2.4.4 Systematics of Defect Reactions in Ionic Crystals and Brouwer Diagrams

- There are essentially three fundamental situations for defects in ionic crystals.
  - *Intrinsic defects*; i.e. the defects present in the bulk of a crystal in thermodynamic equilibrium. This includes the Frenkel and Schottky defects considered before, but also some other kinds not yet discussed.
  - *Defect Doping* ; i.e. the intentional manipulation of defect types and concentrations by the incorporation of specific impurities into the (bulk of the) crystal.
  - *Defect reactions at interfaces*, e.g. the incorporation of atoms or molecules from the "outside" into the crystal via defects - or the opposite, the loss of crystal atoms to the outside world generating defects in the crystal.
- There are not always clear distinctions, but lets look at these three cases separately for a start.

Intrinsic Defects in Ionic Crystals

- This case includes all defect situations that one could find in a perfect ionic crystal. Besides Schottky and Frenkel disorder or any mixture of the two, we could have many more defects - any combination of interstitials and vacancies for any kind of atom in the crystal is admissible.
  - One example: In an **AB** crystal, instead if two oppositely charged vacancies (the Schottky defects), we could also have two interstitials of the two kinds of atoms carrying different charge.
  - This kind of defect is called an "**Anti Schottky defect**", it would be formed according to the (Kröger-Vink) reaction

$$\boxed{\mathbf{AB + 2V_i = A_i^{\cdot} + B_i^{/}}}$$

  - Following our recipe, we obtain after rearranging and "translating" to Schottky notation:

$$\boxed{\begin{gathered}\mathbf{(A_i^{\cdot} - V_i) + (B_i^{/} - V_i) = AB} \\ \mathbf{A^{\cdot} + B^{/} = AB}\end{gathered}}$$

- This is essentially the same result as for the regular Schottky defects. However, in using the mass action law, we would have to use the formation energies for interstitials (and take care of the additional degrees of freedom for arranging interstitials as in the case of Frenkel defects).
  - In reality, the formation energies of interstitials are mostly larger than those for vacancies; this is certainly true for the "big" negatively charged anion interstitial.
  - Anti Schottky defects therefore have not been observed as the dominating defect type so far. But they are not only perfectly feasible, but also always present - only their concentration is so small that it can not be measured; consequently they do not play a role in anything interesting connected with defects.
- We could also conceive of "**anti site defects**", i.e. **A**-atoms on **B**-places and vice versa; $\mathbf{A_B}$ and $\mathbf{B_A}$, of combinations like a $\mathbf{V_A}$ and $\mathbf{A_B}$, and of plenty more intrinsic defects for more complicated crystals, e.g. for $\mathbf{YBa_2Cu_3O_7}$ (the famous first high temperature superconductor with a critical temperature larger than the boiling point of liquid $\mathbf{N_2}$).
  - We could, moreover, include isoelectronic impurity atoms into the list; e.g. **K** instead of **Na**; **Ba** instead of **Ca**, or **F** instead of **Cl**, which could be incorporated into a crystal without the need to change anything else. A little dirt, after all, is always "intrinsic", too.
  - And *all* the reactions that are conceivable will *occur*. The only difference is that some might be frequent and some might be rare - and it is often sufficient to only consider the dominating reaction.
- This teaches us a *major lesson*, especially with respect to the upcoming paragraphs
  - There are far too many defect types and reactions principally possible in simple (ionic) crystals (not to mention complicated ones) for a priori treatments of all possible effects. We must invoke some *additional* information (such as anion interstitials being unlikely) to simplify the situation to a level where it can be handled.
  - For the intrinsic defects mentioned so far, this was easy and has been done all along. It will become an important guiding principle for the other two cases, however.
- But we are not yet done with intrinsic defects: If we look at *semiconducting* ionic or compound crystals, we may have to include *electrons and holes* in our defect systematization. Let's look at this, first assuming that electrons and holes are the *only* defects.
  - Implying a band structure and always using the Boltzmann approximation for the tail of the proper Fermi distribution, we might denote the generation of an electron in the conduction band in complete analogy to the Kröger-Vink system.by

$$\mathrm{e_V}^{/} + \mathrm{h^{\cdot}_C} = \mathrm{e}^{/}_{\mathrm{C}} + \mathrm{h^{\cdot}_V}$$

- Rearranging gives

$$(\mathrm{e_C}^{/} - \mathrm{h^{\cdot}_C}) + (\mathrm{h^{\cdot}_V} - \mathrm{e}^{/}_{\mathrm{V}}) = 0$$

