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# Defect Chemistry in Solid State Ionics

Tutorial lecture at SSI-20, Keystone, Colorado, June 14, 2015

## Main purposes

Introduce defect chemistry to newbies

Focus on some important principles and good practices for oldies

## Outline

What are defects and why are they important?

Random diffusion and ionic conductivity

Defect reactions and equilibrium thermodynamics

Examples include MO,  $ZrO_2$ ,  $BaZrO_3$

Li ion battery materials

Computational defect chemistry

Summarising conclusions

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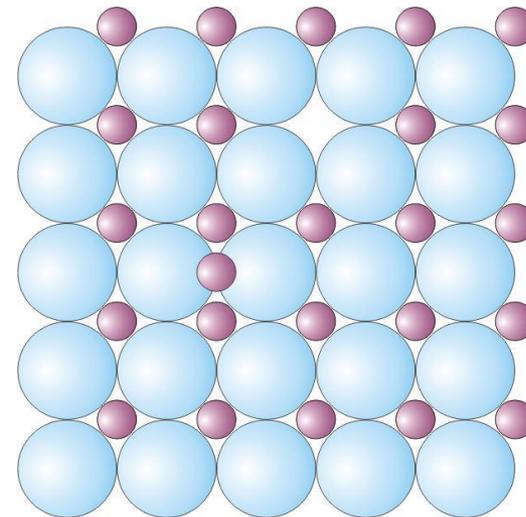
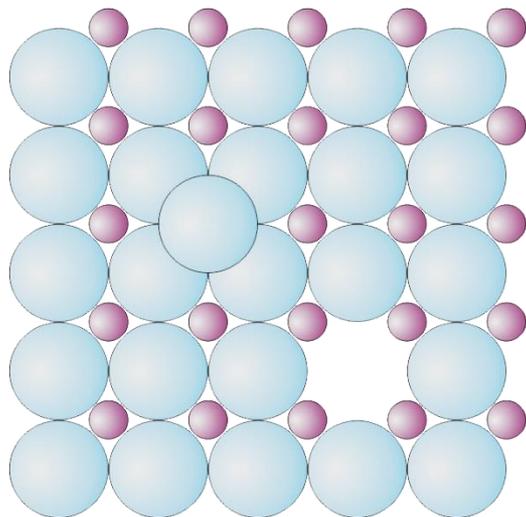
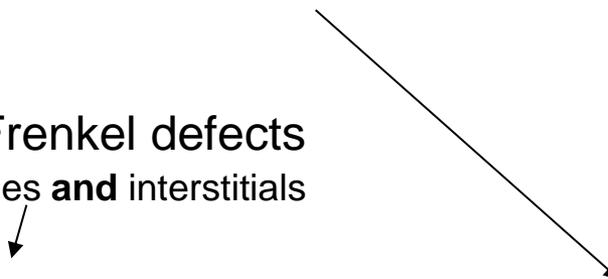
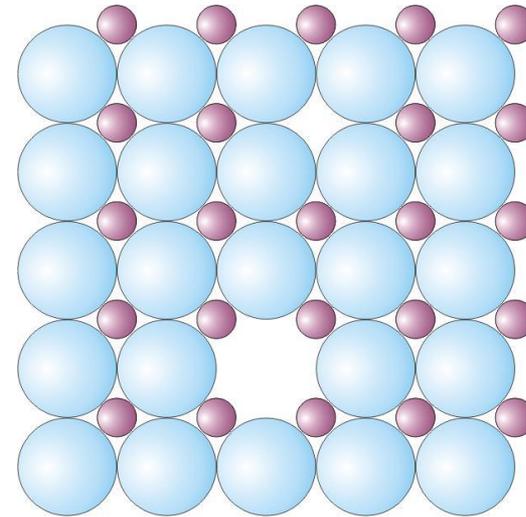
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# Stoichiometric compounds;

## Point defects form in pairs: Intrinsic point defect disorders

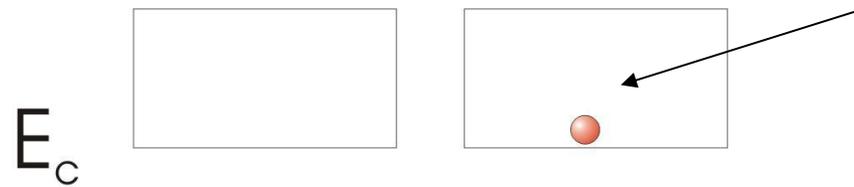
- Schottky defects
  - Cation and anion **vacancies**
- Frenkel defects
  - **Cation** vacancies and interstitials
- Anti- or anion-Frenkel defects
  - **Anion** vacancies and interstitials



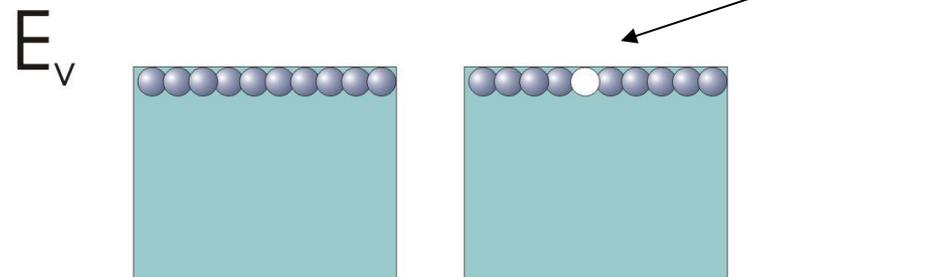
# Stoichiometric compounds:

## Electronic defects: Intrinsic electronic disorder

- Dominates in undoped semiconductors with moderate bandgaps



Defect electrons in the conduction band  
and



electron holes in the valence band

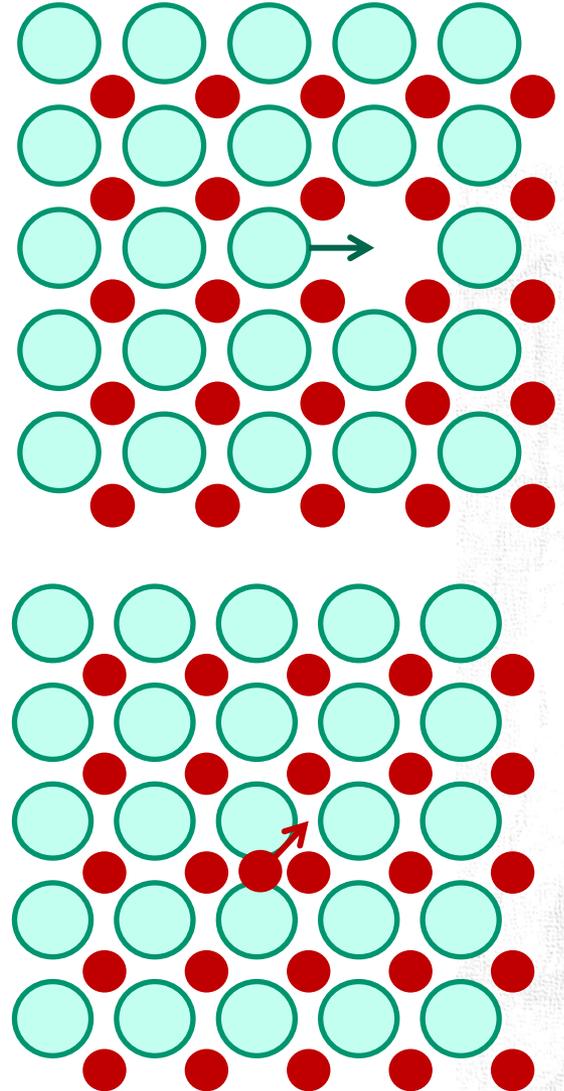
# Random diffusion and self diffusion

- Mass transport in crystalline solids is driven by **thermal energy  $kT$**
- Leads to **random diffusion**
- If the diffusing species is a constituent it is also called **self-diffusion**
- Two most important mechanisms:

