

## 2. Defect reactions

### Introduction

As discussed in the previous chapter several different types of point defects may be formed in metal oxides and other inorganic compounds. In principle, all types of defects will be present, but in general, only a small number of different defects will predominate.

When defect-dependent properties are to be interpreted, it is important that the defect concentrations as a function of temperature and the activities of the crystal components are known. In order to understand these functions, it is necessary to formulate chemical reaction equations for the formation (or annihilation) of the defects.

The defect formation may either occur internally in the solid or through reactions with the environment. In the following, the rules for formulating defect reactions will be described and applied to different defect structure systems, while in the next chapter, conditions for equilibrium and equations relating equilibrium defect concentrations to temperature, activities (partial pressures) of the components in a compound, impurity concentrations, etc., will be discussed.

### The three rules for writing defect reactions

From a thermodynamic point of view a solid containing point defects constitutes a solid solution where the point defects are dissolved in the solid. In analogy with liquid solutions, the solid may be considered to be the solvent and the point defects the solute. Similarly, the defect equilibria may be treated in terms of the thermodynamics of chemical reactions and solutions.

In analogy with reactions in aqueous solutions, the rules for writing defect reactions include requirements of electroneutrality and mass balance. But for defect reactions in a crystalline compound it is also necessary to require that the ratio of regular structure sites in the metal and oxygen sublattices must be maintained, even if the total number of sites may increase or decrease during the reaction. The rules may be summarised as follows:

#### Conservation of mass – mass balance

The defect reaction must balance with respect to the mass, i.e. the number and types of atoms involved in the defect reaction must be the same before and

after the defect formation or annihilation. Vacancies, which only represent empty sites, have zero mass and do not count. Also electronic defects are considered not to count in the mass balance.<sup>1</sup>

### Conservation of charge

The compounds are and should remain electrically neutral. With the perfect crystal as reference, this means that the total effective charge is the same before and after the formation or annihilation of the defects.

This means that the net charge on the left and right hand sides of a reaction equation must be the same. This charge may be counted in terms of effective charges or of real charges. However, effective and real charges may in general not be balanced against each other, and one must therefore avoid using both effective and real charges in the same equation.

### Conservation of the ratio of structure sites

The ratio(s) of the number of cation and anion structure sites in a crystalline compound is constant. For instance, in an oxide MO the ratio of regular M and O sites is 1:1 regardless of whether the actual composition is stoichiometric or nonstoichiometric. Correspondingly, in a compound M<sub>2</sub>O<sub>3</sub> the ratio of regular cation to anion sites is 2:3, and if 3 oxygen sites are created in M<sub>2</sub>O<sub>3</sub> through a defect reaction, two regular M-sites - vacant or filled - in the metal sublattice must also simultaneously be created.

This rule is special to defect chemistry in crystalline solids, and requires special attention and some practice to avoid its pitfalls. As an exception, this rule does not apply to oxides with infinitely adaptive structures.

Despite the requirement of the constancy in the ratio of regular sites, the total number of regular structure sites may change in a defect reaction, and therefore, the defect equation may include the formation or annihilation of structure sites as long as the proper ratios are maintained.

It should be noted that no sites are created in the formation of electronic defects.<sup>2</sup>

In the many defect equations and equilibria which will be discussed, surface atoms will not be considered separately. All atoms will be considered to be bulk atoms, and this means that the treatment only applies to sufficiently large

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<sup>1</sup> One may choose to count and balance also the mass of electrons, but then one must be sure to include also non-defect electrons (electrons in the valence band).

<sup>2</sup> One may choose to operate with sites – or energy levels - for electronic defects, and one must then take into account the empty levels of the conduction band and the occupied levels of the valence band.

crystallite sizes for which the number of surface atoms is insignificant compared to that of the bulk atoms.

Defect reactions generally do not result in significant changes in the number of surface atoms. In the formation of a vacancy, for instance, a bulk atom is transferred to the surface, but in the same process a previous surface atom, in turn, becomes a bulk atom. (It is worth mentioning, however, that the creation of the new bulk atom has consequences for the energy involved, as we shall discuss in the next chapter.)

### **Examples of reaction equations for defects**

We will now go directly to formation of defects in ionic compounds such as metal oxides, as this will illustrate the three rules. As we move on, the reader is encouraged to check the equations and the three rules against each other to promote understanding of how they apply from the simpler to the somewhat more challenging cases.

In view of the many types of point defects that may be formed in inorganic compounds and that each type of defect may have varying effective charge, numerous defect reactions may in principle be formulated. In the following, a few simple cases will be treated as examples. First, we will consider defect structure situations in stoichiometric compounds (Schottky, Frenkel and intrinsic electronic disorders) and then defect structure situations in nonstoichiometric oxides will be illustrated. Finally, examples of defect reactions involving foreign elements will be considered.

The treatment and examples of defect reactions will not only provide training in applying the rules of defect reactions, but also broaden the description of defect structures and of the individual point defects.

### **Stoichiometric compounds – intrinsic disorders**

As described in the previous chapter, the defect structures in stoichiometric compounds contain equivalent concentrations of negatively and positively charged point defects. These are formed as a result of internal equilibria in the crystal and do not involve reactions with the surroundings. For this reason the defect structures in stoichiometric compounds are also termed internal disorder.

#### *Schottky disorder*

As described in the previous chapter, the Schottky disorder involves the presence of equivalent amounts of cation and anion vacancies. In an oxide MO this means that the crystal contains equal concentrations of metal and oxygen vacancies. The overall formation of such a defect pair within the crystal involves

the transfer of a pair of cations and anions on regular structure sites from the bulk to the surface. In reality the defects are formed at external and internal surfaces or dislocations and subsequently diffuse into the crystal until they are randomly distributed. In writing the equation, one is only interested in the initial and final states, and one disregards the kinetics of the defect reaction.

If one starts with a pair of cations and anions on regular structure sites within the crystal, one must also take into account that the formation of the Schottky pair results in the formation of two new structure sites, and the overall equation may thus be written



However, in this equation the normally occupied sites on both sides may be cancelled, and the net equation therefore becomes



where 0 (nil) designates a perfect crystal.

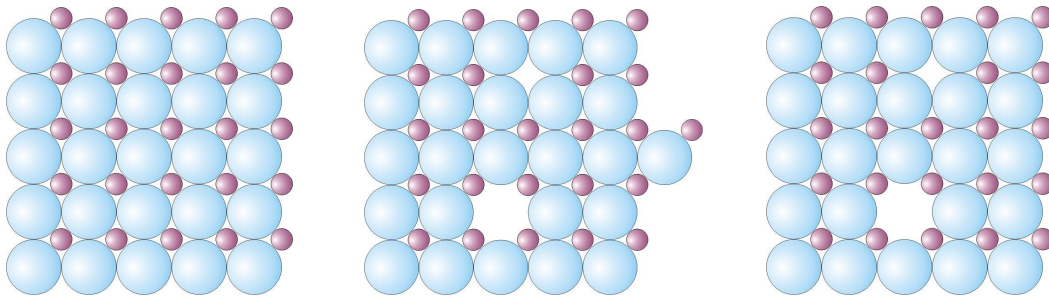


Figure 2-1. Formation of Schottky defect pair in MO. Left: Perfect schematical structure. Middle: One M and one O have left vacancies in the structure and formed a new structural unit on the surface. Right: Equivalent representation.