- The obvious translation to Schottky notation yields

$$\mathrm{e}^{/} + \mathrm{h}^{\cdot} = 0$$

- Adding electroneutrality, i.e. $\mathbf{e}^{/} = \mathbf{h}^{\cdot}$, makes the analogy to Frenkel defects complete, and we obtain

$$\mathrm{e}^{/} = \mathrm{h}^{\cdot} = c \cdot \exp - \frac{E}{\mathrm{k}T}$$

- There is a big difference, however. We know that the constant c in front of the exponential is the effective density of states N_{eff} (or more precisely $[N^{\mathrm{C}}{}_{\mathrm{eff}} \cdot N^{\mathrm{V}}{}_{\mathrm{eff}}]^{1/2}$) and the formation energy is given by $E = E_{\mathrm{g}}/2$, with E_{g} = band gap.
  - This is knowledge that comes from quantum theory and there is simply *no way* to deduce this from classical thermodynamics.
- However, the mass action law is based on considering the minimum of the free enthalpy - a principle that is always valid. It is only the chemical potential of electrons and holes that cannot be directly expressed in the standard form. Mass action, however, remains valid.

Defects and Doping

- Lets now consider some typical doping reactions. Most common and important is the doping of semiconductors with substitutional impurities, i.e. **P**, **As**, or **B** in **Si**.
  - If we call the substitutional dopant atoms **D** (for **D**onor) or **A** (for **A**cceptor), we may express the doping reaction, i.e. the exchange of electrons or holes with the bands, as follows

$$\mathrm{D} = \mathrm{D}^{\cdot} + \mathrm{e}^{/}$$

$$\mathrm{A} = \mathrm{A}^{/} + \mathrm{h}^{\cdot}$$

  - Kröger-Vink and Schottky notation are identical in this case (figure it out!), and we have the mass action law

$$\frac{[\mathrm{D}]}{([\mathrm{D}^{\cdot}] \cdot [\mathrm{e}^{/}])} = k_{\mathrm{D}}$$

$$[\mathrm{e}^{/}] = \frac{[\mathrm{D}]}{[\mathrm{D}^{\cdot}]} \cdot k_{\mathrm{D}}{}^{-1}$$

  - Lets consider a simple situation with just one type of doping, say donors, with a concentration **[D]**, giving us $[\mathrm{e}^{/}] = k_{\mathrm{D}}{}^{-1}[\mathrm{D}]/[\mathrm{D}^{\cdot}]$ as stated above. But we have no holes so far. We need some other reaction to produce holes, what comes to mind is

$$h^{\cdot} \; + \; D \; = \; D^{\cdot}$$

$$\Rightarrow \quad \frac{h^{\cdot} \cdot [D]}{[D^{\cdot}]} \; = \; k_A$$

- Can we get the "universal" mass action law for semiconductors, as we know it from semiconductor physics from this, i.e.

$$[e^{/}] \cdot [h^{\cdot}] \; = \; n_i^2$$

  - If we form the product with the equation from above we obtain

$$[h^{\cdot}] \cdot [e^{/}] \; = \; k_D^{-1} \cdot k_A$$

  - We have the mass action law as we know it with, however, unspecified constant. In order to obtain the absolute concentrations, we need one more equation, which, in the absence of other charged defects, is supplied by the electroneutrality condition

$$[h^{\cdot}] \; + \; [D^{\cdot}] \; = [e^{/}]$$

- OK, we are on safe grounds again. But there seems to be a certain ambiguity. Instead of the reaction **$h^{\cdot}$ + D = $D^{\cdot}$**, we also could have chosen the "normal" intrinsic reaction **$e^{/}$ + $h^{\cdot}$ = 0** from above.
  - So what is it? *Both*, of course. The equations above are dominating at low temperatures where thermal carrier generation can be neglected, i.e. not too high temperatures, the other one dominates at high temperatures.
  - But *both* occur independent of each other and, since there is only *one* equilibrium value for the respective concentrations, *both* must give the same numerical values for the same quantity if evaluated.
- This teaches us an important lesson for the treatment of defect equilibria:
  - Since the mass action law and the electroneutrality condition supply only *two* equations for possibly more than two unknown defect types, *any* sensible reaction equation that comes to mind and contains the unknown quantities can be used to supply the required additional information! The equilibrium concentration of defect type **i** is always the same - no matter in which equation it comes up!
- As we see, even for pure semiconductors it is possible to describe the electron-hole equilibrium in terms of reaction equations.
  - But the notion of chemical potentials becomes somewhat strained for calculating concentrations or "activities". Considering densities of states and distribution functions (Fermi distribution in full generality or Boltzmann distribution in the proper approximation) may be more advantageous as long as only electrons and holes are considered.
- Now lets look at a different kind of doping: We intentionally change the vacancy concentration, i.e. we **dope a crystal with vacancies**.
  - In a simple example we may look back at the introductory paragraph of this subchapter, and consider a reaction equation for the incorporation of **Ca** into a **NaCl** crystal (in Schottky notation right away - can you figure out the Kroeger-Vink notation?)