**Vacancy mechanism**

**Interstitial mechanism**

- ***Defects are needed in both***



# Diffusivity: a matter of geometry and jump rates

- Constituent by vacancy mechanism

Orthogonal directions

Jump rate

Number of neighbouring sites

$$D_{r,c} = \frac{1}{6} s^2 \Gamma_c = \frac{1}{6} s^2 \omega Z X_v$$

Likelihood of target site to be vacant

Jump distance

Rate of sufficiently energetic attempts

- Vacancy

$$D_{r,v} = \frac{1}{6} s^2 \Gamma_v \approx \frac{1}{6} s^2 \omega Z$$

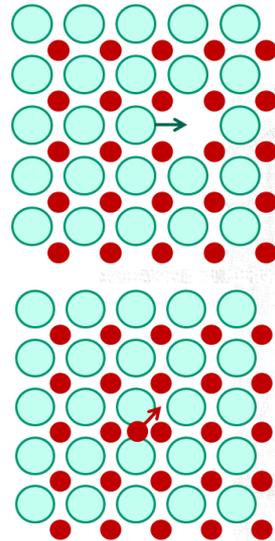
- Constituent by interstitial mechanism

$$D_{r,c} = \frac{1}{6} s^2 \Gamma_c \approx \frac{1}{6} s^2 \omega Z X_i$$

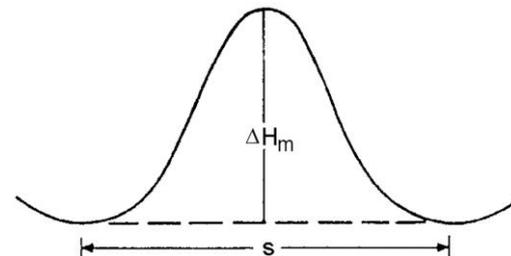
Likelihood to be interstitial

- Interstitial

$$D_{r,i} = \frac{1}{6} s^2 \Gamma_i = \frac{1}{6} s^2 \omega Z (1 - X_i) \approx \frac{1}{6} s^2 \omega Z$$



$$\omega = \nu \exp \frac{-\Delta G_m}{RT} = \nu \exp \frac{\Delta S_m}{R} \exp \frac{-\Delta H_m}{RT}$$



## The Nernst-Einstein relation – linking mobility and diffusivity

- Application of a force  $F_i$  gives the randomly diffusing particles  $i$  a net drift velocity  $v_i$ :

$$v_i = B_i F_i$$

- The proportionality  $B_i$  is called **mechanical mobility** («beweglichkeit»)
- Mechanical mobility  $B_i$  (beweglichkeit) is the diffusivity  $D_i$  over the thermal energy  $kT$ :

$$B_i = \frac{D_i}{kT}$$

$$D_i = B_i kT$$

- This is the Nernst-Einstein relation

# Electrical field; force, flux density, and current density

- An electrical field is the downhill gradient in electrical potential:

$$E = -\frac{d\phi}{dx}$$

- It gives rise to a force on a charged particle  $i$  given as

$$F_i = z_i e E = -z_i e \frac{d\phi}{dx}$$

- The flux density  $j_i$  is the volume concentration  $c_i$  multiplied with the drift velocity  $v_i$ :

$$j_i = c_i v_i = c_i B_i F_i = c_i B_i z_i e E$$

- Current density by multiplication with charge:

$$i_i = z_i e j_i = z_i e c_i v_i = c_i B_i (z_i e)^2 E$$

# Mobilities and conductivity

- We now define a **charge mobility**  $u_i$

$$u_i = z_i e B_i$$

Charge mobility  $u$  is in physics often denoted  $\mu$ . We here use  $u$  to avoid confusion with chemical potential.

- We then obtain for the current density:

$$i_i = c_i B_i (z_i e)^2 E = z_i e c_i u_i E$$

- We now define **electrical conductivity**  $\sigma_i$

$$\sigma_i = z_i e c_i u_i$$

**Very important! Know it!**  
Charge x concentration x charge mobility

- and obtain

$$i_i = z_i e c_i u_i E = \sigma_i E$$

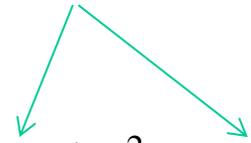
This is one form of Ohm's law.  
Conductivity has units S/cm or S/m.

# Ionic conductivity for vacancy mechanism

- Constituent by vacancy mechanism

$$\sigma_i = z_i e c_{i,c} u_{i,c} = (z_i e)^2 c_{i,c} B_{i,c} = \frac{(z_i e)^2 c_{i,c} D_{i,c}}{kT} = \frac{(z_i e)^2 c_{i,c} \frac{1}{6} s^2 \omega Z X_{i,v}}{kT}$$

Volume concentration of vacancies



- Vacancy

$$\sigma_i = z_i e c_{i,v} u_{i,v} = (z_i e)^2 c_{i,v} B_{i,v} = \frac{(z_i e)^2 c_{i,v} D_{i,v}}{kT} = \frac{(z_i e)^2 c_{i,v} \frac{1}{6} s^2 \omega Z}{kT}$$

Volume concentration of vacancies

Charge mobility of vacancies (~ concentration independent)

Regardless of whether you consider the constituent or the defect, you need the concentration of the defect – indirectly or directly.

## Formal oxidation number – integer charges

- We know that bonds in ionic compounds are not fully ionic, in the sense that all valence electrons are *not* entirely shifted to the anion.
- But if the bonding is broken - as when something, like a defect, moves – the electrons have to stay or go. Electrons cannot split in half.
- And mostly they go with the anion - the most electronegative atom.
- That is why the ionic model applies in defect chemistry and transport
- And it is why it is very useful to know and apply the rules of formal oxidation numbers, the number of charges an ion gets when the valence electrons have to make the choice
- $z$  are integer numbers



# Defect chemistry

- Allows us to describe processes involving defects
- Allows application of statistical thermodynamics
  - Equilibrium coefficients; Enthalpies and entropies
- Yields defect structure (concentrations of all defects) under given conditions
- The defect concentrations for transport coefficients (e.g. conductivity)
- Requires nomenclature
- Requires rules for writing proper reactions
- Additional requirements: Electroneutrality, site balances...

**Now, we'll learn  
exactly that!**

# Kröger-Vink notation

- In modern defect chemistry, we use Kröger-Vink notation. It can describe any entity in a crystalline structure; defects and “perfects”.
- Main symbol A, a subscript S, and a superscript C:
- **What** the entity is, as the main symbol (**A**)
  - Chemical symbol
  - or v (for vacancy)
- **Where** the entity is – the site - as subscript (**S**)
  - Chemical symbol of the normal occupant of the site
  - or i for interstitial (normally empty) position
- Its **charge**, real or effective, as superscript (**C**)
  - +, -, or 0 for real charges
  - or ·, /, or x for effective positive, negative, or no charge
- The use of **effective charge** of a few defects over the real charge of all the “perfects” is preferred and **one of the key points in defect chemistry**.
  - We will learn what it is in the following slides



A large diagram showing the components of Kröger-Vink notation. A large capital letter 'A' is on the left. To its right, a capital letter 'S' is positioned below a capital letter 'C'. This represents the notation A<sub>S</sub><sup>C</sup>.