In terms of the three rules of defect chemical reactions, both (2.1) and (2.2) conserve mass, both conserve charge (being neutral on either side), and both conserve the structure site ration of 1:1 by forming one new M and one new O site.

### *Frenkel disorder*

For the Frenkel disorder the predominant defects are either limited to the cations and anions, and the disorder involves the presence of equal numbers of vacancies and interstitial ions in a sublattice in a crystal. In the formation of a Frenkel defect pair, a cation on a normal site is transferred to an interstitial site, and no new structure sites are created in the process. If the interstitial ion and the resulting vacancy are assumed to be doubly charged, the formation of a Frenkel defect pair may be written



Note that we choose to have an empty interstitial site as a reactant. This has not been usual in defect chemistry, but it helps visualise that such a site is needed, and it keeps track of it through the reaction.

A corresponding equation may be written for the formation of an anion or anti Frenkel defect pair (anion vacancy and anion interstitial).

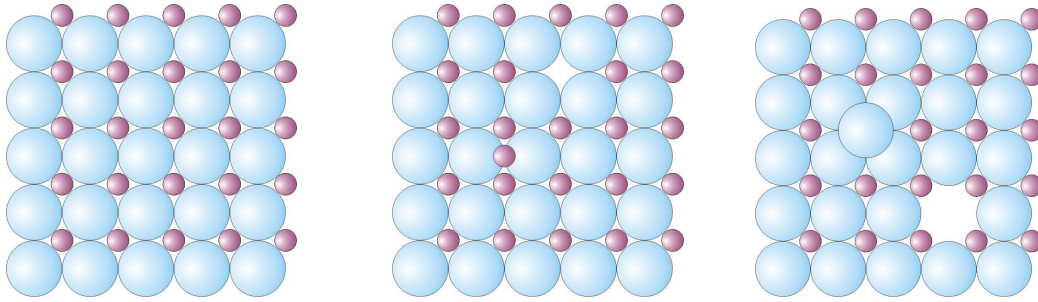


Figure 2-2. Formation of Frenkel-type defect pairs in MO. Left: Perfect schematical structure. Middle: Frenkel defect pair; One M leaves a cation vacancy and takes an interstitial position. Right: Anti (anion) Frenkel defect pair; O vacancy and interstitial O.

### Intrinsic ionisation of electrons

The excitation of an electron from the valence band to the conduction band, thereby leaving an electron hole in the valence band, is written

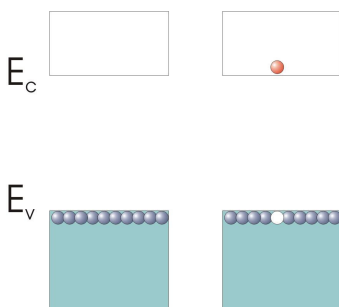


Figure 2-3. Intrinsic ionisation of an electron-hole pair over the band gap between the valence band edge  $E_v$  and conduction band edge  $E_c$ .

As mentioned above we can choose to apply the conservation of mass of electrons in which case we might rewrite the equation as follows:



We can also choose to keep track of the sites – or energy levels – for electrons;

$$e_v^x + h_c^x = h_v^\bullet + e_c^{\prime} \quad (2.6)$$

However, by convention, the three are equivalent, and the first and simplest suffices.

As mentioned earlier, the electronic defects may be localized and then denoted valence defects. In these cases the reactions are connected with individual atomic sites. For instance the intrinsic ionization (disproportionation) of  $Fe^{3+}$  ions into  $Fe^{2+}$  and  $Fe^{4+}$  ions would be written



Similarly, intrinsic ionization may also take place by charge transfer. In ilmenite,  $FeTiO_3$ , we may for instance observe the reaction  $Fe^{2+} + Ti^{4+} = Fe^{3+} + Ti^{3+}$ , which in terms of defects is written:



## Nonstoichiometry

The ratio of cation to anion structure sites is the same whether a compound is stoichiometric or nonstoichiometric. But as nonstoichiometry means that there is an excess or deficit of either cations or anions, nonstoichiometry also means that there is an excess of a certain type or types of defects relative to that in the stoichiometric condition. If the predominating type of defects are charged, electronic defects of the opposite effective charge are created in order to conserve electrical neutrality. The extent of nonstoichiometry and the defect concentrations in inorganic compounds are functions of temperature and activities (e.g. expressed as partial pressures) of their components.

First we consider, as an example the formation of oxygen deficiency in an oxide  $MO_2$ . The overall reaction may be written



From this equation it is qualitatively seen using le Chatelier's principle that the oxygen deficit increases with decreasing oxygen pressure. Conversely, for oxides

with excess oxygen the nonstoichiometry increases with increasing oxygen pressure.

In the following various defect reactions which are encountered in oxides with oxygen or metal excess or deficit will be considered. As the activity of the metal component is usually negligibly small compared to that of the oxygen activity under most experimental conditions, the nonstoichiometry in metal oxides is correspondingly a result of the interaction and exchange of oxygen between the metal oxide and the surrounding gas atmosphere. In the following examples of formation of nonstoichiometric defects, only cases where the metal oxides interact with gaseous oxygen are illustrated. However, it should be borne in mind that the corresponding nonstoichiometry and defects may be formed by interaction with metal if it is experimentally feasible to control the activity of the metal component in the surroundings of the crystal.

### *Oxygen-deficient oxides*

An oxygen vacancy is formed by the transfer of an oxygen atom on a normal site to the gaseous state. There is no change in the number of structure sites. This defect reaction may be written



In this equation it is assumed that the oxygen vacancy is neutral, i.e. the two electrons of the  $O^{2-}$  ion that were there have stayed behind. They are associated with the vacancy or its immediate neighbourhood and the vacancy as a result has zero effective charge.