$$Ca^{\cdot}_{\;Na} \; + \; V^{/}_{Na} \; = \; 0$$

  - In words: A **Ca-V_{Na}** pair is introduced (or taken out) of the crystal.
  - The mass action law demands that **$[Ca^{\cdot}_{Na}] \cdot [V^{/}_{Na}]$ =** constant; and charge neutrality is conserved if **$[V^{/}_{\;Na}] = [Ca^{\cdot}_{\;Na}]$**.
  - If, and *only* if there is no other way to achieve charge neutrality, e.g. by generating electrons or holes, we will now produce *vacancies* by incorporating a doping element in perfect analogy to producing electrons or holes in semiconductors.
- Of course, we could also have incorporated **Ca** by generating **$Cl^{/}$** interstitials, a mix of vacancies and interstitials, or even worse, a mix of vacancies, interstitials, holes and electrons. All those possible reactions *will* occur and we cannot know a priori what will dominate. In a real case we must use some additional knowledge as pointed out above if we want to get results.

  - Well, "we" do know that vacancy doping can indeed be achieved in this way in **ZrO_2** doped with e.g. **Y_2O_3** or **CaO**, generating **$V_O^{\bullet\bullet}$**, i.e. doubly positively charged oxygen vacancies. This is a particularly relevant example, because it is part of the working principle of the oxygen sensor in your car exhaust system that feeds the controller of the car engine in order to keep emissions at the lowest possible level.
  - The technical importance is the same as in semiconductors: Whatever the intrinsic defect concentrations might be in the perfect intrinsic material, with doping you have a more or less fixed concentration of vacancies that can be far larger than the intrinsic concentration and may not depend sensitively on temperature.

- Great if you need lots of vacancies because you want to make an ionic conductor where the conductivity depends on the diffusion of oxygen via a vacancy mechanism. However, vacancy doping is not such a hot issue at low temperatures (like room temperature) if the vacancies - and therefore the oxygen ions, too - are not mobile at reasonable temperatures - in contrast to electrons and holes which get rather more mobile with decreasing temperature.
  - But if there is *some* mobility, you have now increased the *ionic* conductivity by orders of magnitude - exactly as you increase the *electronic* conductivity in semiconductors by doping.
  - Moreover, you *know* the concentration of the vacancies, and within some parameter range, you can treat it as *constant* which means you can remove **[V]** from the business end of the mass action law and multiply it into the general reaction constant. Life is easier.
- There are more examples for technical uses of doping, but we will now consider the *third* basic reactions, the defect reactions at interfaces.

Defect Reactions at Interfaces

- Considering that *all* chemical reactions between a solid and anything else occur at the surface of the solid, i.e. at the solid-gas, solid-liquid, or solid- solid interface, this headline covers a good part of general chemistry.
  - Indeed, it has become clear in recent years that reactive solid-solid interfaces generate or consume point defects. However, here we will only look at reactions between a gas and a (simple) ionic crystal as they are used in sensor technology. In other words, we consider the possible reactions between a **MeX** crystal and a **X_2(g)** gas in a first simplified treatment. We do not consider charges for the time being, to keep things simple.
  - The crystal may then incorporate **X_2(g)** (or emit it) via several reactions which we can easily formulate with the the Kröger-Vink notation:

1. $$\tfrac{1}{2}X_2\,(g) + V_X = X_X$$

  - i.e. an atom of the gas occupies a fitting empty place (= vacancy) of the crystal.

2. $$\tfrac{1}{2}X_2(g) + V_i = X_i$$

  - i.e. an atom of the gas occupies a fitting empty place (= vacancy) in the interstitial lattice and is now an interstitial.

3. $$\tfrac{1}{2}X_2\,(g) + V_M = X_M$$

  - i.e. an atom of the gas occupies a (probably not well fitting) empty place (= vacancy) in the metal ion lattice and is now an anti-site defect.
  - And there will be even more possibilities as is shown below.

