial positions. Such type of defects leads to increase in crystal density.
- **Frenkel defects** - in general the defect forms when an atom or ion leaves its place in the lattice, creating a vacancy, and becomes an interstitial by lodging in a nearby location not usually occupied by an atom. During our classes by the "**Frenkel defect**" we will mean a defect in which interstitial cation is formed, while "**Anti-Frenkel defect**" will mean a defect in which interstitial anion is formed.
- **Antisite defects** - the defect forms when atoms/ions of different type exchange places

To describe defects we will need a proper notation. In or case we will use Kröger-Vink notation. Some basic symbols are included in the table below:

Defect	Symbol
Cation in a cation sublattice site	Me_{Me}
Anion in an anion sublattice site	X_X
Cation vacancy (no charge)	V_{Me}
Anion vacancy (no charge)	V_X
Cation vacancy (charge -2)	V_{Me}''
Anion vacancy (charge +2)	$V_X^{\bullet\bullet}$
Interstitial atom (Me)	Me_i
Interstitial atom(X)	X_i
Interstitial cation (Me) (charge +2)	$Me_i^{\bullet\bullet}$
Interstitial anion(X) (charge -2)	X_i''
Electron	e^-
Electron hole	h^\bullet

Now we can describe the process of defect creation for Schottky/Frenkel defects:

- Schottky defects



- Anti-Schottky defects



- Frenkel defects



- Anti-Frenkel defects



Here we can observe a very important rule: electroneutrality. Due to the conservation law, the charge in the system must be preserved, so always the overall charge on the left side of our equation must be equal to the overall charge on the right side, or in other words, total charge in our system must be equal zero:

$$\sum_i z_i c_i = 0 \quad (5.5)$$

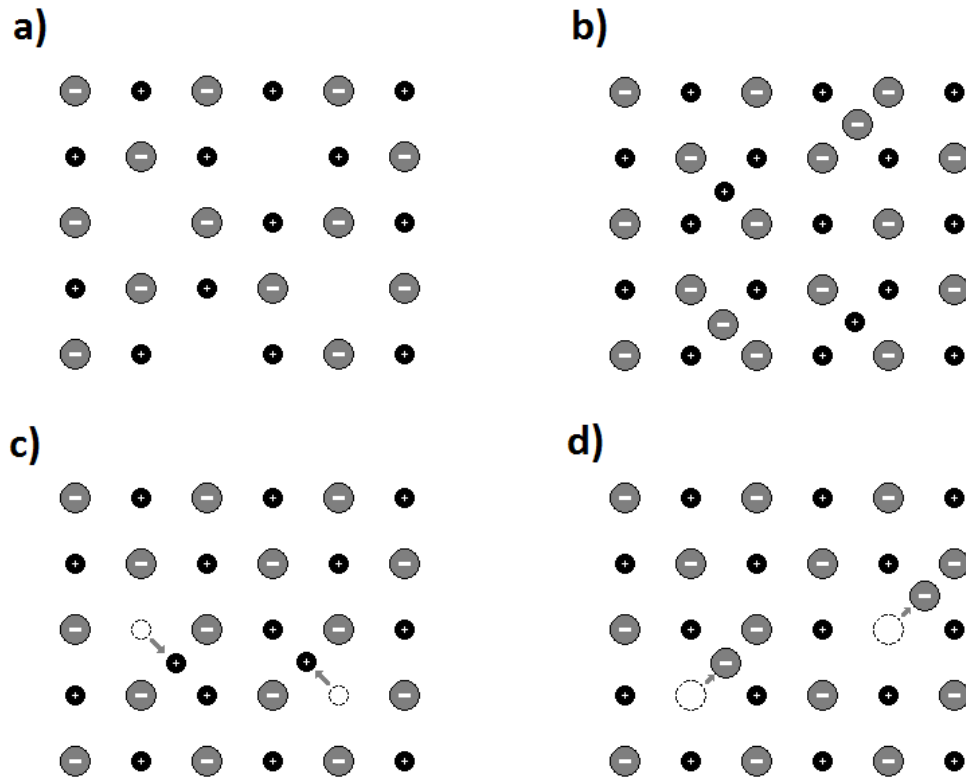


Fig.5.1. a) Schottky defects, b) Anti-Schottky, c) Frenkel defects, d) Anti-Frenkel defect