Kröger and Vink used uppercase V for vacancies and I for interstitial sites, perhaps because that is natural for nouns in German.

I say: How would you then do defect chemistry for vanadium iodide  $\text{VI}_3$ ? I claim that lowercase v and i are much better in all respects, and hereby use v and i. Basta.

# Effective charge

- The effective charge is defined as

*the charge an entity in a site has*

*relative to (i.e. minus)*

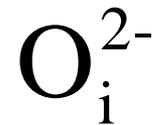
*the charge the same site would have had in the ideal structure.*

- Example: An oxide ion  $O^{2-}$  in an interstitial site (i)

Real charge of defect: -2

Real charge of interstitial (empty) site in ideal structure: 0

Effective charge:  $-2 - 0 = -2$



# Effective charge – more examples

- Example: An oxide ion vacancy

Real charge of defect (vacancy = nothing): 0

Real charge of oxide ion  $O^{2-}$  in ideal structure: -2

Effective charge:  $0 - (-2) = +2$



- Example: A zirconium ion vacancy, e.g. in  $ZrO_2$

Real charge of defect: 0

Real charge of zirconium ion  $Zr^{4+}$  in ideal structure: +4

Effective charge:  $0 - 4 = -4$



# Kröger-Vink notation – more examples

- Dopants and impurities

$\text{Y}^{3+}$  substituting  $\text{Zr}^{4+}$  in  $\text{ZrO}_2$



$\text{Li}^+$  interstitials

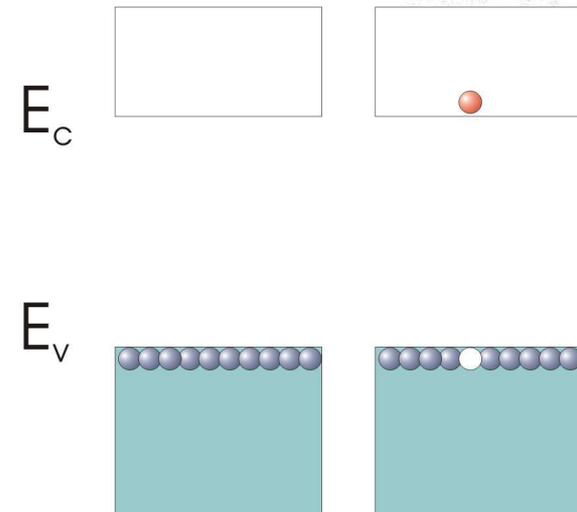


- Electronic defects

Defect electrons in conduction band



Electron holes in valence band



**We will now make use of the thermodynamics of chemical reactions comprising defects**

**In order to do that correctly, we need to obey 3 rules for writing and balancing defect chemical reaction equations:**

- **Conservation of mass - mass balance**
- **Conservation of charge - charge balance**
- **Conservation of site ratio (host structure)**

**MUST KNOW!**

## Schottky defects in MO

- We start by writing the relevant defect formation reaction:



- which we can simplify to

$$0 = v_O^{\bullet\bullet} + v_M^{//}$$

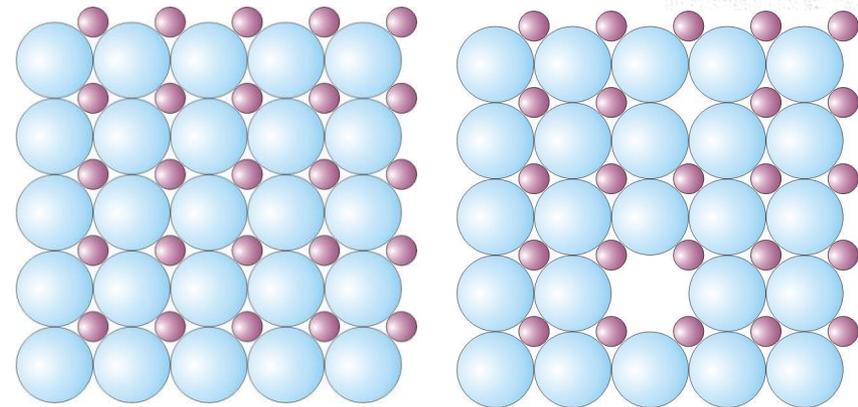
- We then write its equilibrium coefficient:

$$K_S = a_{v_O^{\bullet\bullet}} a_{v_M^{//}} = X_{v_O^{\bullet\bullet}} X_{v_M^{//}} = \frac{[v_O^{\bullet\bullet}]}{[O]} \frac{[v_M^{//}]}{[M]}$$

Activities  $a$

For point defects, activities are expressed in terms of site fractions  $X$

The site fraction is the concentration of defects over the concentration of sites



# Schottky defects in MO

$$0 = v_{\text{O}}^{\bullet\bullet} + v_{\text{M}}^{\prime\prime}$$

- $K$ 's are often simplified. There are various reasons why:
  - Because you sometimes *can* do it *properly*;
  - Because the simplification often is a *reasonable approximation*;
  - Because you are perhaps *not interested* in the difference between the exact and simplified  $K$  (this often means that you disregard the possibility to assess the entropy change);
  - Because neither the full nor simplified forms make much sense in terms of entropy, so they are equally useful or accurate (or inaccurate), and then we may well *choose the simplest*.
- If we express concentrations in molar fractions (mol/mol MO), then  $[M] = [O] = 1$ , and we may simplify to

$$K_s = \frac{[v_{\text{O}}^{\bullet\bullet}]}{[O]} \frac{[v_{\text{M}}^{\prime\prime}]}{[M]} = [v_{\text{O}}^{\bullet\bullet}] [v_{\text{M}}^{\prime\prime}]$$

# Schottky defects in MO



- NOTE: At equilibrium, an equilibrium coefficient expression is always valid and must be satisfied at all times!

$$K_S = [v_{\text{O}}^{\bullet\bullet}][v_{\text{M}}^{\prime\prime}]$$

- Thus the product of the concentrations of oxygen and metal vacancies is always constant (at constant T). We may well stress this by instead writing:

$$[v_{\text{O}}^{\bullet\bullet}][v_{\text{M}}^{\prime\prime}] = K_S$$

- While  $K_S$  represents information about the system, we have two unknowns, namely the two defect concentrations, so this is not enough. We need one more piece of independent input.

# Schottky defects in MO

$$0 = v_{\text{O}}^{\bullet\bullet} + v_{\text{M}}^{\prime\prime}$$

- The second piece of input is the *electroneutrality expression*. If the two defects of the Schottky pair are the dominating defects, we may write

$$2[v_{\text{O}}^{\bullet\bullet}] = 2[v_{\text{M}}^{\prime\prime}] \quad \text{or} \quad [v_{\text{O}}^{\bullet\bullet}] = [v_{\text{M}}^{\prime\prime}]$$

- It is now important to understand that this is NOT an “eternal truth”...the electroneutrality statement is a *choice*: We choose to believe or assume that these are the dominating defects.
- The next step is to combine the two sets of information; we insert the electroneutrality into the equilibrium coefficient:

$$[v_{\text{O}}^{\bullet\bullet}][v_{\text{M}}^{\prime\prime}] = K_S \quad \longleftarrow \quad [v_{\text{O}}^{\bullet\bullet}] = [v_{\text{M}}^{\prime\prime}]$$

$$[v_{\text{M}}^{\prime\prime}]^2 = K_S$$

$$[v_{\text{M}}^{\prime\prime}] = K_S^{1/2}$$

$$[v_{\text{O}}^{\bullet\bullet}] = [v_{\text{M}}^{\prime\prime}] = K_S^{1/2}$$

Voila! We have now found the expression for the concentration of the defects. In this case, they are only a function of  $K_S$ .

