2.4.3 Schottky Notation and Working with Notations

Schottky Notation

The Kröger-Vink notation defined *structure elements* - atoms, molecules, point defects and even electrons and holes relative to *empty space*. Despite the problem with the inapplicability of the mass action law, this notation is in use throughout the scientific community dealing with point defects.

The other important notation - the "**Schottky notation**" or "**building element notation**" is defined as follows:

- Defects are defined relative to the *perfect crystal*.

- Charges are notated as in the Kröger-Vink way, i.e. *relative to the perfect crystal*. We again use the "▪" for positive (relative) charge and the "**/**" for (relative) negative charge.

To make things a bit more complicated, there are *two* ways of writing the required symbols, the "**old**" and the "**new**" Schottky notation.

- The "*old*" Schottky notation used special graphical symbols, like black circles or squares which are not available in **HTML** anyway.

- So we only give the *new* Schottky notation in direct comparison with the Kröger-Vink notation, again for the example **NaCl** with **Ca** impurities, i.e.
  $A = Na^+, B = Cl^-, C = Ca^{++}.$

	A on B site	A-vacancy	A-interstitial
Schottky (new)	Na|Cl| ⋅⋅	|Na|$^/$	Na ⋅
Kröger-Vink	Na_{Cl} ⋅⋅	$V_{Na}{}^/$	Na_i ⋅

So far, the difference between the Schottky notation and the Kröger-Vink notation seems superficial. The important difference, however, becomes clear upon writing down defect reactions. Lets look at the formation of Frenkel and Schottky defects in the two notations.

|	Frenkel defects	Schottky defects
Schottky (new)	$\|Ag\|^/ + Ag\ ^\bullet = 0$	$\|Ag\|^/ + \|Cl\|^\bullet + AB = 0$
Kröger-Vink	$Ag_{Ag} + V_i = V^/{}_{Ag} + Ag\ ^\bullet{}_i$	$Ag_{Ag} + Cl_{Cl} = V^/{}_{Ag} + V\ ^\bullet{}_{Cl} + AB$

In words, the Schottky notation says:

- For *Frenkel defects*: A negatively charged **Ag** vacancy plus a positively charged **Ag** interstitial gives zero.

- For *Schottky defects*: A neatively charged **Ag** vacancy plus a positively charged **Cl** vacancy plus a **AgCl** "lattice molecule" gives zero.

This is clear enough for these simple cases, but not as clear and easy as the Kröger-Vink notation.

But, and that is the big advantage, we can apply the mass action law directly to the reactions in the Schottky notation.

- This is not directly obvious. After all, Frenkel defects, e.g., do not only *appear* to be linked (where there is an interstitial, there is also a vacancy), but actually *are* linked if the defects are charged (otherwise there would be neither net charge in the crystal, or we would have to invoke electrons or holes to compensate the ionic charge - but then we would have to include those into the reaction equation).

- *Theoretically*, however, you can introduce one more vacancy or one more interstitial into a crystal with a given concentration of each and look at the change of the free enthalpy, i.e. the chemical potential of the species under consideration. The independence condition does not require that it is *easy* to change individual concentrations, only that it is *possible*!

- If you do neglect the energy associated with charge (i.e. you look at the chemical and not the electrochemical potential), the answers you get will not contain the coupling between the defects and you have to consider that separately. We will see how this works later.

Now, why don't we use just the Schottky notation and forget about Kröger-Vink? We asked that question before; the answer hasn't changed: If we look at more complicated reactions, e.g. between point defects in an ionic crystal, a gas on its outside, and with electrons and holes for compensating charges, it is *much easier* to formulate possible reaction in the Kröger-Vink notation. The trick now is, to convert your reaction equations from the Kröger-Vink structure elements to the Schottky building elements. There is a simple recipe for doing this.

Converting Kröger-Vink to Schottky

All we have to do, is to combine the two *structure elements* of Kröger-Vink that refer to the *same place* in the lattice and view the combination as a *building element*.

Lets first look at an example and then generalize. Consider the Frenkel disorder in **AgCl**. Using structure elements, we write

$$ Ag_{Ag} + V_i = V^/_{Ag} + Ag^._i $$
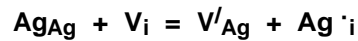
- Combining the terms referring to the same place in the lattice (with the actual defects always as the first term in the combination) yields

$$ (V^/_{Ag} - Ag_{Ag}) + (Ag_i - V_i) = 0 $$
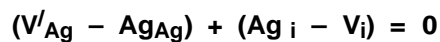
- Now all we have to do is to write down the corresponding Schottky notation and identify the terms in brackets with the Schottky structure elements. We see that

$$ (V^/_{Ag} - Ag_{Ag}) = |Ag|^/ $$

$$ (Ag^._i - V_i) = Ag^. $$

We can generalize this into a "**translation table**":