Similarly to the chemical reactions, we can use for defect formations processes, mass-action law which will allow us to obtain reaction constants (values in brackets are molar concentrations):

- Schottky defects

$$K_S = [V_{Me}''][V_X^{\bullet\bullet}] \quad (5.6)$$

- Anti-Schottky defects

$$K'_S = [Me_i^{\bullet\bullet}][X_i''] \quad (5.7)$$

- Frenkel defects

$$K_F = [Me_i^{\bullet\bullet}][V_{Me}''] \quad (5.8)$$

- Anti-Frenkel defects

$$K'_F = [X_i''] [V_X^{\bullet\bullet}] \quad (5.9)$$

Due to the electroneutrality of the system, on the basis of for example (5.8), we can write:

$$K_F^{1/2} = [Me_i^{\bullet\bullet}] = [V_{Me}''] \quad (5.10)$$

because the concentrations of positive and negative defects must be the same to preserve the charge.

There is one more thing that has to be remembered: **all types of defects are correlated**. It means that if for example we have concentration of vacancies of given component, the same concentration

have to be used in all reaction constants for given system. As a result, for a M_mX_n compound we can write:

$$K_F^m K_F'^n = K_S K_S' \quad (5.11)$$

For every chemical reaction, reaction constant is correlated with the change of Gibbs free energy by equation:

$$K = \exp \left(\frac{-\Delta G}{RT} \right) \quad (5.12)$$

Since:

$$\Delta G = \Delta H - T\Delta S \quad (5.13)$$

we can rewrite (5.12) as:

$$K = \exp \left(\frac{-\Delta H}{RT} \right) \exp \left(\frac{\Delta S}{R} \right) \quad (5.14)$$

After applying equation (5.14) to for example Frenkel defects (it can be done for the other types of defects as well), we will obtain:

$$K_F = \exp \left(\frac{-\Delta H_F}{RT} \right) \exp \left(\frac{\Delta S_F}{R} \right) \quad (5.15)$$

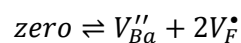
Where: ΔH_F - molar enthalpy of creation for Frenkel defects

ΔS_F - molar entropy change due to creation of Frenkel defect

Example 5.1

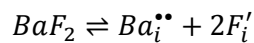
For BaF_2 , write down the defect formation processes (Schottky, Anti-Schottky, Frenkel, Anti-Frenkel) and suitable reaction constant for each. Write down electroneutrality condition.

- Schottky



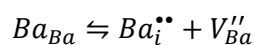
$$K_S = [V_F^\bullet]^2 [V_{Ba}'']$$

- Anti-Schottky



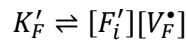
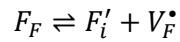
$$K_S' = [Ba_i^{\bullet\bullet}] [F_i']^2$$

- Frenkel



$$K_F = [Ba_i^{\bullet\bullet}] [V_{Ba}'']$$

- Anti-Frenkel



- Electroneutrality:

$$+2[Ba_i^{\bullet\bullet}] + 1[V_F^\bullet] - 2[V_{Ba}''] - 1[F_i'] = 0$$

Until now we were talking about stoichiometric compounds, now it's time to talk about **nonstoichiometric** ones. **The nonstoichiometric compounds are compounds in which there is excess or shortage of a given component of the crystal lattice.** In general we can define two types of compounds:

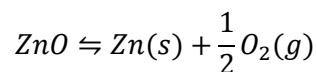
- **Compounds with dominance of more electropositive component**
 - Excess of a metal ($Me_{1+y}X$)
 - Shortage of an oxidant (MeX_{1-y})
- **Compounds with dominance of more electronegative component**
 - Shortage of a metal ($Me_{1-y}X$)
 - Excess of an oxidant (MeX_{1+y})

Defects created in nonstoichiometric compounds are called chemical defects (!!!).