# Schottky defects in MO

$$0 = v_{\text{O}}^{\bullet\bullet} + v_{\text{M}}^{\prime\prime}$$

- From the general temperature dependency of K,

$$K_s = \exp \frac{-\Delta G_s^0}{RT} = \exp \frac{\Delta S_s^0}{R} \exp \frac{-\Delta H_s^0}{RT}$$

- we obtain

$$[v_{\text{O}}^{\bullet\bullet}] = [v_{\text{M}}^{\prime\prime}] = K_s^{1/2} = \exp \frac{\Delta S_s^0}{2R} \exp \frac{-\Delta H_s^0}{2RT}$$

- In or log defect concentrations vs 1/T (van 't Hoff plots):

$$\ln[v_{\text{O}}^{\bullet\bullet}] = \ln[v_{\text{M}}^{\prime\prime}] = \frac{\Delta S_s^0}{2R} + \frac{-\Delta H_s^0}{2R} \frac{1}{T}$$

$$\log[v_{\text{O}}^{\bullet\bullet}] = \log[v_{\text{M}}^{\prime\prime}] = \frac{\Delta S_s^0}{2R \ln 10} + \frac{-\Delta H_s^0}{2R \ln 10} \frac{1}{T}$$

Note: This *not* the Gibbs energy change (which becomes zero at equilibrium)

It is the *standard* Gibbs energy change.

What does *standard* refer to?

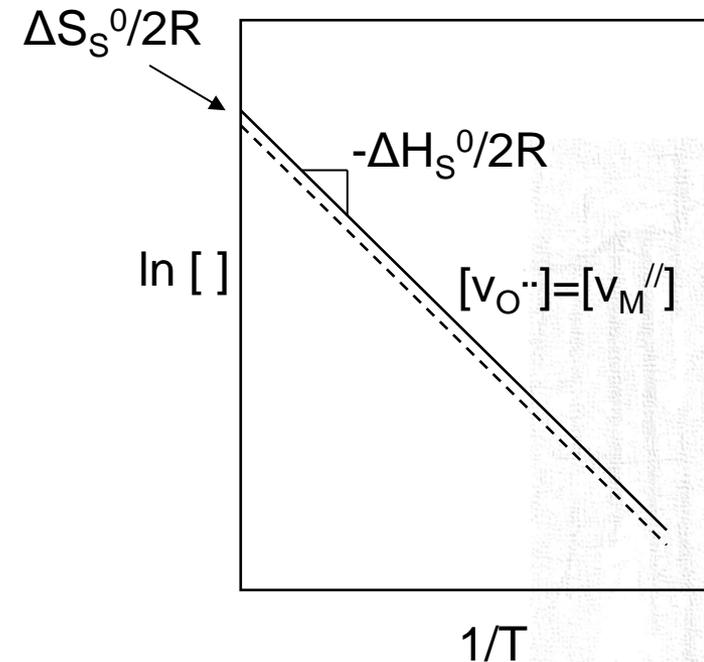
The square root and number 2 arise from the reaction containing 2 defects.

$\ln 10 = 2.303$

# Schottky defects in MO

$$0 = v_{\text{O}}^{\bullet\bullet} + v_{\text{M}}^{\prime\prime}$$

- van 't Hoff plot
- Standard entropy and enthalpy changes can be found from intercept with y axis and slope, respectively, after multiplication with  $2R$  and  $-2R$ .
- $\log[ ]$  plots can be more intelligible, but require the additional multiplications with  $\ln 10 = 2.303$ .
- The standard enthalpy change can have any value: Finding it is a *result!*
- The standard entropy change can be estimated: Finding it is therefore a *control!*
- Dare to try?
- Get interested in preexponentials and entropies!



Main contribution to entropy changes is gas vs condensed phases:  $\sim 120 \text{ J/molK}$  !

## Recap before we move on... $0 = v_{\text{O}}^{\bullet\bullet} + v_{\text{M}}^{\prime\prime}$

- The solution we found assumes that the two Schottky defects are dominating.
- The *standard entropy and enthalpy changes* of the Schottky reaction refer to the reaction when the reactants and products are in the *standard state*.
- For our defects, that means that the *site fraction is unity!* This is a *hypothetical state*, but nevertheless the state we have agreed on as standard.
- Therefore, the entropy as derived and used here is only valid if the point defect concentrations are entered (plotted) in units of *site fraction* (which in MO happens to be the same as mole fraction).
- Other species – gases, electrons, condensed phases – should be expressed as activities, referring to their defined standard states, if possible.
- The model also assumes ideality, i.e. that the activities of defects are proportional to their concentrations. It is a dilute solution case.

## Intrinsic ionisation of electronic defects

- For conduction band electrons and valence band holes, the relevant reaction is



$$N_C = \left( \frac{8\pi m_e^* kT}{h^2} \right)^{3/2}$$

- The equilibrium coefficient may be written

$$K_i = a_{e'} a_{h^\bullet} = \frac{[e']}{N_C} \frac{[h^\bullet]}{N_V} = \frac{n}{N_C} \frac{p}{N_V}$$

$$N_V = \left( \frac{8\pi m_h^* kT}{h^2} \right)^{3/2}$$

Here, the activities of electrons and holes are expressed in terms of the fraction of their concentration over the density of states of the conduction and valence bands, respectively. The reason is that electrons behave quantum-mechanically and therefore populate different energy states rather than different sites.

- The standard state is according to this:  $n^0 = N_C$  and  $p^0 = N_V$

# Intrinsic ionisation of electronic defects

- If we choose to apply the concepts of standard Gibbs energy, entropy, and enthalpy changes as before, we obtain

$$K_i = \frac{n}{N_C} \frac{p}{N_V} = \exp \frac{-\Delta G_i^0}{RT} = \exp \frac{\Delta S_i^0}{R} \exp \frac{-\Delta H_i^0}{RT}$$

- This is possible and useful, but not commonly adopted.
- In semiconductor physics it is instead more common to use simply:

$$K_i' = [e'] [h^\bullet] = n p = N_C N_V \exp \frac{-E_g}{RT}$$

This states that the product of  $n$  and  $p$  is constant at a given temperature, as expected for the equilibrium coefficient for the reaction. However, the concept of activity is not applied, as standard states for electronic defects are not commonly defined. For this reason, we here use a prime on the  $K_i'$  to signify the difference to a “normal”  $K$  from which the entropy could have been derived.

# Intrinsic ionisation of electronic defects

- From 
$$K_i = \frac{n}{N_C} \frac{p}{N_V} = \exp \frac{-\Delta G_i^0}{RT} = \exp \frac{\Delta S_i^0}{R} \exp \frac{-\Delta H_i^0}{RT}$$

and 
$$K_i' = [e'] [h^\bullet] = np = N_C N_V \exp \frac{-E_g}{RT}$$

we see that the band gap  $E_g$  is to a first approximation the Gibbs energy change of the intrinsic ionisation, which in turn consists mainly of the enthalpy change.

- We shall not enter into the finer details or of the differences here, just stress that  $np = \text{constant}$  at a given temperature. Always!
- Physicists mostly use  $E_g/kT$  with  $E_g$  in eV per electron, while chemists often use  $E_g/RT$  (or  $\Delta G^0/RT$ ) with  $E_g$  in J or kJ per mole electrons. This is a trivial conversion (factor 1 eV = 96485 J/mol = 96.485 kJ/mol).