- The thing to note once more is: If these reactions *can* occur, they *will* occur - independently of each other. Only their probabilities (or reaction rates) are (wildly) different, and we are well off if we know (or can make an educated guess) at the dominating reaction. And the equilibrium concentrations **[D_i]** of some defect type **D_i**, no matter in which equation it appears, are always identical in equilibrium.
  - In other words, we should know

    1. What kind of defect situation dominates in our **MeX** crystal (Frenkel- or Schottky defects etc.); i.e. which reaction constant is smallest?
    2. How can charge neutrality be achieved (only with ions and defects; only with electrons and holes, or in a mixture)? In other words are we dealing with an ionic conductor, a semiconductor, or a mixed case? Of course, the answer to this question may well depend on the temperature.
    3. Is there intentional (or unintentional) ionic or electronic doping that imposes specific conditions on the defect situation?

- This only looks hopeless, but rejoice, it is not - albeit for a sad reason: After all, we are not so much interested in defects per se, but in their uses. Typically, we want to do something "electrical" - make a better battery, a fuel cell, a sensor giving of a voltage or a current in response to the stuff to be sensed - and this demands that we use only ionic crystals that are **ionic conductors** of some sort.
  - Unfortunately, not too many ionic crystal are useful ionic conductors; it's just a handful of crystal families. And only those families we have to know. The search for a real good (and affordable) ionic conductor at room temperature is still on - if you find it, you may not make the Nobel prize, but certainly a great deal of money.
  - So all it takes is to study some **4** or **5** typical cases which contain practically everything encountered in ionic defect engineering.
- The paradigmatic case is an undoped crystal with Frenkel defects and some semiconducting properties. We start assuming that the electron/hole concentration is far smaller than the Frenkel defect concentration.
  - Thermal equilibrium of the **MeX** crystal by itself thus means that we have

$$[M^{\cdot}_i] = [V^{/}_M]$$

$$[e'] = [h^{\cdot}] << [V_M]$$

- Now we establish equilibrium with the gas X_2 **(g)**. It could be H_2, O_2, Cl_2, F_2 , whatever.
  - How are **X** atoms to be incorporated? Surprisingly, perhaps, none of the three possibilities given above is the preferred reaction. We do not have **X**- vacancies (V_X) available in our case, and we are not going to generate very unlikely **X** interstitials (X_i') or anti site defects. We want to incorporate **X** on a regular lattice site.
  - Now you see why the Kröger-Vink notation is useful. Playing around a bit with what you have (and putting in charge neutrality right away), gives

$$½\, X_2(g) \;+\; M_M \;=\; MX \;+\; V^{/}_M \;+\; h^{\cdot}$$

  - In words: An **X**-atom takes out a **M** atom from its position on the crystal surface, forming a **MX** molecule that is added to the crystal somewhere, leaving back a vacancy on a **M**-site and a hole.
  - This is not so easily expressible in Schottky notation (try it), but leads easily to the mass action law noticing that $[M_M] = [MX] =$ const $= 1$ and thus not needed in the "business end" of the mass action law.
  - We could come up with other reaction equations achieving the same result; but the one we have is good enough for the time being.
- We thus obtain two "master" equations for this case, one from mass action and one from charge neutrality exactly along the lines discussed before.
  - Mass action law

$$\frac{[X_2(g)]^{1/2}}{[V^{/}_M]\cdot[h^{\cdot}]} \;=\; \text{const.}$$

  - Charge neutrality

$$[V^{/}_M] \;+\; [e^{/}] \;=\; [M_i^{\cdot}] \;+\; [h^{\cdot}]$$

  - We have *two* equations for the *four* unknowns $V^{/}$, $e^{/}$, $M_i^{\cdot}$, and $h^{\cdot}$ which determine the electrical conductivity σ as a function of the concentration (or partial pressure) of the gas $[X_2$ **(g)]** via

$$\sigma([X_2(g)]) \;=\; \Sigma_i\,(q_i \cdot c_i \cdot \mu_i)$$

  - With q = charge carried by the defect **i**, c_i = concentration and μ_i = mobility of defect **i**, resp.
- Again, we need to have additional information about our system if we want quantitative relations between a measurable parameter like the defect-dependent conductivity.
  - Doping, as described above, could be helpful. It would provide a more or less constant value for e.g. the vacancy or electron concentration and thus remove one (or two) unknowns.
  - Without that, however, we have to resort to case studies making reasonable assumptions and considering the important quantities for the task at hand. As an example, if we want to measure the $[X_2$ **(g)]** concentration, we are not so much interested in the absolute value of σ, but in its change with the gas concentration, $d\sigma/d[X_2(g)]$.