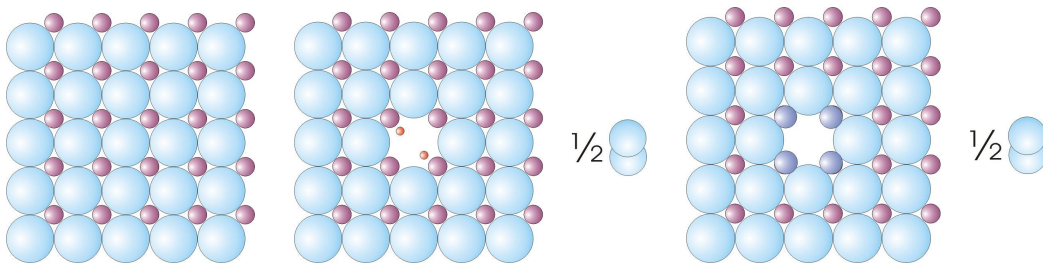
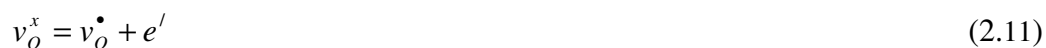


Figure 2-4. Formation of a neutral oxygen vacancy in MO. Left: Schematic perfect structure. Middle: An oxygen atom escapes as gas and leaves a vacancy with two associated electrons. Right: The two electrons shown delocalised on neighbouring cations.

As described in Chapter 1, the two electrons trapped at or near the vacancy may, depending on the temperature and vacancy concentration, be excited and transferred away from the vacancy. Thus, the oxygen vacancy acts as a donor and may become singly and doubly charged:



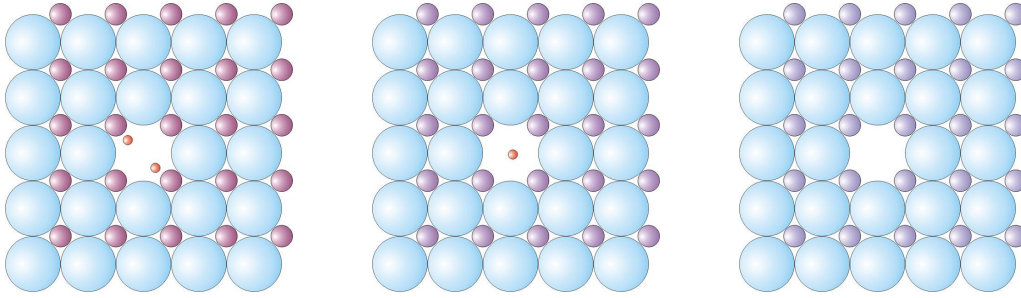


Figure 2-5. Ionisation of an oxygen vacancy. Left:  $v_o^x$ . Middle:  $v_o^\bullet + e'$ . Right:  $v_o^{\bullet\bullet} + 2e'$ .

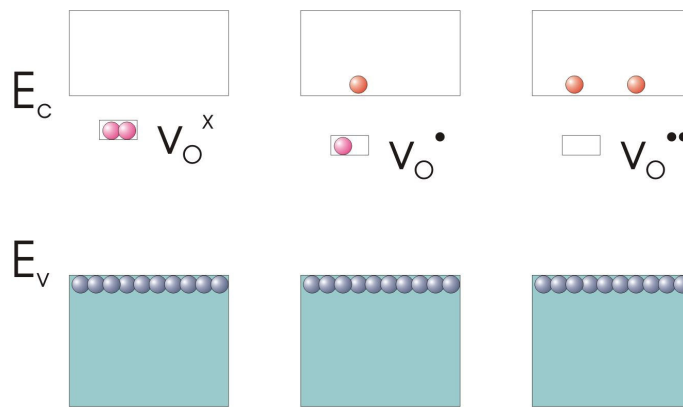


Figure 2-6. Electron energy band picture of the same ionisation steps.

The formation of the doubly ionized oxygen vacancy can be written as the total reaction:



At high temperatures, the ionisation is typically complete, so that this equation is one of the most commonly encountered in high temperature defect chemistry. We will thus use it extensively.

In the equations above the free electrons are considered delocalised in the conduction band. If they are localised at a metal ion on a normal structure site the last equation could be reformulated as follows:



If this takes place in the oxide  $MO_2$  the valence of the M atoms then partly reduces from +4 to +3 when the oxide becomes non-stoichiometric ( $MO_{2-y}$ ).



*Oxides with excess metal*

The oxygen deficiency in an oxide may alternatively be equivalent to the presence of excess metal relative to stoichiometric composition, and in this case the predominant defects constitute interstitial atoms. Correspondingly the composition of the oxide  $MO_2$  should then be written  $M_{1+x}O_2$ . The formation of an interstitial M atom in this oxide involves the transfer of a regular  $M_M$  atom to an interstitial site. As a metal structure site is annihilated in this process, two oxygen structure sites must simultaneously be annihilated in the oxygen sublattice and this is achieved by transferring two oxygen atoms to the gas phase. The defect equation then becomes



The neutral interstitial  $M_i$  atoms may be successively ionised to singly, doubly, triply or quadruply charged interstitial ions, e.g.



From this we can state that the metal interstitial, like the oxygen vacancy, is an electron donor. It may be noted that in both cases it is the effectively neutral or incompletely ionized defects that is a donor, not the fully ionized defects.

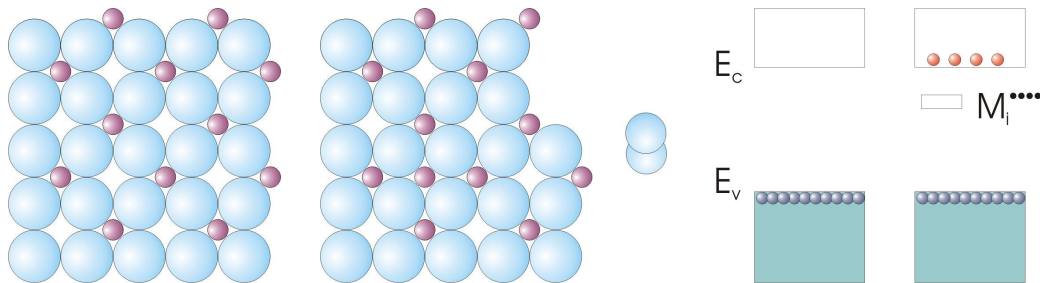


Figure 2-7. Formation of cation interstitials. Left: Schematic perfect  $MO_2$  structure. Middle: Formation of metal interstitial by loss of  $O_2$ . Right: Electron energy band diagram of the process.