# Intrinsic ionisation of electronic defects

- If we *choose* that electrons and holes dominate the defect structure;

$$n = p$$

- We insert into the equilibrium coefficient expression and get

$$n p = n^2 = K'_i = N_C N_V \exp \frac{-E_g}{RT}$$

$$n = p = K_i'^{1/2} = (N_C N_V)^{1/2} \exp \frac{-E_g}{2RT}$$

- A logarithmic plot of  $n$  or  $p$  vs  $1/T$  will thus have a slope that seems to reflect  $E_g/2$  as the apparent enthalpy.
- Because of the temperature dependencies of the density of states it should however be more appropriate to plot  $nT^{-3/2}$  or  $pT^{-3/2}$  vs  $1/T$  to obtain a slope that reflects  $E_g/2$  more correctly.

## Oxygen deficient oxides

- Oxygen vacancies are formed according to



This big expression may seem unnecessary, but is meant to help you understand...

$$K_{vO} = \frac{a_{v_o^{\bullet\bullet}} a_{e'}^2 a_{O_2(g)}^{1/2}}{a_{O_o^x}} = \frac{\frac{[v_o^{\bullet\bullet}]}{[O]} \left(\frac{n}{N_C}\right)^2 \left(\frac{p_{O_2}}{p_{O_2}^0}\right)^{1/2}}{\frac{[O_o^x]}{[O]}} = \frac{[v_o^{\bullet\bullet}]}{[O_o^x]} \left(\frac{n}{N_C}\right)^2 \left(\frac{p_{O_2}}{p_{O_2}^0}\right)^{1/2}$$

- It is common for most purposes to neglect the division by  $N_C$ , to assume  $[O_o^x] = 1$  and to remove  $p_{O_2}^0 = 1$  bar, so that we get

$$K'_{vO} = N_C^2 K_{vO} = [v_o^{\bullet\bullet}] n^2 p_{O_2}^{1/2}$$

I use again the prime in  $K'$  to signify this neglectance

# Oxygen deficient oxides

- We now choose to assume that the oxygen vacancies and electrons are the two dominating defects. The electroneutrality then reads

$$2[v_o^{\bullet\bullet}] = n$$

- We now insert this into the equilibrium coefficient and get

$$K'_{vO} = 4[v_o^{\bullet\bullet}]^3 p_{O_2}^{1/2}$$

- We finally solve with respect to the concentration of defects:

$$[v_o^{\bullet\bullet}] = \left(\frac{1}{4} K'_{vO}\right)^{1/3} p_{O_2}^{-1/6}$$

$$n = 2[v_o^{\bullet\bullet}] = (2K'_{vO})^{1/3} p_{O_2}^{-1/6}$$

# Oxygen deficient oxides

- We split  $K'_{vO}$  into a preexponential and the enthalpy term:

$$n = 2[v_o^{\bullet\bullet}] = (2K'_{vO})^{1/3} p_{O_2}^{-1/6} = (2K'_{vO,0})^{1/3} \exp \frac{-\Delta H_{vO}^0}{3RT} p_{O_2}^{-1/6}$$

- From this, to a first approximation, a plot of the logarithm of the defect concentrations vs  $1/T$  will give lines with slope of  $-\Delta H_{vO}^0/3R$
- The number 3 relates to the formation of 3 defects in the defect reaction

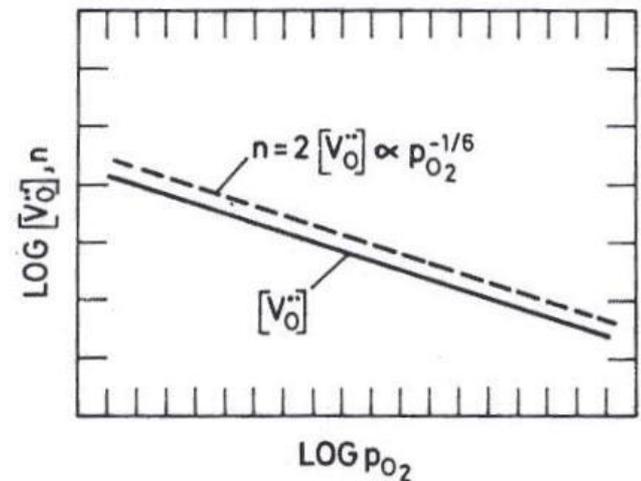
# Oxygen deficient oxides

$$n = 2[v_{O}^{\bullet\bullet}] = (2K'_{vO})^{1/3} p_{O_2}^{-1/6}$$

- By taking the logarithm:

$$\log n = \log 2 + \log[v_{O}^{\bullet\bullet}] = \frac{1}{3} \log(2K'_{vO}) - \frac{1}{6} \log p_{O_2}$$

- we see that a plot of  $\log n$  vs  $\log p_{O_2}$  gives a straight line with a slope of  $-1/6$ .
- This kind of plot is a **Brouwer diagram**
- Note that  $\log[v_{O}^{\bullet\bullet}]$  is a parallel line  $\log 2 = 0.30$  units lower.



# Electroneutrality

- One of the key points in defect chemistry is the ability to express electroneutrality in terms of the few defects and their effective charges and to skip the real charges of all the normal structural elements
- $\Sigma \text{ positive charges} = \Sigma \text{ negative charges}$

can be replaced by

- $\Sigma \text{ positive effective charges} = \Sigma \text{ negative effective charges}$
- $\Sigma \text{ positive effective charges} - \Sigma \text{ negative effective charges} = 0$

# Electroneutrality

- The number of charges is counted over a volume element, and so we use the concentration of the defect species  $s$  multiplied with the number of charges  $z_s$

$$\sum_s z_s [s^{z_s}] = 0$$

- Example: MO with oxygen vacancies, metal interstitials, and electrons:

$$2[v_{\text{O}}^{\bullet\bullet}] + 2[M_{\text{i}}^{\bullet\bullet}] - [e'] = 0 \quad \text{or} \quad 2[v_{\text{O}}^{\bullet\bullet}] + 2[M_{\text{i}}^{\bullet\bullet}] = [e']$$

- If oxygen vacancies dominate over metal interstitials we can simplify:

$$2[v_{\text{O}}^{\bullet\bullet}] \approx [e']$$

- Note: These are not chemical reactions, they are mathematical relations and must be read as that. For instance, in the above: Are there two vacancies for each electron or *vice versa*?

# Equilibria and electroneutralities

- In defect chemistry, we combine information from equilibrium coefficients and electroneutrality expressions
- There is a potential pitfall
- For defect equilibria, you should use *site fractions* in order to get the entropies right
  - Different defects have different reference frames
- For electroneutralities, you must use *volume concentrations, molar fractions, or formula unit fractions*
  - All defects must have the same frame when counting their charges
- They can be the same, but are in general not