  - That implies that we are mainly interested in those defects which react sensitively to concentration changes of $[X_2(g)]$.

- For our example we postulated the two conditions

$$[M^{\cdot}_i] = [V^{/}_M]$$

$$[e^{/}] = [h^{\cdot}] << [V_M^{/}]$$

  - This is valid as long as we are considering stoichiometric **MX** which is neither losing nor adding **X**. In other words, the crystal is kept at the **stoichiometric point** - at a certain partial pressure of X_2.
  - It is now important to notice that the reaction with the outside gas at partial pressures different from that belonging to the stoichiometric point changes the stoichiometry - no matter how you look at it. For ambient (or standard) pressure, there is no reaction and the stoichiometry is perfect - we are at the stoichiometric point. For large partial pressures of X_2, we will produce $MX_{1+\delta}$, , for low pressures $MX_{1-\delta}$, .

- Now lets see what happens if we work around the stoichiometric point. The absolute concentration of the vacancies and interstitials may change a little, and this means that the electron and hole concentration has to change exactly the same amount in order to maintain charge neutrality.
  - However, since we assumed that the absolute concentration of the electrons and holes at the stoichiometric point is much smaller than that of the vacancies and interstitials, the *relative change* of $[e^{/}]$ and $[h^{\cdot}]$ is much larger than that of $[M_i^{\cdot}]$ and $[V^{/}_M]$.
  - Accordingly, we may assume that $[M_i^{\cdot}]$ and $[V^{/}_M] \approx$ **constant** around the stoichiometric point, i.e. within a certain range of partial pressures of X_2 below and above the standards pressures which simplifies the relevant equations to

$$\frac{[X_2(g)]^{1/2}}{[h^{\cdot}]} = \text{const.}$$

  - With a different value of the constant, however.
  - The concentration of holes and electrons, on the other hand, changes markedly, but their *absolute* concentrations are still much smaller than that of vacancies and interstitials.

- This leads us to an *extremely important generalization*:
  - As far as the *mass action law* is concerned, only *variable* concentrations, i.e. concentrations that are not (approximately) constant, count. The absolute concentration is of no special importance - it becomes part of the reaction constant.
  - As far as *charge neutrality* is concerned, only *absolute* concentrations count. Minority carriers can simply be neglected in a first approximation.

- This give a first direct result: We can write dow the following simplified mass action law and electroneutrality condition:

Mass action	$[h^{\cdot}] = \text{const} \cdot [X_2(g)]^{1/2}$
Electro-neutrality	$[V^{/}_M] = [M_i^{\cdot}]$

- How about the electron concentration? Since our approximations imply that there is no interaction between the point defects and the electrons and holes, we must have $[h^{\bullet}] \cdot [e'] = \text{const.}$ and thus

$$[e^{/}] = \text{const} \cdot [X_2(g)]^{-1/2}$$

  - But we will derive that result now by using different reaction equation just to show that in equilibrium you always must obtain the same results.

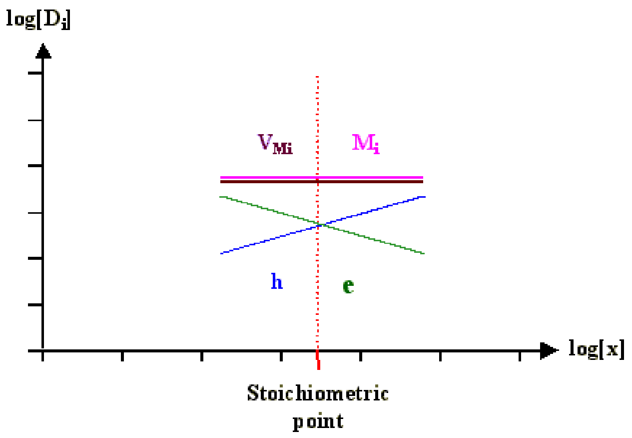
- Lets consider the reaction

$$\tfrac{1}{2} X_2(g) + M^{\cdot}_i + e^{/} = MX + V_i$$

- In words: A positively charged metal interstitial plus an electron and a gas atom form a crystal molecule and a vacancy on the interstitial lattice.
- Neglecting **$M^{\cdot}_i$**, **MX**, and **V_i** with the same arguments as before, we have, as we know that it must be

$$[e^{/}] = \text{const}\cdot[X_2(g)]^{-1/2}$$

In a **log [i] - log [X_2(g)]** plot we have straight lines with a slope of **1/2** for holes, **– 1/2** for electrons and **0** for the interstitials and vacancies, respectively. This looks like this:



