

2.4.2 Kröger-Vink Notation

How do we treat point defects in perfect analogy to atoms and molecules in chemical reaction equations? A very clear way was suggested by **Kröger** and **Vink**, it is therefore called "**Kröger-Vink notation**" or notation by "**structure elements**" - we already had a [glimpse of this](#).

- We define vacancies and interstitials as particles which occupy a defined site in a crystal and which may have a charge.
- Sites in a crystal are the points where the atoms, the interstitials, or the vacancies can be. For a crystal composed of two kinds of atoms we have, e.g., the "**A-sites**" and the "**B-sites**". An **A-atom** on an **A-site** we denote by **A_A**, a vacancy on a **B-site** is a **V_B**
- This leaves the interstitials out of the picture. We therefore simply name all possible interstitial sites with their own place symbol and write **A_i** or **B_i** for an **A-atom** or a **B-atom**, resp., on its appropriate interstitial site.
- An interstitial site *not* occupied by an interstitial atom then, by definition, is occupied by a vacancy and symbolized by **V_i**. A perfect crystal in the Kröger-Vink notation thus is full of vacancies on interstitial sites!

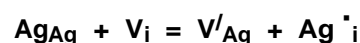
In order to facilitate book keeping with respect to the electrical charge, we only note the **excess charge relative to the neutral lattice**. Positive excess charge is marked by a point (e.g. **A[•]**), negative charge by a hyphen or dash or whatever you like to call it (e.g. **A[']**) to distinguish this relative charge from the absolute charge. If we consider a positively charged **Na⁺** ion in the **NaCl** lattice, we write **Na_{Na}** as long as it is sitting on its regular lattice position, i.e. without a charge symbol. If we now consider a vacancy on the **Na-site**, the **Na-ion** as interstitial, or a **Ca⁺⁺** ion on the **Na-site**, we write

- V[']_{Na}**, **Na[•]_i**, and **Ca[•]_{Na}** because this defines the charge relative to the neutral lattice.
- Running through all the possible combinations for our **NaCl** crystal with some **Ca**, we obtain the matrix

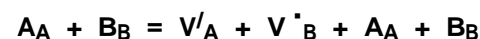
	A atom (Na ⁺)	B atom (Cl ⁻)	Vacancy	C atom (Ca ⁺⁺)
A-site	Na _{Na}	Cl ['] _{Na}	V ['] _{Na}	Ca [•] _{Na}
B-site	Na ^{••} _{Cl}	Cl _{Cl}	V [•] _{Cl}	Ca ^{•••} _{Cl}
i-site	Na [•] _i	Cl ['] _i	V _i	Ca ^{••} _i

What have we gained by this? We now can describe all kinds of structure elements - atoms, molecules and defects - and their reactions in a clear and unambiguous way *relative to the empty space*. Lets look at some examples

- Formation of [Frenkel defects](#) in, e.g., **AgCl**:



- We see why we need the slightly strange construction of a vacancy on an interstitial site.
- Formation of [Schottky defects](#) for an **AB** crystal



- The second equation simply considers the two dislodged atoms as a molecule that must be put somewhere.

This looks *good*. The question is, if we now can use the [mass action law](#) to determine equilibrium concentrations. If the Frenkel defect example could be seen as analogous to the chemical reaction **A + B = AB**, we could write a mass action law as follows:

$$\frac{[\text{Ag}_{\text{Ag}}] \cdot [\text{V}_{\text{i}}]}{[\text{V}_{\text{Ag}}^{\prime}] \cdot [\text{Ag}_{\text{i}}^{\bullet}]} = \text{const}$$

- with **[A]** meaning "concentration of **A**". The reaction constant is a more or less involved function of pressure **p** and temperature **T**, and especially the *chemical potentials* of the particles involved.

Unfortunately, this is wrong!

Why? Well, the notion of **chemical equilibrium** and thus the mass action law, at the normal conditions of constant temperature T and pressure p , stems from finding the minimum of the **free enthalpy** G (also called *Gibbs energy*) which in our case implies the equality of all chemical potentials. You may want to read up a bit on the concept of **chemical potentials**, this can be done in the link.

- In other words, we are searching for the equilibrium concentration of the particles n_i involved in the reaction, which, at a given temperature and pressure, lead to $dG = 0$.
- The equation $dG = 0$ can always be written as a **total differential** with respect to the variables dn_i :

$$dG = \frac{\partial G}{\partial n_1} \cdot dn_1 + \frac{\partial G}{\partial n_2} \cdot dn_2 + \dots$$

- The partial derivatives are defined as the **chemical potentials** of the particles in question and we always have to keep in mind that the **long version** of the above equation has a subscript at every partial derivative, which we, like many others, conveniently "forgot". If written correctly the partial derivative for the particle n_i reads (in **HTML** somewhat awkwardly),

$$\frac{\partial G}{\partial n_i} \Big|_{p, T, n_j \neq i = \text{const}}$$

- Meaning that T , p , and all **other** particle concentrations must be kept constant.

Only if that condition is fulfilled, a mass action equation can be formulated that involves all particles present in the reaction equation! And fulfilling the condition means that you can - at least in principle - change the concentration of **any** kind of particle (e.g. the vacancy concentration) **without** changing the concentration of all the other particles.

- This "**independence condition**" is automatically **not fulfilled** if we have additional constraints which link some of our particles. And such constraints **we do have** in the Kröger-Vink notation, as **alluded to before!**
- There is no way within the system to produce a vacancy, e.g. V_A without removing an **A**-particle, e.g. generating an A_i or adding another **B**-particle, B_B .

S... ! We now have a very useful way of describing chemical reactions, including all kinds of charged defects, but we cannot use simple thermodynamics! That is the point where other notations come in.

You now may ask: Why not introduce a notation that has it all and be done with it?

- The answer is: It could be done, but only by losing simplicity in describing reactions. And simplicity is what you need in real (research) life, when, in sharp contrast to text books, you do **not** know what is going on, and you try to get an answer by mulling over various possibility in your mind, or on a sheet of paper.

So "defects-in-ceramics" people live with several kinds of notation, all having pro and cons, and, after finding a good formulation in one notation, translate it to some other notation to get the answers required. We will provide a glimpse of this in the next subchapter.