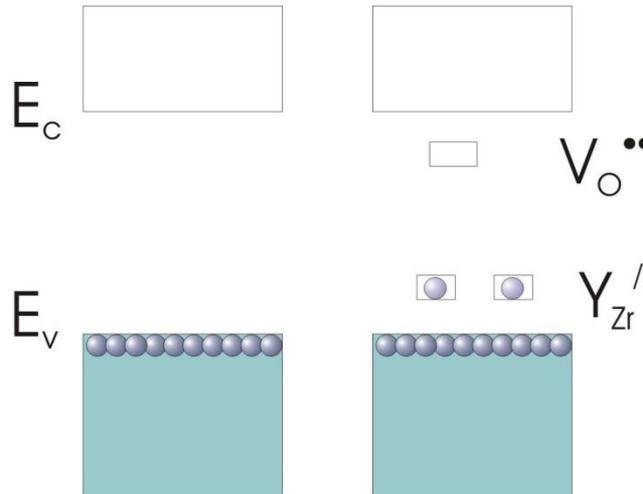
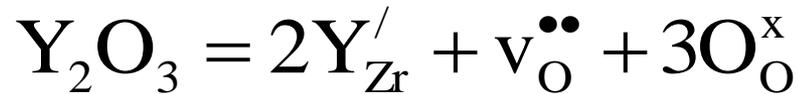
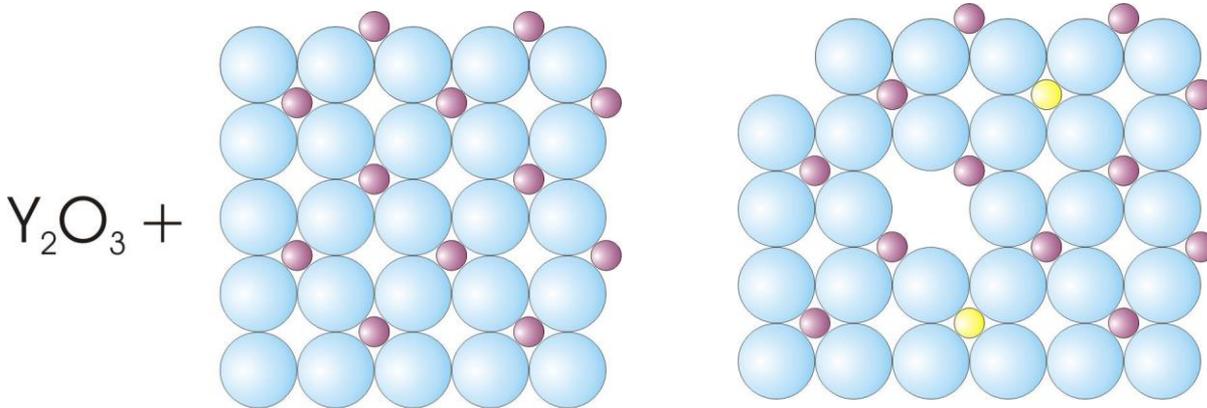
**Impurities**

**Doping**

**Substitution**



# ZrO<sub>2-y</sub> doped substitutionally with Y<sub>2</sub>O<sub>3</sub>

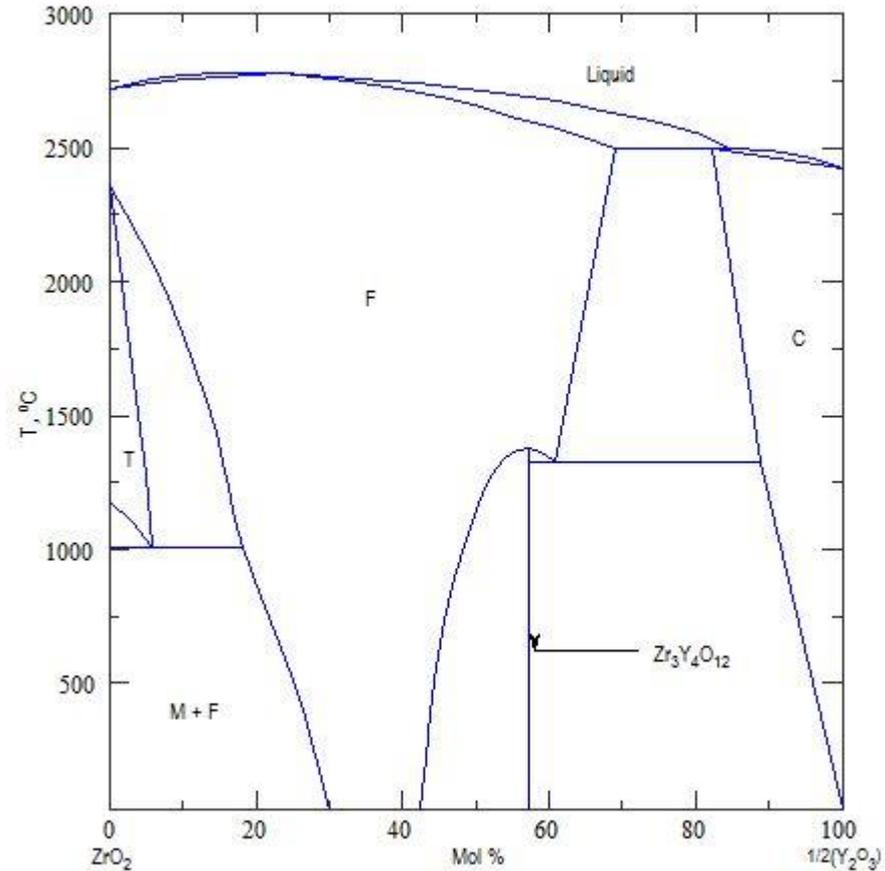


Note: Electrons donated from oxygen vacancy are accepted by Y dopants; no electronic defects in the bands.

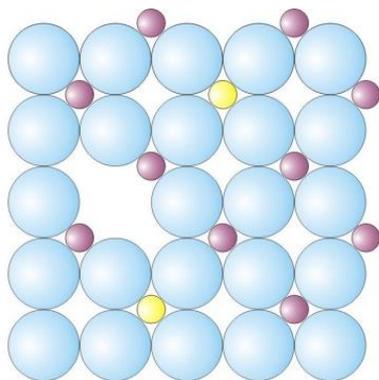
- Note: Doping reactions are almost *never* at equilibrium!
- They are most often fixed or frozen!
- What would it take to have them in equilibrium?
- Dopant (secondary) phase must be present as source and sink
- Temperature must be very high

# Phase diagrams and defect chemistry

- All solid solutions and their phase boundaries are determined by defect thermodynamics
- But surprisingly few studies attempt at taking advantage of this, e.g. to rationalise solubility and phase diagram studies