- Without looking at the reaction constants, we know that the cross over of the **$e^{/}$** and **$h^{\cdot}$** concentration lines must be at the stoichiometric point.
- It is clear that for large deviations from the stoichiometric point the approximations used are no longer valid. For very small or very large partial pressures of **X_2**, we now may consider the other two possible extremes by simply extrapolating the lines in the illustration:
- **1.** For very large partial pressures of **X_2** the **$e^{/}$** concentration becomes negligible while the hole concentration becomes comparable to the point defect concentration. Charge neutrality can only be maintained by decreasing the positively charged metal interstitials and increasing the negatively charged vacancies. In the extreme, we may only consider **$[V^{/}_M] = [h^{\cdot}]$** for charge neutrality. Inserting that in the reaction equation from above, we have .

$$\tfrac{1}{2}\,X_2(g) + M_M = MX + 2h^{\cdot}$$

- which gives the mass action equation

$$\frac{[X]^{1/2}}{[h^{\cdot}]^2} = \text{const}$$

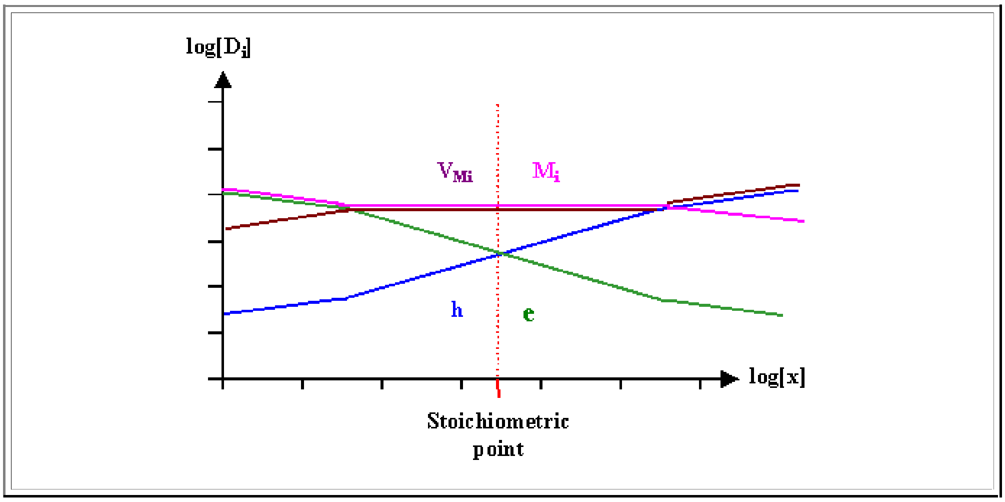
$$[h^{\cdot}] = \text{const.}\cdot[X]^{1/4}$$

- For very low partial pressures we obtain exactly along the same line of arguments **$[e^{/}] = \text{const.}\cdot[X]^{-1/4}$**.

With these relations, we may also calculate the concentrations of the minority point defects by simply inserting the above equations in the appropriate reaction equation and applying mass action which yields

High pressure side	$[M_i^{\cdot}] = \text{const}\cdot[X]^{-1/4}$
Low pressure side	$[V^{/}_M] = \text{const}\cdot[X]^{1/4}$

- Putting everything together in on single graph, we obtain a schematic **Kröger-Vink** or **Brouwer diagram**:



- Of course, the change-over would be smooth in reality; and we cannot tell easily where it will occur. It is also obvious that there are no discontinuities of the concentration curves, which tells us something about the "const." in the mass action equation.
- In the consideration above we did not assign values to the "const." and carry it through. That might be a interesting exercise one of those days.

- In any case, we now have seen how Kröger-Vink reaction equations, mass action, charge neutrality and some additional knowledge or educated guesses allow to come up with a pretty good idea of what will happen in a reaction involving point defects.
  - The possibilities of electronic and ionic doping together with the temperature dependence of point defect equilibria now give us a powerful tool for designing materials for specific applications.
  - " **Ionics**", in research and application, is slowly coming into its own. Together with the good old "electronics" it may well open up new fields for materials scientists.