We have until now written the formation of metal defects by exchange with oxygen in the surrounding atmosphere. We may in principle choose to write the same in terms of exchange with the metal component in the surroundings. For instance, metal interstitials in  $MO$  can be formed in equilibrium with the metal vapour:



*Metal-deficient oxides*

In metal-deficient compounds metal vacancies are the predominating point defects. In an oxide MO a metal vacancy is formed by reacting oxygen gas with the oxide. This creates new oxygen structure sites and therefore an equivalent number of new metal structure sites - which are vacant - is also formed:



In this reaction it is assumed that the vacancy that is formed is effectively neutral, that is, two electrons are taken from the surroundings of the vacancy in order to form the  $O^{2-}$  ion. The lacking electrons may be taken up from the valence band, forming electron holes here;



The overall reaction is thus

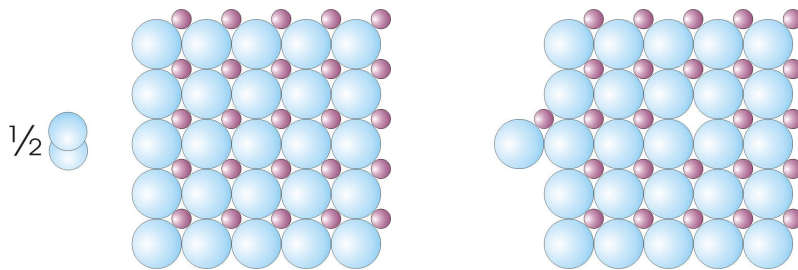


Figure 2-8. Formation of cation deficiency in MO. Left: Oxygen gas and perfect schematical MO structure. Right: Cation vacancy formed by making new formula unit on surface.

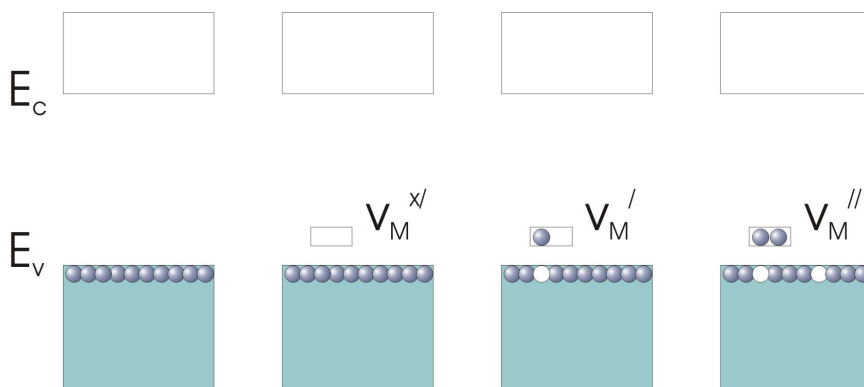


Figure 2-9. Electron energy band structure changes accompanying the formation and ionisation of cation deficiency.

By experience, this is the most difficult to comprehend and reproduce of the simple defect reactions. New sites are formed in the ratio required to maintain the ratio of the structure. One type of sites is empty as formed.

The formation of electron holes may alternatively be expressed in terms of valence defects, so that overall reaction becomes:



This correspondingly means that the valence for some M atoms changes from +2 for to +3; creation of charged metal vacancies involves oxidation.

The metal vacancy, whether it is effectively neutral (electrons missing from its neighbourhood) or ionized (electrons supplied from the rest of the crystal) illustrates that the effective size of a point defect may extend beyond the site itself; the charge may be distributed over at least the closest neighbours of the defect. Accordingly, defect chemistry works fine under the ionic model and with the assumption of integer charges, even if the compound is far from ideally ionic – the point defect is just a little bigger than one site. It works because in defect chemical as in other chemical reactions, the electrons have to choose to go or stay – no half electrons are involved. It then does not matter how close that electron was of the point defect – as long as it was associated with it. For most defect chemical considerations, it then also suffices to consider the defect as a true point defect, and that the electrons are associated with the point defect itself.

#### *Oxides with excess oxygen*

In metal oxides with excess oxygen the predominating point defects are interstitial oxygen atoms or ions. The formation of a neutral interstitial oxygen atom through reaction of oxygen with the oxide is written



No new structure sites are formed in this reaction. The neutral interstitial oxygen atoms may in principle be ionised to yield electron holes and interstitial oxide ions with negative effective charges, so that the total reaction becomes, for instance,



#### *Summary of fundamental reactions for oxide $M_aO_b$*

For reference, the table below contains all the fundamental reactions we have been through, with fully ionised defects, and oxygen as component to exchange for non-stoichiometry. The reactions are made for a binary oxide of

general formula  $M_aO_b$ , i.e., containing cations with formal oxidation state  $M^{\frac{2b}{a}+}$ . It may be noted that the reactions involving no metal defects are unaffected by the coefficients  $a$  and  $b$ .

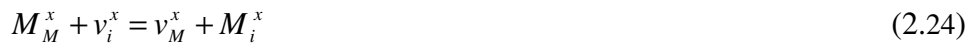
Table 2-1. Summary of fundamental reactions for formation of fully ionized defects in binary oxide  $M_aO_b$ . Oxygen gas chosen for reactions creating non-stoichiometry.

Schottky disorder	$0 = v_M^{\frac{2b}{a}} + \frac{b}{a} v_O^{\bullet\bullet}$
Frenkel disorder	$M_M^x + v_i^x = v_M^{\frac{2b}{a}} + M_i^{\frac{2b}{a}\bullet}$
Anti-Frenkel disorder	$O_O^x + v_i^x = v_O^{\bullet\bullet} + O_i^{\prime\prime}$
Intrinsic electronic ionisation	$0 = e^{\prime} + h^{\bullet}$
Oxygen deficiency	$O_O^x = v_O^{\bullet\bullet} + 2e^{\prime} + \frac{1}{2} O_2(g)$
Metal excess	$M_M^x + \frac{b}{a} O_O^x + v_i^x = M_i^{\frac{2b}{a}\bullet} + \frac{2b}{a} e^{\prime} + \frac{b}{2a} O_2(g)$
Metal deficiency	$\frac{b}{2a} O_2(g) = v_M^{\frac{2b}{a}} + \frac{b}{a} O_O^x + \frac{2b}{a} h^{\bullet}$
Oxygen excess	$\frac{1}{2} O_2(g) + v_i^x = O_i^{\prime\prime} + 2h^{\bullet}$

### Defect reactions for elemental solids

Before we continue, we briefly stop by some reactions for elemental solids, e.g. metals such as Ni and halfmetals such as Si or Ge. In comparison with compounds – especially ionic compounds – the equations are simple and the three rules of defect reactions mainly reduce to one: mass balance.

With the element M as example we can describe the formation of a pair of vacancy and interstitial – a Frenkel pair – as:



What we may call Schottky defects involves only vacancies of M. The atoms removed can be placed in a new structure site on the surface of the crystal,



or removed to the gas phase,



but the latter are equivalent as the solid and gaseous phases are in unvariable equilibrium with each other.

In semiconducting solids the vacancies and interstitial atoms may have a tendency to accept or donate electrons, respectively, from the valence band or to the conduction band and become effectively charged. With Si as example we thus have:

$$v_{Si}^x = v_{Si}' + h^\bullet \quad (2.27)$$

$$Si_i^x = Si_i^\bullet + e' \quad (2.28)$$

### Dissolution of foreign elements

The presence of impurities or dopants may significantly affect or even control the concentrations of the native defects in a compound. The effects are to a large extent dependent upon the relative valences of the ions in the parent compound and those of the impurities or dopants and what sites the impurities and dopants occupy. When the principal valence is the same as that of the host site, we say that the foreign element is homovalent. When it is unequal to that of the host site, we say that the foreign element is heterovalent – or aliovalent.