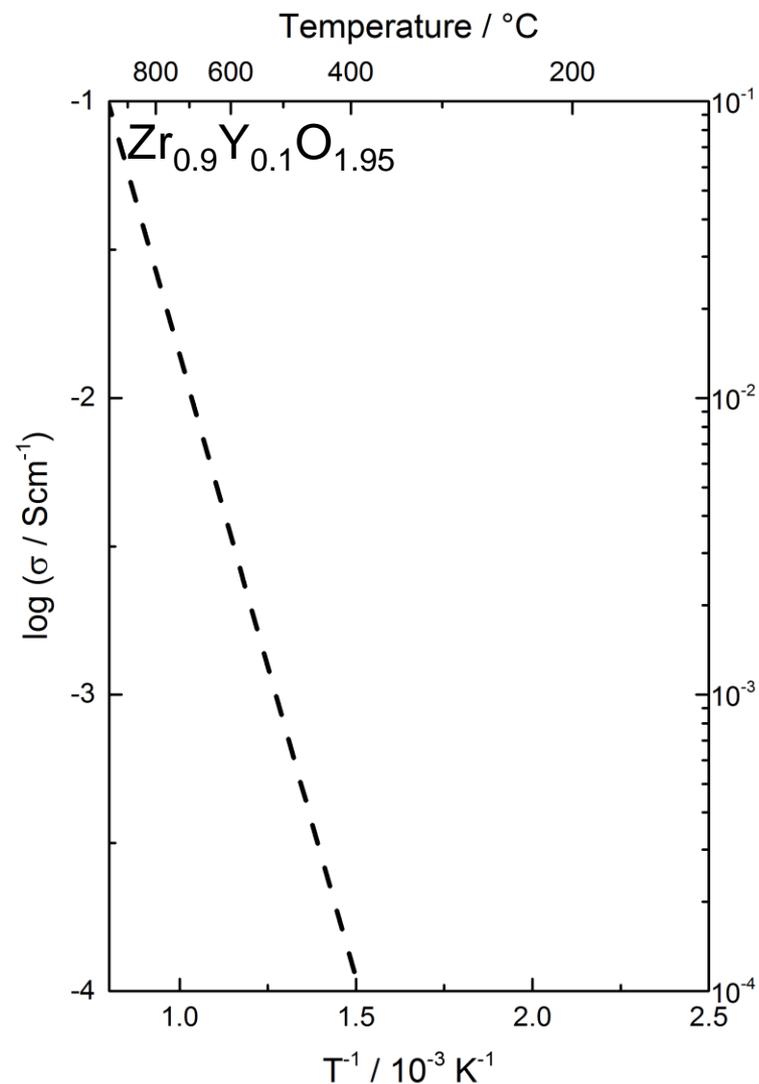
## Oxide ion conduction of YSZ



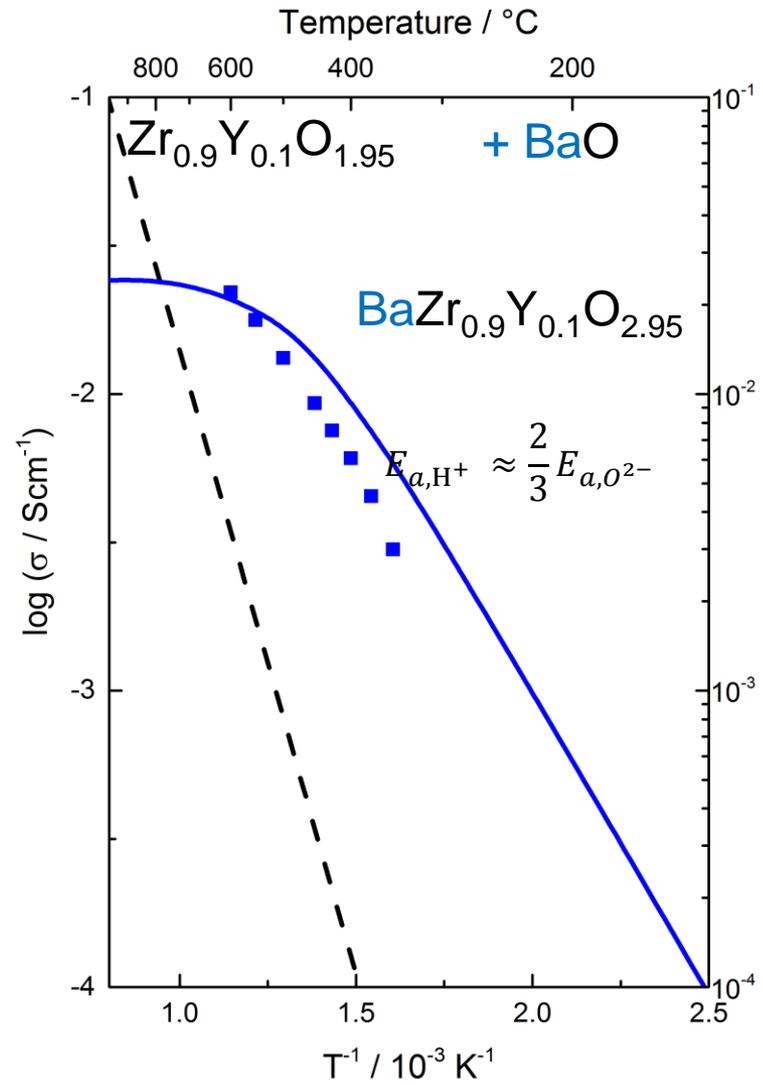
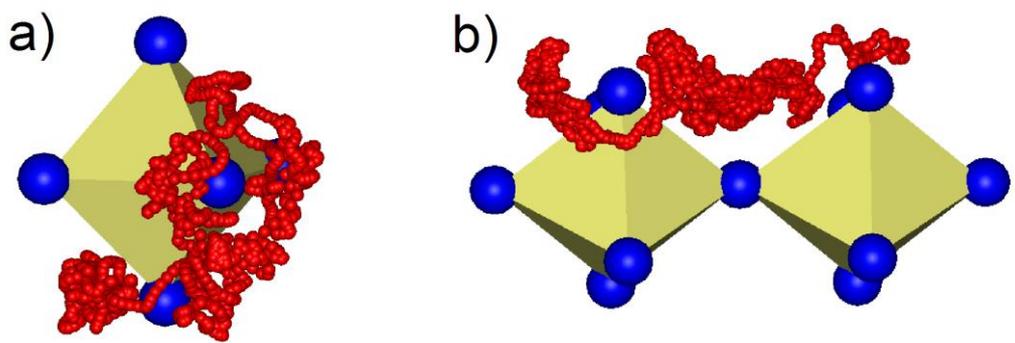
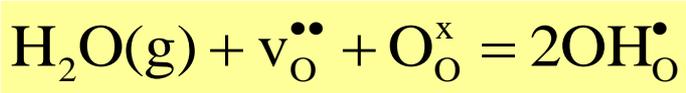
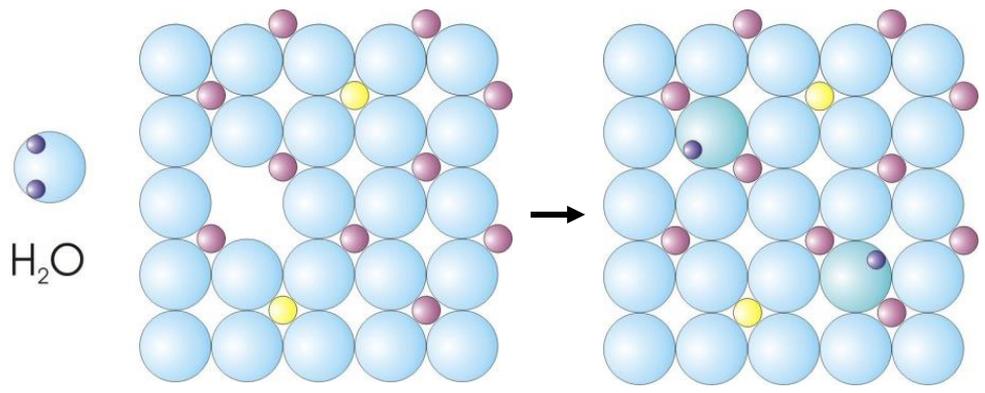
The conductivity has to a first approximation a simple temperature dependency given only by the mobility and hence random diffusivity of the constant concentration of oxygen vacancies.

I have chose to neglect two things:

- \* Only a plot of  $\log(\sigma T)$  would give a truly straight line (remember why?)
- \* Defects interact: Oxygen vacancies and acceptor dopants associate, lowering the concentration of free mobile vacancies - or their mobility if you prefer – at lower temperatures.



# Y: BaZrO<sub>3</sub> : A proton conducting oxide



From Kreuer, .K-D.