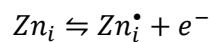
$Me_{1+y}X$ compounds

Typical compound from this group is ZnO. The process of defect formation can be described as follows:

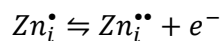
- In temperature higher than 0[K] the compound is unstable, what leads to decomposition on the surface (s) - solid state, (g)-gas



- Atoms of Zn "dissolve" in lattice and locates in interstitial positions forming Zn_i
- Interstitial atoms can be ionized... :



- ...even twice:



- Created electrons stay within the lattice (quasi-free electrons)

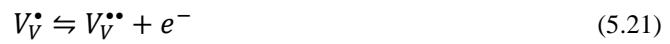
In general case process of defect formation in $Me_{1+y}X$ compounds can be described with equations:



There is one important logical rule which helps to remember this equations: if there is an excess of component, it must locate somewhere in a crystal lattice - sites are already occupied, so it must locate in interstitial positions.

MeX_{1-y} compounds

In general case process of defect formation in MeX_{1-y} compounds can be described with equations:



Again, there is a logic here. Because there is a shortage of a component, not all its sites are occupied, what means that some are empty - there are vacancies instead.

Me_{1-y}X compounds

In general case process of defect formation in Me_{1-y}X compounds can be described with equations:



MeX_{1+y} compounds

In general case process of defect formation in MeX_{1+y} compounds can be described with equations:



Reaction constants

Now let's focus on the reaction described by equations (5.16)-(5.18). Using mass-action law following constants can be derived:

$$K_{16} = [Me_i]p_{X_2}^{1/2} \quad (5.28)$$

$$K_{17} = \frac{[Me_i^\bullet][e^-]}{[Me_i]} \quad (5.29)$$

$$K_{18} = \frac{[Me_i^{\bullet\bullet}][e^-]}{[Me_i^{\bullet}]} \quad (5.30)$$

Let's assume, that we want to know, how the concentration of the electrons changes with the pressure. First, we will rewrite (5.28)-(5.30) in a following form:

$$[Me_i] = K_{16} p_{X_2}^{-1/2} \quad (5.31)$$

$$[Me_i^{\bullet}] = K_{17} \frac{[Me_i]}{[e^-]} = K_{16} K_{17} \frac{1}{[e^-] p_{X_2}^{1/2}} \quad (5.32)$$

$$[Me_i^{\bullet\bullet}] = K_{18} \frac{[Me_i^{\bullet}]}{[e^-]} = K_{18} K_{17} K_{16} \frac{1}{[e^-]^2 p_{X_2}^{1/2}} \quad (5.33)$$

Now we will use the electroneutrality condition:

$$[e^-] = [Me_i^{\bullet}] + 2[Me_i^{\bullet\bullet}] \quad (5.34)$$

After substituting equations (5.30) and (5.31) into (5.32) we will get:

$$[e^-] = K_{17} K_{16} \frac{1}{[e^-] p_{X_2}^{1/2}} + 2 K_{18} K_{17} K_{16} \frac{1}{[e^-]^2 p_{X_2}^{1/2}} \quad (5.35)$$

$$[e^-]^3 = K_{17} K_{16} p_{X_2}^{-1/2} ([e^-] + 2 K_{18}) \quad (5.36)$$

If we assume, that $[e^-] \gg 2 K_{18}$:

$$[e^-] = \sqrt{K_{17} K_{16} p_{X_2}^{-1/2}} \quad (5.37)$$

If we assume, that $[e^-] \ll 2 K_{18}$:

$$[e^-] = \sqrt[3]{2 K_{18} K_{17} K_{16} p_{X_2}^{-1/2}} \quad (5.38)$$

Because in general, the higher the temperature, the more interstitial ions will undergo reaction (5.18), equation (5.37) will be true in low temperatures, while equation (5.38) should be suitable for very high temperatures.