Foreign aliovalent elements may dissolve in the host structure with zero effective charge. However, their difference from the host atom makes them easily donate or accept one or more electrons – they are donors or acceptors. We will briefly analyse the reason for this and describe the processes in terms of defect reactions.

When boron, B, or phosphorous, P, dissolve as dopants in elemental silicon, Si, they have one too few or one too many valence electrons, respectively, compared to Si. However, they are in this state effectively neutral since the electron number in each case is compensated by the nuclear charge. Nevertheless, the missing or extra electrons form local states in the band structure that easily accept or donate electrons:

$$B_{Si}^x = B_{Si}' + h^\bullet \quad (2.29)$$

$$P_{Si}^x = P_{Si}^\bullet + e' \quad (2.30)$$

The neutral defects, the acceptor and donor, were here formed by dissolving the foreign elements in the same oxidation state as the host, namely 0. It is the desire of the crystal to fulfil the octet rule around each atom – the covalent nature of the bond – that causes the ionization in this case.

We may do something similar with ionic compounds such as oxides. For instance, hypothetical LiO, containing divalent lithium,  $Li^{2+}$ , may be dissolved in NiO to form effectively neutral  $Li_{Ni}^{2+}$  species;  $Li_{Ni}^x$ . Since Li is unstable in oxidation state +2, it easily accepts an electron from the valence band of the crystal:

$$Li_{Ni}^x = Li_{Ni}' + h^\bullet \quad (2.31)$$

Thus, in this case, it is the formal oxidation state according to an ionic model that is the argument for why the acceptor is ionised. Similar arguments hold for donors in ionic compounds.

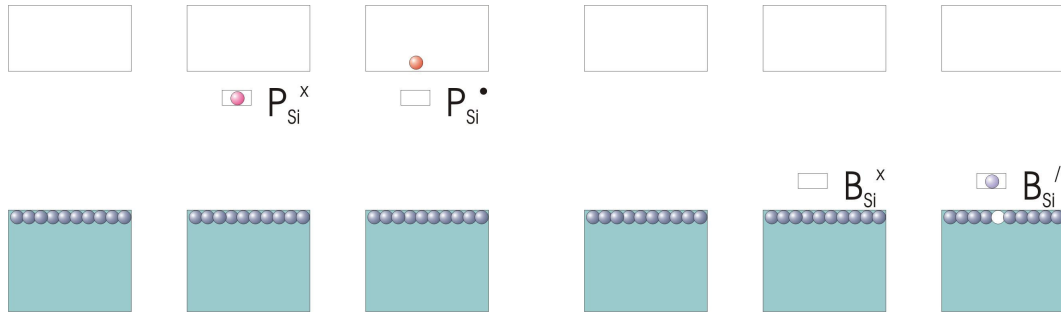


Figure 2-10. Electron energy band representation of pure Si, Si with unionised and ionised P donors (left) and similarly B acceptors (right).

When dealing with aliovalent foreign elements it is common to assume directly the ionisation of the donor or acceptor into an effectively charged state. We often refer to the cases as donor- or acceptor-doped systems, but keep in mind that it is the unionised species that constitutes the donor or the acceptor.

#### *Effects of dissolution of aliovalent oxides in the metal-deficient oxide $M_{1-x}O$ .*

Let us assume that the parent oxide is metal-deficient  $M_{1-x}O$  and that the majority point defects in  $M_{1-x}O$  are charged metal vacancies, e.g.  $v_M''$ , compensated by electron holes,  $h^\bullet$ . The oxide is thus a p-type electronic conductor. Assume now that a higher valent oxide  $Mh_2O_3$  is added. (Mh is used as an arbitrary chemical symbol for a higher valent metal.) Some  $Mh_2O_3$  dissolves in the  $M_{1-x}O$ . The Mh-ions have in this case a valence of +3, and if it is assumed that the Mh-ions occupy normal M-sites in  $M_{1-x}O$ , the dissolved Mh-ions will have one positive effective charge,  $Mh_M^\bullet$ . These additional positive effective charges must for electroneutrality reasons be balanced by creation of an equivalent concentration of negative effective charges or annihilation of an equivalent concentration of positive effective charges. Let us consider these two alternatives.

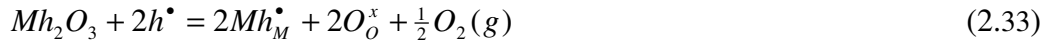
The dissolution of  $Mh_2O_3$  may in the first case be compensated by the formation of additional M-vacancies with two negative effective charges. In this case the equation for the dissolution of  $Mh_2O_3$  is written



and thus the dissolution of  $Mh_2O_3$  in  $M_{1-x}O$  increases the concentration of metal vacancies in the parent oxide.

But as will be discussed in detail in the next chapter an increased concentration of charged metal vacancies simultaneously results in a decrease in

the concentration of electron holes. The dissolution of  $Mh_2O_3$  may thus alternatively be written with a defect reaction involving annihilation of electronic holes:



When the dissolution of  $Mh_2O_3$  is written in this way, the equation emphasises that the concentration of electron holes is reduced. However, as the concentration of metal vacancies and electron holes are interrelated, it should be emphasised that both processes take place. Actually, the dissolution of the higher valent cation decreases the concentration of all effectively positive defects and increases the concentration of all negatively charged defects. Qualitatively, this may simply be seen as a consequence of the electroneutrality equation or, if one wishes, of Le Chatelier's principle. Details of these aspects will be further discussed using defect diagrams in Chapter 4.

If one has the choice of writing a doping reaction by creation or annihilation of defects, it is usually more meaningful to choose the creation of defects, since this can describe the doping reaction to levels beyond the defect concentrations that existed in the undoped oxide, and since this describes the defects that will dominate when the doping level gets high.

So far we have added a higher valent dopant oxide to  $M_{1-x}O$ . Let us alternatively consider what takes place when a lower valent dopant oxide,  $Ml_2O$ , is added to  $M_{1-x}O$ . If the  $Ml^+$  ions dissolve substitutionally in  $M_{1-x}O$ , the dissolved  $Ml^+$  ions have one negative effective charge,  $Ml_M'$ . This will be compensated by the formation of positive effective charge or the annihilation of negative effective charge. In our example oxide this will mainly affect electron holes and metal vacancies, and the two defect reactions may thus be written

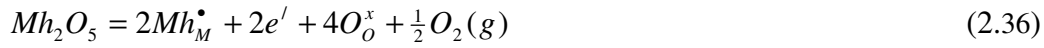


Thus, the addition of  $Ml_2O$  to  $M_{1-x}O$  has the opposite effect of addition of  $Mh_2O_3$ ; it increases the concentration of electron holes and decreases the concentration of metal vacancies. One may note that the first of the two reactions is an oxidation and thus involves uptake of oxygen, while the latter is not. It is typical of such dissolutions of foreign aliovalent elements in oxides that they can be charge compensated by means of electronic defects – in which case we are dealing with reduction or oxidation and uptake or release of oxygen – or by means of point defects – in which case we have no change in oxidation states and no exchange of oxygen gas.