## Ternary and higher compounds

- With ternary and higher compounds the site ratio conservation becomes a little more troublesome to handle, that's all.
- For instance, consider the perovskite  $\text{CaTiO}_3$ . To form Schottky defects in this we need to form vacancies on both cation sites, in the proper ratio:



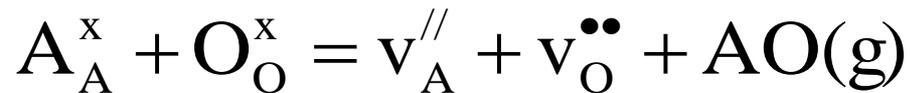
- And to form e.g. metal deficiency we need to do something similar:



- ...but oxygen deficiency or excess would be just as simple as for binary oxides, since the two cations sites are not affected in this case ☺...

# What if a ternary oxide has a strong preference for *one* of the cation defects?

- It can choose to make a selection of the defects by throwing out one of the components, in order to not brake the site ratio conservation rule.
- Example: Schottky defects in  $ABO_3$  with only A and O vacancies:



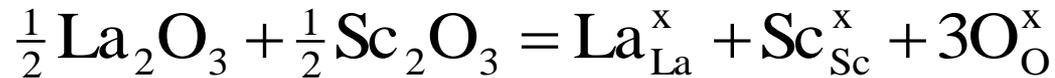
- Example: Oxidation of  $ABO_3$  by forming metal deficiency only on the A site:



- Note: Choice of  $AO(s)$  (secondary phase) or  $AO(g)$  (evaporation) are arbitrarily hosen to illustrate the possibilities...

# Doping of ternary compounds

- The same rule applies: Write the doping as you imagine the synthesis is done: If you are doping by substituting one component, you have to remove some of the component it is replacing, and thus having some left of the other component to react with the dopant.
- For instance, to make undoped LaScO<sub>3</sub>, you would probably react La<sub>2</sub>O<sub>3</sub> and Sc<sub>2</sub>O<sub>3</sub> and you could write this as:



- Now, to dope it with Ca<sup>2+</sup> substituting La<sup>3+</sup> you would replace some La<sub>2</sub>O<sub>3</sub> with CaO and let that CaO react with the available Sc<sub>2</sub>O<sub>3</sub>:



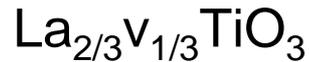
- The latter is thus a proper doping reaction for doping CaO into LaScO<sub>3</sub>, replacing La<sub>2</sub>O<sub>3</sub>.

**Defect chemistry of battery materials?**

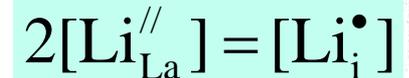
**Yes, Of Course**

# Solid-state Li ion conductor: Li : La<sub>2/3</sub>TiO<sub>3</sub>

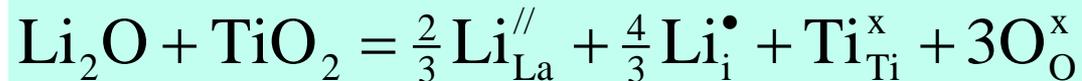
- The perovskite has two structurally different A sites; 2/3 La, and 1/3 empty:



- Substitute 1 Li for 1 La on the La site, and add 2 Li on the empty site:



- Doping reaction:



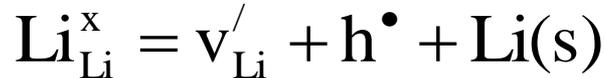
# LiFePO<sub>4</sub> cathode material

- Main defect disorder is Li deficiency
- Can be written in several ways:

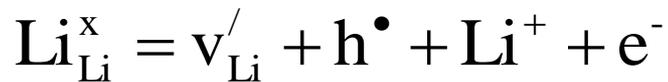
- Written as an extraction of Li<sub>2</sub>O:



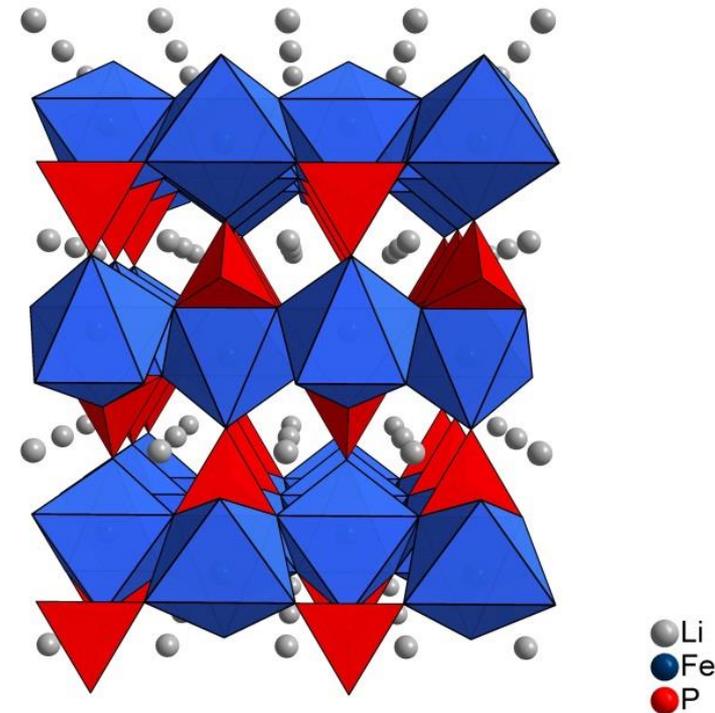
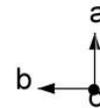
- More relevant: Extraction of Li(s) to the anode:



- Even more relevant: Extraction of Li<sup>+</sup> ions to the electrolyte:



- Often donor doped. Total electroneutrality:



Normally, never mix real and effective charges

For battery electrode materials, it may still be useful: Both types of charges must then be conserved separately

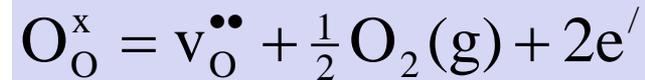
# Computational defect chemistry

- Generate a computational cell with many atoms (ions) and few defects
- Try to make it charge neutral
- Establish boundary conditions by surrounding the cell with copies of itself
- Calculate energy minimum by density functional theory (DFT)
- Defect formation Gibbs energy; difference between defective and perfect lattice;

$$\Delta E_{\text{defect}}^f = E_{\text{defect}}^{\text{tot}} - E_{\text{perfect}}^{\text{tot}} + \sum_i \Delta n_i \mu_i + q \mu_e$$

- Chemical potential of gas species:

$$\mu_i(T, p) = \mu_i^\circ(T, p^\circ) + k_B T \ln(p/p^\circ)$$



- Defect concentrations:

$$c_{\text{defect}} = N \exp\left(-\frac{\Delta E_{\text{defect}}^f}{k_B T}\right)$$

- The standard entropy of gases is a first approximation of entropies, that enables you to calculate equilibrium defect concentrations at finite  $T$ ,  $p\text{O}_2$ , etc.
- We can also calculate lattice and hence defect entropies – a further refinement.

- Numerically fit to electroneutrality.
- You enter  $p$ 's (e.g.  $p\text{O}_2$ ) and you *obtain* the Fermi level  $\mu_e$
- You can obtain all defect concentrations vs  $T$ ,  $p\text{O}_2$ , doping level, etc.

# Summarising conclusions

- Be honest! Admit and admire your defects!
- Ramble! That's what your defects do and keep you doin'!
- Learn! The nomenclature, the three rules, and writing electroneutralities!
- Combine! Defect equilibria and the limiting electroneutrality!
- Practice!
- Be brave! Do the statistical thermodynamics right (standard states and site fractions) and get the pre-exponentials and entropies. *Check!*
- Combine DFT and defect chemistry!
- Become an Almighty Computational Defect Chemist! (ACDC)
  - Not a UCDP