	A on B site	A-vacancy	A-interstitial	AB molecule	C on B site	Free electron	hole
	All defects neutral					*Always charged*	
Schottky (new) *Building elements*	A|B|	|A|	A	AB	C|B|	$e^/$	$h^.$
Kröger-Vink *Structure elements*	A_B	V_A	A_i	AB	C_B	$e^/$	$h^.$
Combined structure elements = Building elements	$A_B - B_B$	$V_A - A_A$	$A_i - V_i$	AB	$C_B - B_B$	$e^/$	$h^.$

The General Recipe for Point Defect Reactions and First Example

If you now stick to the full formalism, what you do is:

- **1.** Write down the possible reaction with structure elements (= Kröger-Vink notation).
- **2.** Translate that to building elements (= Schottky notation).
- **3.** Consider charges and check for electroneutrality. If the sum of all charges is not zero, search for mistakes and if there are none, *throw in holes or electrons*, as your system provides.
- **4.** Use the mass action law with the final (building element) equation (including holes or electrons).
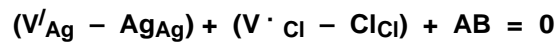
First Example: Schottky Defects

We take the Schottky defect as a fitting elementary example and go through the movements:
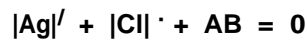
- **1.** Kröger-Vink *structure element* equation

$$Ag_{Ag} + Cl_{Cl} = V'_{Ag} + V^{\cdot}_{Cl} + AB$$

- After rearranging (remember, the defect comes first!) so we can use the translation table, we have

$$(V'_{Ag} - Ag_{Ag}) + (V^{\cdot}_{Cl} - Cl_{Cl}) + AB = 0$$

- **2.** Switch to *building elements* using the the expressions in brackets; we have

$$|Ag|' + |Cl|^{\cdot} + AB = 0$$

- **3.** *Charge neutrality* demands

$$\Sigma(\text{pos. charge}) = \Sigma(\text{neg. charge})$$

$$[|Ag|'] = [|Cl|^{\cdot}]$$

- **4.** *The mass action* law now gives

$$\frac{[|Ag|'] \cdot [|Cl|^{\cdot}]}{[AB]} = \exp{-\frac{\Sigma \nu_i \mu_i^0}{kT}}$$

- And this leads to

$$[|Ag|'] = [|Cl|^{\cdot}] = [AB] \cdot \exp{-\frac{\Sigma \nu_i \mu_i^0}{kT}}$$

- With μ_i = standard chemical potentials of the two vacancies and a lattice molecule, resp., and ν_i = stoichiometric coefficients of the reaction (**1**,**1**, and **− 1** in our case).

This sure looks strange compared to the formula derived in the "physical" way. *But it is the same.* Lets see why.

- First, the activity (or concentration) of the lattice molecule **AB** is simply **[AB] = 1** since it is nothing but the number of mols of **AgCl** molecules in one mol of **AgCl**; i.e. it is **= 1**. This gives us

$$[|Ag|'] \cdot [|Cl|^{\cdot}] = \exp{\frac{\Sigma \nu_i \mu_i^0}{kT}}$$

- Now lets look at the energies in the exponent. As always, the energy scale is relative. From whatever zero point you measure your energy to make an **Ag** vacancy or a **Cl** vacancy, you must subtract the energy of the **AB** molecule as measured in that system. If you take it to be zero - which then defines the energy origin of your standard system - the standard chemical potentials of the two vacancies are just the usual formation energies.

Note that as in treatment given before, the mass action law alone does *not* specify the vacancy concentration, *only their product.*

- Only invoking the electroneutrality condition, which demands **[|Ag|'] = [|Cl|$^{\cdot}$]**, allows to compute the individual concentrations. Writing **H$^+$** and **H$^−$** for the formation enthalpies of the positively or negatively charged vacancy, resp., we obtain the familiar result

$$[|Ag|^{/}] = [|Cl|^{\cdot}] = \exp - \frac{H^+ + H^-}{2kT}$$

Second Example: Frenkel Defects

First we write down the reaction with *structure elements* (= Kröger-Vink notation).
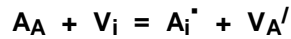
$$A_A + V_i = A_i^{\cdot} + V_A^{/}$$

- After rearranging (remember, the defect comes first!) so we can use the translation table, we have

$$(A_i^{\cdot} - V_i) + (V_A^{/} - A_A) = 0$$

- **2.** The expressions in brackets are the *building elements*, we have

$$|A|^{\cdot} + |A|^{/} = 0$$

- **3**. *Charge neutrality* demands

$$|A|^{\cdot} = |A|^{/}$$

- **4.** *The mass action* law now gives

- *A problem*? What are we going to do with the "**0**"? Well, there really is no problem with the zero - just take the mass action law as it is

$$\prod(a_i)^{\nu_i} = \exp - \frac{G^0}{kT} = K = \text{Reaction Constant}$$

- Nowhere was it required that in the product there must be terms with negative stoichiometry coefficients ν_i. This gives us

$$[A^{\cdot}] \cdot [|A|^{/}] = \exp \frac{G_F}{kT}$$

- And we identify **G^0** with the formation energy **G_F** of a Frenkel pair as before.