*Effects of dissolution of aliovalent oxides on the oxygen-deficient oxide  $MO_{2-y}$*

The examples in the previous section show the effects of additions of higher and lower valent oxide to the p-conducting, metal-deficient  $M_{1-x}O$ . Let us also briefly consider the effects of doping an oxygen-deficient oxide  $MO_{2-y}$  with higher and lower valent oxides, respectively. The predominating defects in  $MO_{2-y}$  are oxygen vacancies compensated by defect electrons. The oxide is thus an n-type electronic conductor.

When the dopant oxide is higher valent, e.g.  $Mh_2O_5$ , and the dopant cation,  $Mh^{5+}$ , dissolves substitutionally, the dopant ions get one effective positive charge,  $Mh_M^\bullet$ . This charge must be compensated either by formation of negative effective charges in the form of electrons or by annihilation of positive effective charges, oxygen vacancies. These defect reactions may be written



Thus when  $MO_{2-y}$  is doped with a higher valent oxide  $Mh_2O_5$  the concentration of electrons is increased and the concentration of oxygen vacancies is decreased.

When the same oxide,  $MO_{2-y}$ , is doped with a lower valent oxide,  $MI_2O_3$ , the negative effective charge of the dissolved atoms  $MI_M'$  is compensated by annihilation of electrons or formation of oxygen vacancies:



The latter is exemplified by yttria-stabilised zirconia where the acceptor doping is compensated by mobile oxygen vacancies that lay ground for this material as a solid electrolyte:



This important example is illustrated in Figure 2-11.

Numerous other examples may be formulated, depending on the defect structure of the parent oxide, the valence of the foreign ion and the site it



occupies. It may be noted that a foreign cation dissolving interstitially always will have a positive effective charge and thus affect the defect structure in a similar manner as a higher valent cation dissolved substitutionally. We shall return to this and other examples in subsequent chapters and in connection with the review and discussion of a few individual oxides systems.

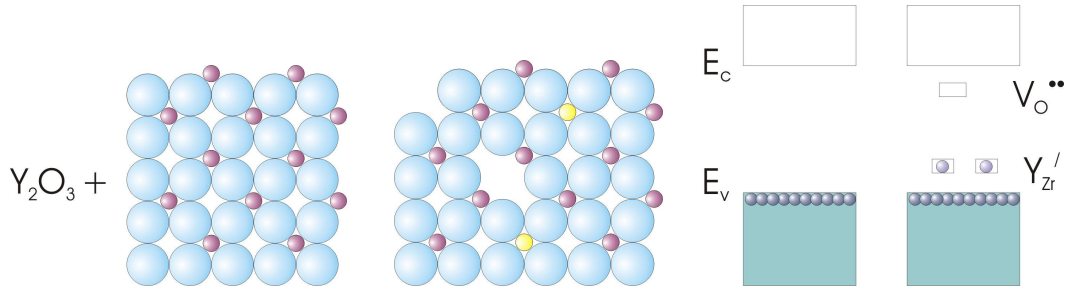
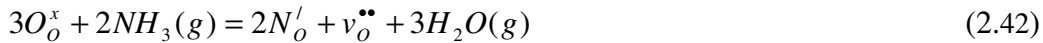


Figure 2-11. Y-doping of ZrO<sub>2</sub>. Left: Y<sub>2</sub>O<sub>3</sub> is added to ZrO<sub>2</sub>. Middle: ZrO<sub>2</sub> gets new Zr sites and O sites in ratio 1:2. Y dissolves substitutionally and one oxygen vacancy compensates the effective charge of two dopant ions. Right: Electron energy band representation of the process.

### Foreign anions in oxides

In oxides, homovalent foreign anions comprise S<sup>2-</sup>, while aliovalent foreign anions comprise F<sup>-</sup> and N<sup>3-</sup>. They can enter as impurities during synthesis, or dissolve from gaseous species under reducing atmospheres, e.g.,



### Dissolution of hydrogen and water vapour in metal oxides

When metal oxides are exposed to gas atmospheres containing water vapour or other hydrogen containing gases, hydrogen will dissolve in the oxides. Under oxidizing or mildly reducing conditions, the hydrogen atoms ionise to protons and associate with oxygen atoms on normal structure sites and thereby form hydroxide ions on normal oxygen sites, OH<sub>o</sub><sup>•</sup>. We may thus for instance write the hydrogenation as



(see Figure 2-12) in which case the protons dissolved are charge compensated by the formation of defect electrons. In terms of defect chemistry the dissolved proton, located on a normal oxide ion as hydroxide, may also be considered to constitute an interstitial hydrogen ion, and as such it is also in the literature

alternatively written  $H_i^\bullet$ . One just has to bear in mind that the protons do not occupy regular interstitial positions (voids).

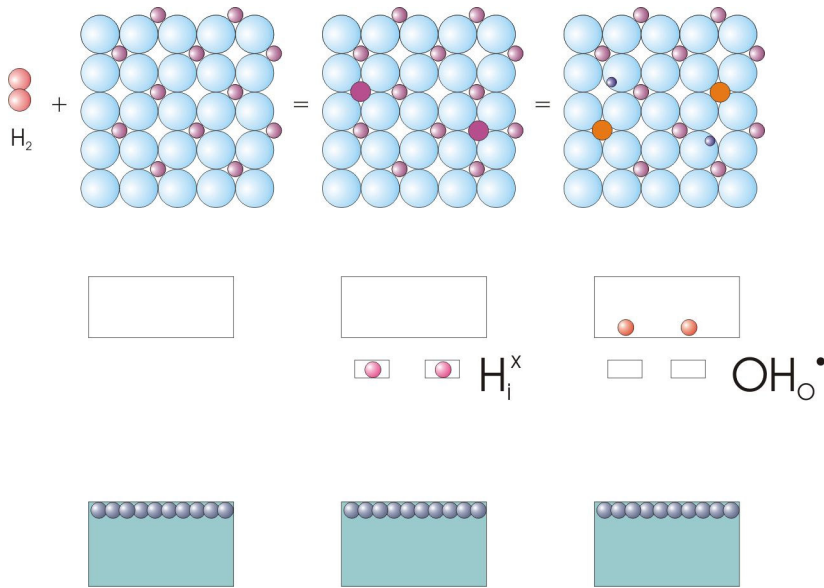
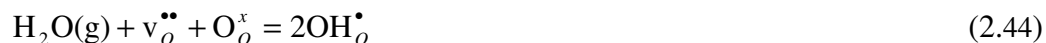


Figure 2-12. Schematic hydrogenation of an oxide  $MO_2$  and ionisation of the hydrogen interstitial atoms into protons in OH groups and electrons.

