

## 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<sub>A</sub>**, a vacancy on a **B-site** is a **V<sub>B</sub>**
- This leaves the interstitials out of the picture. We therefore simply name all possible interstitial sites with their own place symbol and write **A<sub>i</sub>** or **B<sub>i</sub>** 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<sub>i</sub>**. A perfect crystal in the Kröger-Vink notation thus is full of vacancies on interstitial sites!

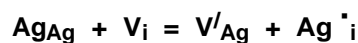
In order to facilitate book keeping with respect to the electrical charge, we only note the **excess charge relative to the neutral lattice**. Positive excess charge is marked by a point (e.g. **A<sup>•</sup>**), negative charge by a hyphen or dash or whatever you like to call it (e.g. **A<sup>'</sup>**) to distinguish this relative charge from the absolute charge. If we consider a positively charged **Na<sup>+</sup>** ion in the **NaCl** lattice, we write **Na<sub>Na</sub>** 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<sup>++</sup>** ion on the **Na-site**, we write

- V<sup>'</sup><sub>Na</sub>**, **Na<sup>•</sup><sub>i</sub>**, and **Ca<sup>•</sup><sub>Na</sub>** 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 <sup>+</sup> )	B atom (Cl <sup>-</sup> )	Vacancy	C atom (Ca <sup>++</sup> )
A-site	Na <sub>Na</sub>	Cl <sup>'</sup> <sub>Na</sub>	V <sup>'</sup> <sub>Na</sub>	Ca <sup>•</sup> <sub>Na</sub>
B-site	Na <sup>••</sup> <sub>Cl</sub>	Cl <sub>Cl</sub>	V <sup>•</sup> <sub>Cl</sub>	Ca <sup>•••</sup> <sub>Cl</sub>
i-site	Na <sup>•</sup> <sub>i</sub>	Cl <sup>'</sup> <sub>i</sub>	V <sub>i</sub>	Ca <sup>••</sup> <sub>i</sub>

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.