- Together with the charge neutrality condition we have

$$[A^{\cdot}] = [|A|^{/}] = \exp - \frac{G_F}{2kT}$$

- *almost* the familiar result - *except that we do not have the factor $(N/N')^{1/2}$*.

- OK - we do have a problem, but *not with the zero*. Where did we lose the factor $(N/N')^{1/2}$?

Lets look at equilibrium another way. We do not involve the mass action law but go one step back to the equilibrium condition for the chemical potentials: $\mu_{A^{\cdot}} = \mu_{|A|^{/}}$. We write the chemical potentials in the standard form and obtain

$$\mu_{A^\bullet} = \mu^0_{A^\bullet} + kT \cdot \ln \frac{n_{A^\bullet}}{N'}$$

$$\mu_{|A|/} = \mu^0_{|A|/} + kT \cdot \ln \frac{n_{|A|/}}{N}$$

🔵 For equilibrium we now obtain (if you wonder at the n/N and n/N, consult the link)

$$n_{A^\bullet} \cdot n_{|A|/} = N \cdot N' \cdot \exp - \frac{\mu^0_{A^\bullet} + \mu^0_{|A|/}}{kT}$$

🔵 Charge neutrality tells us that

$$n_{A^\bullet} = n_{|A|/} = n_{FP}$$

🔵 For the concentration of Frenkel pairs $c_{FP} = n_{FP}/N$ we now obtain the correct old formula

$$c_{FP} = \left(\frac{N}{N'}\right)^{1/2} \cdot \exp - \frac{\mu^0_{A^\bullet} + \mu^0}{2kT} = \left(\frac{N}{N'}\right)^{1/2} \cdot \exp - \frac{G_{FP}}{2kT}$$

🚩 *Aha!* Applying the mass action law uncritically causes a problem: The standard chemical potentials of vacancies and interstitials were for *different* standard conditions:

🔵 In one case (the *vacancies*) the standard condition was for adding N vacancies to the system, in the other case (the *interstitials*) it was for adding $N' = N \cdot I$ interstitials (and I being some factor taking into account that there are more positions for interstitials than for vacancies in a crystal).

🔵 If that appears to be incredibly complicated and prone to errors - *that's because it is*! But take comfort: You get used to it, and working with it is not all that difficult after overcoming an intial "energy barrier".

Some Remarks to Practical Work

🚩 Many books and other texts to not dwell extensively on the fine differences between notations, problems with the standard condition in the chemical potentials, meaning of reaction equations and so on - they write down a reaction equation, in the worst case a mix of Kröger-Vink and Schottky notations, throw in electrons or holes right away to achieve charge neutrality, and write down the mass action law in the form

$$\prod_i (a_i)^{\nu_i} = \exp \frac{G}{kT} = K(T) = const \cdot \exp - \frac{G}{kT}$$

🔵 And not much attention is given to the constant $K(T)$ in front of the exponential.

🔵 Even though it's *faulty thermodynamics*, let's see what happens if we do that for Frenkel defects in the Kröger-Vink notation:

🚩 The reaction equation was

$$Ag_{Ag} + V_i = V'_{Ag} + Ag^\bullet_i$$
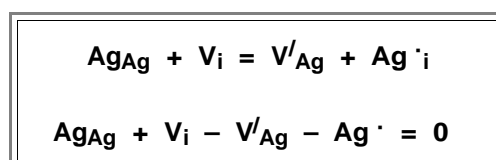
$$Ag_{Ag} + V_i - V'_{Ag} - Ag^\bullet = 0$$

🔵 The mass action law uncritically applied gives

$$\frac{[Ag_{Ag}] \cdot [V_i]}{[V^/] \cdot [Ag^{\cdot}]} = const \cdot exp - \frac{G'}{kT}$$

- As long as the defect concentration is small compared to the concentrations of atoms and lattice sites, we may simply equate

$$[Ag_{Ag}] = 1$$
$$[V_i] = 1$$

- Which leaves us with

$$[V^/] \cdot [Ag^{\cdot}] = const \cdot exp - \frac{G}{kT}$$

- With $G = - G'$, but that is irrelevant - we simply know that the exponential always has a minus sign for the reactions we are interested in and that G must be the formation enthalpy of a Frenkel pair.

That is the correct result, expressed in Kröger-Vink terms. What that means is that you don't have to worry all that much about the finer details as long as you are not terribly interested in the exact value of the constant in front of the exponential - you will mostly get your reaction equation right!

- Luckily, there are only a few fundamental reaction equations involving point defects - everything else can be expressed as linear combinations of the fundamental reactions (like Frenkel and Schottky defect equilibrium) - after some initiation, you will feel quite comfortable with defect reactions.

As shown above for Frenkel defects, it is often advisable not to use the mass action law directly, but to go one step back and use the equilibrium condition for the chemical potentials. This gives not only a clearer view of what constitutes the standard conditions, but also circumvents a number of other problems associated with the law of mass action (if you really want to know, consult the advanced module accessible by the link).