The electrons may interact with other defects in the oxide so that the protons in effect are compensated by formation of other negative defects or by the annihilation of positive defects. From the dissolution reaction and through the interaction with native defects in the oxide it is clear that the dissolution of hydrogen in metal oxides is dependent both on the partial pressure of the hydrogen source (e.g. water vapour or hydrogen) and of oxygen. These aspects will be described in more detail in a later chapter.

Under reducing conditions, where hydrogen is stable in oxidation state 0 (as  $H_2$  in the gas phase) we may foresee neutral hydrogen atoms dissolved in oxides, probably interstitially, as  $H_i^x$ , as mentioned above. Under even much more reducing conditions could also hydride ions be expected to become stable, e.g. as dissolved substitutionally for oxide ions, as the defect  $H_O^\bullet$ .

Protons may also dissolve from water vapour as a source. The dissolution of hydrogen from its oxide,  $H_2O$ , is in principle similar to dissolution of other foreign cations. However, the possibility of a controlled water vapour pressure and the fast diffusion of protons makes it much easier to attain and vary (and more difficult to completely avoid) an equilibrium content of protons in the oxide. Of particular interest is the reaction between water vapour and oxygen vacancies, by which an acceptor-doped oxide compensated by oxygen vacancies in the absence of water (dry state) becomes dominated by protons when hydrated:



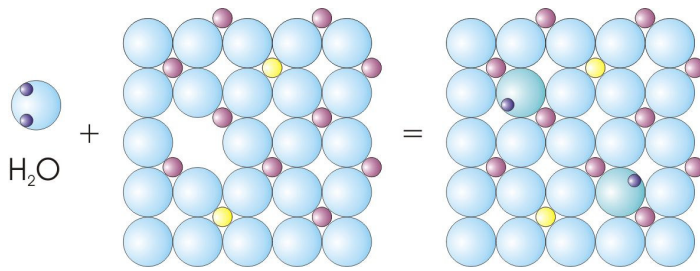


Figure 2-13. Hydration of oxygen vacancies in acceptor-doped  $MO_2$ .

## Ternary and higher compounds

We have so far concentrated on binary compounds, mostly oxides, and only touched upon elemental solids. Ternary and higher compounds fall, however, under exactly the same rules of writing defect reactions.

A typical ternary compound is a ternary oxide such as perovskite,  $CaTiO_3$ . As an example of defect reactions for this case, we consider first the formation of Schottky defects. When we form new structure sites in this reaction, we need to form vacancies on both Ca and Ti sites to maintain the ratio between them, in addition to the appropriate number of oxygen vacancies:

$$0 = v_{Ca}'' + v_{Ti}''' + 3v_O^{\bullet\bullet} \quad (2.45)$$

If we further consider the uptake of oxygen by formation of cation vacancies and electron holes, we again have to balance the cation sites:

$$\frac{3}{2}O_2(g) = v_{Ca}'' + v_{Ti}''' + 3O_O^x + 6h^{\bullet} \quad (2.46)$$

Similar principles should be applied also in cases where one and the same element is distributed on different crystallographic sites. For instance,  $Y_2O_3$  has a structure where all oxide ions are not strictly equal. Similarly, distorted perovskites may have unequal oxygen sites. In the pyrochlore structure,  $A_2B_2O_7$ , there are 6 oxygen sites of one type and 1 of slightly different coordination and energy (and one which is structurally empty and thus to be regarded as an interstitial site). In principle the formation or annihilation of crystal units has to maintain the ratio between those different sites in all such cases. However, this is so far hardly ever practiced in defect chemistry.

Contrary to binary oxides, ternary and higher oxides can have non-stoichiometry not only in terms of the oxygen-to-metal ratio, but also internally between the various cations. This is in practice often a result of synthesis. For instance, it may be difficult to weigh in exactly equal numbers of moles of Ca and

Ti precursors when synthesizing  $\text{CaTiO}_3$ , so that the synthesized material has a permanent number of vacancies on one of the cation sites. Such non-stoichiometry may also be a result of equilibria. For instance, if A-site deficiency is energetically favourable over B-site deficiency in the compound  $\text{ABO}_3$ , we may at very high temperatures (e.g., during sintering) see a preferential evaporation of the A component. For a perovskite  $\text{A}^{2+}\text{B}^{4+}\text{O}_3$  we can for this case write:

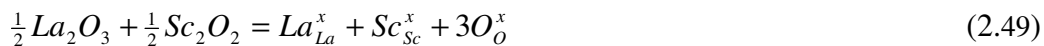


During oxidation we might similarly see a preferential incorporation of A-site vacancies, resulting in a precipitation of an A-rich phase:

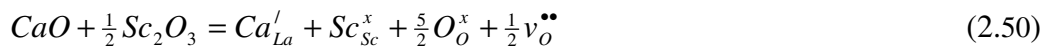


It may be noted that these reaction equations do not violate the site ratio conservation requirement of the ternary oxide.

When we earlier doped elementary or binary compounds the reaction was fairly straightforward. When we dope a ternary or higher compound, however, the reaction may be less obvious – we have some choices. It is quite common, however, to do the synthesis and write the equation in such a way that one takes out a corresponding amount of the host element that is substituted. If we, for instance, want to dope  $\text{LaScO}_3$  with Ca substituting for La, we go for a composition  $\text{La}_{1-x}\text{Ca}_x\text{ScO}_3$ . In order to see how we write the doping reaction in this case we first just look at the trivial normal synthesis:



Accordingly, we then write the defect reaction for the doping in the way that we let there be  $\text{Sc}_2\text{O}_3$  reserved for the  $\text{CaO}$ :



## Summary

Defect reactions can be written in a similar manner as ordinary chemical reactions. They must confer with the requirements for conservation of mass,

charge, and ratios of structure sites, but are allowed to increase or decrease the total number of structure units.

We have treated defect reactions mostly in cases for binary ionic compounds, notably oxides. Reactions for elemental crystalline solids follow the same basic rules and principles, but without the site ratio conservation requirement. Also higher compounds, e.g. ternary oxides, follow the same rules, only often with slightly more complex site conservation considerations and more defects.

Normally, one should seek to use reactions that create rather than annihilate defects, and one should avoid using reactions that form more defects than necessary (as such reactions are then a sum of simpler reactions).

We have formulated defect reactions which describe intrinsic ionic and electronic disorder, nonstoichiometry, variable ionisation of point defects, and substitutional dissolution of aliovalent cations and anions. Aliovalent elements may be compensated by electronic defects or by point defects, of which the former involve red-ox-reactions.

We have treated hydrogen defects specially, as they arise from a special source and in its most stable form, the proton, take on a special size and type of defect.

## Problems

The Problems in this chapter mainly provide training in 1) formulating a reaction in terms of the appropriate reactants and products, and 2) balancing and checking them with respect to a) mass conservation, b) charge conservation, and c) site ratio conservation.

1. Write a reaction for the formation of Schottky defects in NaCl.
2. Write a reaction for the formation of Schottky defects in  $\text{MO}_2$ .
3. Write a reaction for the formation of Schottky defects in  $\text{Cu}_2\text{O}$ .
4. Write a reaction for the formation of anion Frenkel defects in MO.
5. Write a reaction for the formation of anion Frenkel defects in  $\text{CaF}_2$ .
6. Write a reaction for a charge transfer between the cation and anion in  $\text{CeO}_2$ , i.e. for reduction of the cerium ion and oxidation of the oxide ion. Write the same process as an intrinsic ionisation assuming delocalised electronic defects. (Last part is trivial...just to check your understanding.)
7. Write a reaction for the formation of fully ionised oxygen vacancies and electrons when oxygen is lost in the reaction  $\text{M}_2\text{O}_3 = \text{M}_2\text{O}_{3-y} + y/2 \text{O}_2(\text{g})$ .
8. Write reactions for the direct formation of fully ionised metal interstitials in MO,  $\text{M}_2\text{O}_3$ , and  $\text{MO}_2$ .

9. Write reactions for the direct formation of fully ionised metal vacancies in  $\text{MO}$ ,  $\text{M}_2\text{O}_3$ , and  $\text{MO}_2$ .
10. Write reactions for formation of sodium vacancies in  $\text{NaCl}$  by exchange with a) chlorine gas and b) sodium gas.
11. We have in the text claimed that charges can be associated directly with ideal point defects, even if the compound is not ideally ionic, and that this normally does not affect the results of the calculations. Under what conditions will it start to matter that the charge of the defect actually extends outside the defect itself?
12. Write a reaction for dissolution of  $\text{CaO}$  into the oxide  $\text{ZrO}_{2-y}$ .
13. Write a reaction for dissolution of  $\text{MfO}$  into  $\text{M}_{2-x}\text{O}_3$  when we assume that the foreign metal  $\text{Mf}$  is small and therefore dissolves interstitially.
14. Write a reaction for dissolution of  $\text{CaO}$  substitutionally into the anion-Frenkel dominated  $\text{Y}_2\text{O}_3$ .
15. Write a reaction for dissolution of  $\text{ZrO}_2$  substitutionally into the anion-Frenkel dominated  $\text{Y}_2\text{O}_3$ .
16. Write a reaction for dissolution of  $\text{CaF}_2$  into  $\text{CaO}$ , assuming that  $\text{F}$  dissolves substitutionally and that  $\text{CaO}$  is dominated by Schottky defects in the pure, undoped state.
17. Write a reaction for dissolution of protons in an oxide with water vapour as source and with oxygen interstitials as compensating defects.
18. Write a reaction for dissolution of protons in an oxide  $\text{M}_{1-x}\text{O}$  with water vapour as source.
19. Consider an oxide  $\text{M}_2\text{O}_3$  which is acceptor-doped by dissolving the oxide  $\text{MIO}$ . The dopants are compensated by oxygen vacancies. Write a defect reaction for the dissolution of  $\text{MIO}$ . Write a reaction for the dissolution of protons from water vapour into this acceptor doped oxide, by annihilation of the oxygen vacancies. Finally, write a reaction for the dissolution of  $\text{MIO}$  in the presence of water vapour compensated by protons directly. Can the latter reaction be constructed as a sum of the two previous reactions?
20. Hydride ions  $\text{H}^-$  have been suggested to dissolve in oxides accompanied by protons by disproportionation of hydrogen gas. Write defect reactions for this in the case that the hydride dissolves a) interstitially, and b) substitutionally. (Assume in both cases that the oxide is perfectly stoichiometric and has no defects as a starting point).
21. Write a defect reaction for the formation of Schottky disorder in spinel  $\text{MgAl}_2\text{O}_4$ .
22. Write defect reactions for formation of A-site Frenkel, B-site Frenkel, and anion Frenkel disorders in a perovskite  $\text{ABO}_3$  (assuming both cations are trivalent).
23. Suggest a defect reaction for formation of Schottky-type disorder in  $\text{LaMnO}_3$  when it is assumed that cation vacancies are formed in the La sublattice only.

## 2. Defect reactions

24. Write a defect reaction for dissolution of  $\text{Sc}_2\text{O}_3$  in  $\text{CaTiO}_3$  during synthesis, assuming that Sc substitutes Ti forming acceptors compensated by oxygen vacancies.
25. With reference to Problem 22 in Chapter 1, the material of your choice, and its full and limiting electroneutrality: Straightforward: Write a reaction for the formation of the defects you have selected to be dominating. More difficult: Write a reaction that replaces the dominant positive defect with another positive defect. Do similar with a dominant negative defect.

## Answers and hints to selected Problems, Ch. 2

1.  $0 = v'_{Na} + v_{Cl}$
2. -
3.  $0 = 2v'_{Cu} + v_{O}''$
4. -
5.  $F_F^x + v_i^x = F_i' + v_F$
6.  $Ce_{Ce}^x + O_O^x = Ce_{Ce}' + O_O$  or  $0 = e' + h$
7. hint: easier than you might think...
8. MO: -  $M_2O_3$ :  $2M_M^x + 3O_O^x + 2v_i^x = 2M_i''' + 6e' + \frac{3}{2}O_2(g)$  MO<sub>2</sub>: -
9. MO: -  $M_2O_3$ :  $\frac{3}{2}O_2(g) = 2v_M''' + 3O_O^x + 6h$  MO<sub>2</sub>: -
10.  $\frac{1}{2}Cl_2(g) = v'_{Na} + Cl_{Cl}^x + h$   $Na_{Na}^x = v'_{Na} + h + Na(g)$
11. -
12.  $CaO(s) = Ca_{Zr}'' + O_O^x + v_O''$
13.  $3MfO(s) = 3Mf_i'' + 3O_O^x + 2v_M'''$
14. Hint: forms oxygen vacancies...
15. Hint: Forms oxygen interstitials...
16.  $CaF_2(s) = Ca_{Ca}^x + v_{Ca}'' + 2F_O$
17.  $H_2O(g) + v_i^x + 2O_O^x = O_i'' + 2OH_O$
18.  $H_2O(g) + O_O^x = v_M'' + 2OH_O$
19. -
20. -
21.  $0 = v_{Mg}'' + 2v_{Al}''' + 4v_O''$
22. Hint: easy solutions...think simple
23. -
24.  $2CaO + Sc_2O_3(s) = 2Ca_{Ca}^x + 2Sc_{Ti}' + 5O_O^x + v_O''$
25. -